

SEMICONDUCTOR PHOTOCATALYTIC SYSTEMS FOR THE PRODUCTION OF HYDROGEN BY THE ACTION OF VISIBLE LIGHT

A. L. Stroyuk, A. I. Kryukov, S. Ya. Kuchmii,
and V. D. Pokhodenko

UDC 541.145

Data on investigations of recent years on the creation of semiconductor photocatalytic systems for the production of hydrogen from water and aqueous solutions of electron-donating substrates are reviewed. Physicochemical approaches to extending the range of spectral sensitivity of the semiconductors (the use of sensitizers, semiconducting heterostructures, doping with metals and metalloids) are examined. Possible ways of improving the photocatalytic systems for the production of hydrogen with metal-sulfide and other types of semiconductors are analyzed. A general description of the advances and planned developments in the creation of photocatalytic converters of solar energy is given.

Key words: photocatalytic systems, photocatalysts, hydrogen production, sensitizers, semiconductor heterostructures, total decomposition of water.

INTRODUCTION

The development of the use of solar radiation as an inexhaustible constantly renewable source of energy was promoted substantially at several leading scientific centers of the world more than three decades ago in connection with the threat of a fuel crisis and the strategic necessity of a search for new alternative sources of energy. The basic idea was to create converters of solar energy into electrical and chemical forms, e.g., by the decomposition of water with the production of molecular hydrogen – a high-energy and ecologically clean fuel.

The direct splitting of water into hydrogen and oxygen can only occur under the influence of light quanta with wavelengths $\lambda < 242$ nm [1], but solar radiation with such energy is absorbed by the Earth's atmosphere and does not reach its surface. For this reason photocatalyst materials capable of inducing the transformation of water molecules during absorption of the quanta of light of long-wave light ($\lambda > 300$ nm) are used for the realization of this process.

Among familiar photocatalysts for the decomposition of water the most promising, for the present at least, are inorganic semiconductors (SCR), combining high light sensitivity and photochemical activity with availability and ease of use. It should be noted that the photocatalytic and electrophotocatalytic (photoelectrochemical) processes involving semiconductors are very close in nature. They are based on the same elementary event in the action of light, leading to the generation of an electron–hole pair, and the only differences lie in the mechanism of transportation of these charge carriers to the participants of the reaction. This provides the grounds for regarding them as photocatalytic processes occurring in the ordinary and electrochemical regimes. Subsequently, therefore, examples of both types of photocatalytic processes will therefore be presented during discussion of the properties of the semiconducting systems.

L. V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prospekt Nauky, 31, Kyiv 03028, Ukraine. E-mail: stroyuk@inphyschem-nas.kiev.ua. Translated from *Teoreticheskaya i Éksperimental'naya Khimiya*, Vol. 45, No. 4, pp. 199–222, July–August, 2009. Original article submitted June 19, 2009.

Photocatalytic systems of two types can be used for the production of hydrogen: systems in which the water is decomposed completely with the simultaneous formation of hydrogen and oxygen; the so-called “sacrificial” systems containing an irreversibly consumable electron donor, which is usually called a sacrificial donor.

In the systems for the complete decomposition of water the photo process, which takes place with an energy reserve of $\Delta G = 238 \text{ kJ/mol}$ [2, 3], requires the use of a semiconductor with a valence band (VB) electron potential greater than the oxidation potential of water of 1.23 eV with reference to the normal hydrogen electrode (NHE) and a conduction band (CB) electron potential more negative than the potential of the NHE ($E = 0.0 \text{ V}$ at pH 0). Consequently, the minimum energy that must be received by the system for the photodecomposition of water amounts to 1.23 eV. As a result of the losses due to the existence of interfaces (barriers to the transfer of electrons) and also the overpotential for the release of hydrogen and oxygen this value increases to 1.7-1.9 eV [2, 3]. From this it follows that the photocatalytic conversion of solar energy must occur more successfully in systems based on semiconductors with a wide forbidden band with $E_g = 1.7\text{-}1.9 \text{ eV}$ in which the edge of the absorption band lies at 730-650 nm. This does not exclude the use also of more wide-band semiconductors in principle, but on account of the small fraction of light with $\lambda = 300\text{-}400 \text{ nm}$ in the total solar flux the efficiency of its conversion cannot exceed 1-2%. The use of wide-band semiconductors for the creation of more productive systems requires the conferring on them of sensitivity to visible light, and as will be seen from the following account this can be achieved either during the production of the photocatalyst or by post-synthesis modification.

It should be noted that in semiconductor systems for the total decomposition of water it has not yet been possible to achieve high efficiencies for the conversion of solar energy on account of the insufficiently high effectiveness in the separation of the photogenerated charges in space and the high rate of mutual recombination of the primary radical products from decomposition of the water (hydrogen atoms and hydroxyl radicals).

Photocatalytic systems for the production of hydrogen containing an irreversibly consumable electron donor in addition to water are much more effective and have been more widely investigated. The assortment of employed electron donors is extremely large. They include sulfur compounds (H_2S , Na_2S , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$), hydrazine and aliphatic amines (triethylamine, triethanolamine, etc.), lower aliphatic alcohols (methanol, ethanol, isopropyl alcohol) and carboxylic acids (formic acid, EDTA), carbohydrates, and other organic compounds present, in particular, in the fermented biomass.

In such systems the photocatalytic process is initiated according to the following scheme: After photoexcitation of the semiconductor by light with energy corresponding to the energy of the band-band transition an electron is transferred from the conduction band to an adsorbed water molecule as a result of which it is reduced with the formation of a hydrogen atom ($e^- + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH}^-$), and a hole in the valence band is filled by an electron from the sacrificial donor ($h^+ + \text{D} \rightarrow \text{D}^{+\cdot}$). A thermodynamic condition essential to the occurrence of such a process is a more negative potential for the electrons of the conduction band compared with the potential of the hydrogen electrode and a more positive potential for the holes of the valence band compared with the oxidation potential of the donor.

An essential component of most of the photocatalytic systems for the production of hydrogen is the presence of co-catalysts, i.e., compounds that do not have their own photoactivity in the reduction of water but are capable of increasing the effectiveness of the systems many times. Particles of metals (Pt, Pd, Rh, etc.) deposited on an inert support or on the surface of the photocatalyst are most often used as co-catalysts for the release of hydrogen. The role of the co-catalyst involves the acceptance of photoelectrons photogenerated in the semiconductor crystal and their accumulation, making it possible to reduce the overpotential for the reduction of water substantially and also to avoid losses due to electron-hole recombination.

Investigations in the region of the conversion of solar energy into the chemical energy of molecular hydrogen at the L. V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine over the last few decades [4-28] have made it possible to make a significant contribution to solution of this problem. Thus, the concept of “hybrid” photocatalytic systems, based on the joint action of metal complex and semiconductor photocatalysts, was first introduced, and the principles of the creation of such systems were formulated and substantiated [4-6, 9, 11, 19]. It was also demonstrated that their effectiveness can be increased substantially by the use of various substances – hole mediators [7, 9, 19], dark stage catalysts, etc. Heterostructures consisting of a semiconductor (CdS), conducting organic polymers, and various types of sensitizers that had proved much more effective catalysts than cadmium sulfide for the release of hydrogen during the action of visible light were constructed for the first time [13, 17, 19]. Photocatalytic processes for the production of hydrogen involving metal sulfide microhetero transitions [8, 10, 12, 16, 19], photocatalysts based on mesoporous titanium dioxide [20, 21, 24, 25, 27], nanostructured semiconductors, etc. [14, 15, 18, 19, 22, 23, 26, 28] were also investigated. In the course of these

investigations a series of highly effective photocatalytic compositions sensitive to visible light were created for the production of molecular hydrogen from aqueous organic and aqueous inorganic media.

At the present time researches on the creation of systems for the conversion of solar energy using semiconductor photocatalysts and photoelectrodes are continuing vigorously around the world. Investigations are also being conducted with the aim of using photosynthesizing microorganisms and other photoactive biosystems for the production of molecular hydrogen [29-31]. In view of the impossibility of exhaustive coverage of all the research devoted to the problem in a journal article in the present review an attempt is made to extract from the enormous mass of information the publications that most fully reflect the investigations of recent years directed toward the creation of semiconductor photocatalytic systems sensitive to visible light for the production of hydrogen from water and, by examining their results, to formulate an idea of the contemporary state of the development of the problem.

1. PHOTOCATALYTIC SYSTEMS BASED ON SEMICONDUCTORS AND SENSITIZERS

The large group of the light-sensitive materials that have been investigated as photocatalysts includes fairly wide-band semiconductors, mostly metal oxides, that absorb UV light. One method of extending their light sensitivity to the visible region of the spectrum is the use of colored substances or sensitizers. In systems with sensitizers the dye absorbs visible light and in the excited state injects electrons into the semiconductor, on which hydrogen is then formed usually in the presence of a catalyst such as the particles of a metal (Fig. 1). Systems based on titanium dioxide have been investigated most in this respect. Thus, during irradiation with visible light the release of hydrogen is observed from alkaline suspensions of TiO_2/Pt modified with various diamine and dithiolate complexes of Pt^{IV} [32], eosin [33, 34], copper phthalocyanine and dipyrindyl complexes of ruthenium [33], and also in systems containing mesoporous TiO_2 with a complex of zinc with cytochrome C and EDTA as electron donor deposited on its surface [35].

Eosin adsorbed on the surface of nanotubes of $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ or zeolite MCM-41 modified with TiO_2 nanoparticles (NP) [36] in the presence of photodeposited platinum acts as sensitizer in the release of hydrogen from aqueous solutions of triethanolamine [37]. Spectral sensitization can also be observed in analogous systems based on eosin and TiO_2 nanoparticles doped with nitrogen [38].

The release of hydrogen from mixtures of water, acetonitrile, and KI as a result of the oxidation of I^- occurs during the absorption of visible light by coumarin and merocyanine dyes attached to the surface of platinized TiO_2 or laminar $\text{K}_4\text{Nb}_6\text{O}_{17}$ [39]. In the case of the last system a relation was established between the activity of the photocatalyst and the location of the photodeposited Pt nanoparticles. In particular, it was established that the rate of formation of hydrogen with the participation of $\text{K}_4\text{Nb}_6\text{O}_{17}/\text{Pt}$ composites containing nanoparticles of the metal inside the intergallery space is higher than in the case of systems in which the metal is distributed uniformly between the inner and outer surfaces of the semiconductor or was only applied to the outer surface of the photocatalyst. The reason for this is reduction of the I_3^- complex by the photogenerated electrons of the CB as a side reaction in the outer layer of the semiconductor.

During the adsorption of 1,1'-dinaphthalene-2,2'-diol on the surface of TiO_2 nanoparticles a charge-transfer complex characterized by a strong absorption band with a maximum at 550-600 nm is formed. Photoexcitation of the complex in the presence of a co-catalyst (0.1 wt.% Pt) in this band leads to the release of hydrogen from aqueous solutions of triethanolamine with a quantum yield of 0.02% [40]. The photocatalytic release of hydrogen from aqueous solutions of glycerol by the action of visible light also takes place in systems based on TiO_2/Pt nanoparticles sensitized by the salts of tungsten-containing heteropoly acids [41, 42].

Organic dye-sensitizers have been used not only to extend the spectral sensitivity of oxide photocatalysts for the production of hydrogen but also for semiconductors of different nature and for cadmium sulfide in particular [13].

Starting in 1980-1990 mononuclear bipyridyl complexes of ruthenium have been investigated widely as sensitizers for oxide photocatalysts. Researches in this direction are still topical today. Thus, for example, in [43] a photocatalytic system consisting of trisbipyridyl complexes of Ru^{2+} , TiO_2 nanoparticles, and hydrogenase as co-catalyst was studied for the production of hydrogen. The release of hydrogen from solutions of methanol during the action of visible light takes place in

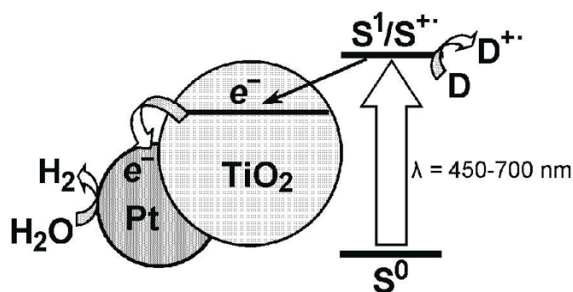


Fig. 1. Diagram of the operation of the photocatalytic system for the release of hydrogen from water based on metal–semiconductor structures and a dye–sensitizer. Legend: S^0 , S^1 , and $S^{+\cdot}$ are the sensitizer in the ground, excited, and one-electron oxidized states respectively.

systems based on mesoporous TiO₂ on the surface of which Pt nanoparticles are formed and mono- and binuclear bipyridyl complexes of Ru²⁺ are adsorbed [44, 45].

Strong electrostatic interaction between the complex cation Ru(bpy)₃²⁺ and the negatively charged surface of the K₄Nb₆O₁₇ “nanoscrolls” produced by the breakdown of the compact niobate creates favorable conditions for electron phototransfer from the excited sensitizer to the semiconductor. On account of this the rate of photocatalytic release of hydrogen from solutions of EDTA is an order of magnitude higher in the case of the K₄Nb₆O₁₇ nanoscrolls than with the compact semiconductor [46]. The yields from the release of hydrogen from solutions of EDTA in the presence of H₄Nb₆O₁₇ and HCa₂Nb₃O₁₀ nanoscrolls modified with platinum nanoparticles and sensitized with Ru(bpy)₃²⁺ and Ru(bpy)₂(4,4′-(PO₃H₂)₂bpy)²⁺ complexes amount to 20-25% during the action of light with wavelength $\lambda > 420 \text{ nm}$ [47].

In [48] new sensitizers of titanium dioxide in the form of binuclear complexes of Ru^{III} where two fragments of this compound are linked with each other by an azobenzene bridge were proposed. In contrast to “classical” sensitizers of such a type, which are strongly adsorbed on the surface of the TiO₂, the bond between these complexes and the semiconductor is weak. This allows the oxidized form of the sensitizer to be desorbed from its surface, which to a considerable hinders electron transfer in the reverse direction and promotes the photocatalytic release of hydrogen from aqueous solutions of methanol or triethanolamine.

2. PHOTOCATALYTIC SYSTEMS BASED ON SEMICONDUCTOR HETEROSTRUCTURES

In binary systems based on narrow-band and wide-band semiconductors the absorption of visible light by the narrow-band component also leads to the injection of an electron into the wide-band semiconductor, on which hydrogen is then formed as a rule in the presence of the co-catalyst. The hole remains spatially separated from the electron and interacts with the electron donor (Fig. 2). Such separation of the charges made it possible to create effective systems for the release of hydrogen based on metal sulfides [8, 10, 12, 16, 19, 49], titanium dioxide materials, and the oxides of a series of other metals. In particular, the photocatalytic decomposition of the complex (NH₄)₂WS₄ in the pores of mesoporous TiO₂ [50] with the subsequent photodeposition of platinum leads to the formation of the nanohetero structure TiO₂/WS₂/Pt, which is active in the release of hydrogen from aqueous solutions of Na₂S under the influence of visible light. The deposition of CdS nanoparticles on the surface of nanocrystalline TiO₂ gives photocatalysts for the release of hydrogen from aqueous solutions of isopropyl alcohol or Na₂S–Na₂SO₃ [51, 52], the activity of which increases with decrease in the size of the CdS nanoparticles due to the appearance of quantum-dimensional effects in them and, in particular, increase in the energy of the photogenerated electrons of the conduction band of cadmium sulfide [53, 54].

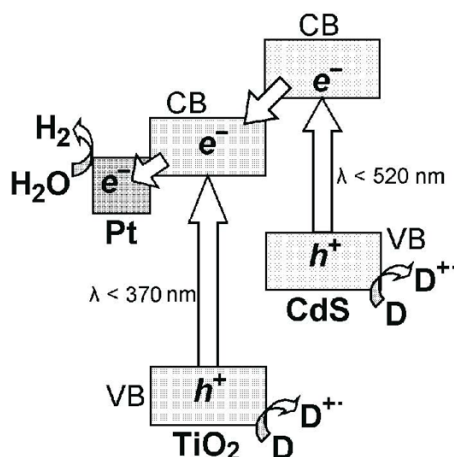


Fig. 2. Diagram of the spatial separation of the photogenerated charges in the CdS/TiO₂ heterostructure and the formation of hydrogen during the action of visible light.

The capacity of zeolite MCM-41 modified with titanium(IV) for ion exchange was used [55] to fix CdS nanoparticles whose average diameter (2.6 nm) was smaller than the diameter of the zeolite pores to its surface. After the photodeposition of platinum on the surface of such a composite it exhibits higher activity in the release of hydrogen from solutions of sodium sulfite during the action of visible light than bulk crystalline CdS. The heterostructures of CdS nanoparticles with TiO₂ nanotubes, produced by ion exchange with subsequent sulfidization by thiourea at 70-80 °C, are active photocatalysts of the release of hydrogen from aqueous solutions of Na₂S/Na₂SO₃ during the action of light with wavelength $\lambda > 420$ nm [56-58].

Heterostructures based on CdS nanoparticles, which are present in the intergallery space of laminar titanates such as K₂Ti₄O₉ [59, 60], potassium niobate [61], and also the compounds K₄Ce₂Nb₁₀O₃₀ and K₄Ce₂Ta₁₀O₃₀ [62], are formed in a similar way. Spatial separation of the photogenerated charges between the components occurs in such nanocomposites. The reduction of water with the formation of hydrogen occurs on nanoparticles of the co-catalyst (Pt, Ni, or RuO₂) deposited on the outer surface, whereas oxidation of the electron donors (Na₂S or Na₂SO₃) occurs with the participation of CdS nanoparticles attached to the inner surface of the laminar material. As a rule the photocatalytic activity of such nanocomposites is substantially higher than the activity of the individual cadmium sulfide or even of a mechanical mixture of CdS and the metallate [59-61].

To create favorable conditions for the formation of heterostructures based on CdS nanoparticles and subsequent photocatalytic processes the laminar metallate materials are sometimes pre-treated in order to extend the intergallery space. Thus, the intercalation of C₃H₇NH₂ together with the [Pt(NH₃)₄]Cl₂ complex into the interlayer space of HNbWO₆ substantially increases the inner cavities between the layers of tungstoniobate; this promotes further intercalation of the mixture of cadmium(II) and zinc(II) ions and the formation, after heating and contact with Na₂S solution, of the nanohetero structure HNbWO₆/Cd_{0.8}Zn_{0.2}S/Pt, which exhibits activity during the action of visible light in the release of hydrogen from aqueous solutions of sodium sulfite [63].

The heterostructure Ni/NiO/KNbO₃ is a fairly effective photocatalyst for the total decomposition of water and release of hydrogen from aqueous solutions of electron donors (ethanol, isopropyl alcohol, etc.) during UV irradiation. The formation of CdS nanocrystals on the surface of such materials makes it possible to realize these reactions during the action of visible light [64].

In [65] a method was proposed for the formation of CdS/TiO₂ nanohetero structures involving titanium(IV) chloride treatment of a mixture of previously synthesized cadmium sulfide and titanium dioxide nanoparticles deposited on conductive glass followed by calcination. Such a procedure improves the mechanical and electrical contact between the CdS and TiO₂ nanoparticles, creating favorable conditions for spatial separation of the charges between the components in the

heterostructure. The highest values for the photocurrent and activity during the release of hydrogen from aqueous solutions of sodium sulfite are achieved with an 80% content of TiO_2 in the initial mixture. In [66] it was proposed to use the $\text{CdS}/\text{TiO}_2/\text{Pt}$ hetero structure for the catalytic release of hydrogen directly from sea water to which Na_2S and Na_2SO_3 impurities had been added.

An important factor determining the activity of ternary systems of the $\text{CdS}/\text{TiO}_2/\text{Pt}$ type in the release of H_2 is the “right” three-dimensional structure of such nanocomposites [67, 68]. Thus, the photocatalysts produced by the photodeposition of platinum on the surface of the binary structure CdS/TiO_2 have characteristics (density of photocurrent and photocatalytic activity in the reduction of water) an order of magnitude worse than for systems in which the deposition of CdS is realized after the photocatalytic formation of the nanoparticles of the metal on the surface of the TiO_2 [67]. The $\text{CdS}/\text{TiO}_2/\text{Pt}$ nanostructures produced by impregnation of H_2PtCl_6 followed by heat treatment or by reduction of the platinum ions have higher activity in the release of hydrogen from $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ solutions than the analogous structures formed during the photocatalytic deposition of platinum [68]. This is due mainly to the fact that in the first case the nanoparticles of the metal are located mainly on the TiO_2 , where the reduction of water occurs, while in the second they are distributed uniformly between the CdS and TiO_2 crystals.

The CdS/TiO_2 nanostructures produced by the sol–gel synthesis of titanium dioxide (particle size 10–20 nm) on the surface of microcrystalline cadmium sulfide after photodeposition of the co-catalyst (platinum nanoparticles, 0.25–2.0 mass %) exhibit activity in the release of hydrogen from aqueous solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ by the action of light with wavelength $\lambda > 420$ nm [69]. Other members of the platinum subgroup are also co-catalysts of the reduction of water and can be arranged in the order $\text{Pt} > \text{Rh} > \text{Pd} > \text{Ru}$ according to their activity. A solution of hydrogen sulfide in concentrated alkali was used as electron donor in such systems [70]. Isotopic investigations showed that the H_2 in this system is formed as a result of the simultaneous decomposition of the H_2O and H_2S molecules.

The spatial separation of unlike photogenerated charges between the matrices of titanosilicates ETS-4 and ETS-10, containing photoactive quantum fibers $(-\text{O}-\text{Ti}-\text{O}-\text{Ti}-\text{O}-)_x$ in their structure, and CdS nanoparticles deposited in their pores gives rise to the high activity of such nanohetero structures in the release of hydrogen from aqueous solutions of Na_2S and Na_2SO_3 during the action of visible light [71].

The solvothermal synthesis of a hetero structure based on CdS nanofibers to the surface of which TiO_2 nanoparticles were attached was reported in [72]. The photocatalytic activity of such nanocomposites in the release of hydrogen from aqueous solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ is much higher than the activity of the original cadmium sulfide nanoparticles. The separation of photogenerated charges between the components of the nanostructure leads also to spatial separation of the oxidation and reduction branches of the photocatalytic process – the reduction of water with the formation of hydrogen takes place on the surface of the TiO_2 nanoparticles while oxidation of the electron donors takes place at the surface of the CdS nanofibers.

The $\text{Bi}_2\text{S}_3/\text{TiO}_2$ nanostructures, characterized by photocatalytic activity in the release of hydrogen from aqueous solutions of Na_2S or Na_2SO_3 , were formed by the hydrolysis of thiourea by heating in the presence of $\text{Bi}(\text{NO}_3)_3$ and nanocrystalline TiO_2 (Degussa P25) [73]. The activity of such a composite is significantly higher than that of the individual bismuth sulfide and reaches a maximum with the components in an equimolar ratio [73].

The spatial separation of the charges in the $\text{Cu}_2\text{O}/\text{TiO}_2$ [74] and CuO/TiO_2 [75] heterostructures and the accumulation of electrons in the copper oxide make it possible to overcome the overpotential for the reduction of water and to realize the release of hydrogen from aqueous solutions of methanol during irradiation with visible light. The photocatalytic formation of hydrogen with a yield of 0.5% is observed during the action of visible light on aqueous solutions of Na_2SO_3 or $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of $\text{CuFeO}_2/\text{SnO}_2$ [76] and $\text{CuAlO}_2/\text{TiO}_2$ [77] nanocomposites.

Together with improvements of the systems based on traditional semiconductor photocatalysts intensive searches are being made for new materials that would combine sensitivity to visible light and would be capable of acting as sensitizers of wide-band semiconductors. Special attention in this direction has been directed toward carbon materials – fullerenes, nanotubes, etc. Thus, in [78] composites were synthesized on the basis of multiwall carbon nanotubes and titanium dioxide modified with metallic nickel. Presumably, the carbon nanotube in such a composite acts as the component sensitive to visible light; after photoexcitation it injects an electron into the CB of the TiO_2 , on which reduction of the water in aqueous solutions of methanol then occurs with the participation of the Ni^0 . Regeneration of the initial state of the nanotube is realized as a result of oxidation of the methanol molecules on its surface.

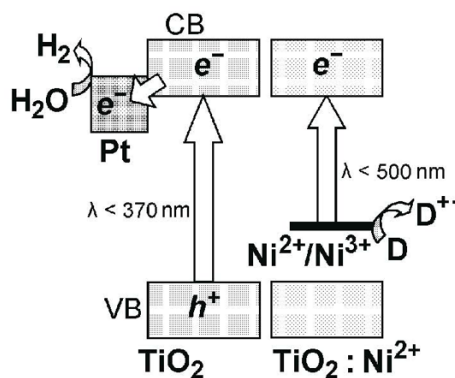


Fig. 3. Diagram of the operation of the photocatalytic system for the release of hydrogen from an aqueous solution of electron donor D with the participation of titanium dioxide doped with Ni^{2+} ($\text{TiO}_2:\text{Ni}^{2+}$).

3. PHOTOCATALYTIC SYSTEMS BASED ON SEMICONDUCTORS DOPED WITH METAL CATIONS

The doping of wide-band semiconductors with transition metals creates local states in the forbidden band the excitation of which by visible light leads to the transfer of electrons into the conduction band (Fig. 3). The water is then reduced by the photogenerated electron, and the donor component is oxidized with participation of the dopant metal [79-84].

Photocatalysts for the release of hydrogen from aqueous solutions of sodium sulfite sensitive to visible light ($\lambda > 420$ nm) were produced by doping ZnS with Pb^{2+} [85], Ni^{2+} [86], or Cu^{2+} [87] cations. The photocatalysts function without additional metallic co-catalysts. The absorption of visible light by them is due to the photoinduced transfer of an electron from the local centers of the dopant cation, substituting zinc in the lattice, into the conduction band of the ZnS. The photocatalytic activity of the $\text{ZnS}:\text{Pb}^{2+}$ system is highest during doping with 1.4 wt.% of Pb and decreases substantially with further increase of the lead content (more than 2%) as a result of the formation of the PbS phase. Further doping of the photocatalyst with the anions of halogens (Cl^- , Br^- , I^-) increases the activity of the system by three times, which the authors [87] attribute to a decrease of tension in the lattice of the semiconductor and of the number of nonradiative recombination centers. With the optimum content of the dopant in the $\text{ZnS}:\text{Cu}^{2+}$ system (4.3%) a quantum yield of 3.7% is achieved [87]. At the same time the maximum activity for the photoreduction of water in the $\text{ZnS}:\text{Ni}^{2+}$ system is observed even at a 0.1% content of the dopant, which corresponds to the composition of the photocatalyst $\text{Zn}_{0.999}\text{Ni}_{0.001}\text{S}$ [86].

Nanocrystals of ZnO doped with Co^{2+} exhibit photocatalytic properties in the reduction of water in water-methanol mixtures and its oxidation to O_2 in solutions of AgNO_3 [88].

A photocatalyst for the release of hydrogen from aqueous solutions of ethanol (20 vol.%), active under the influence of visible light, was produced by doping titanium dioxide with Bi^{3+} cations [89]. By doping SrTiO_3 with Cr^{3+} ions it is possible to obtain a light-sensitive photocatalyst for the release of hydrogen from water-methanol mixtures [90, 91]. Substitution of Ti^{4+} by trivalent chromium is accompanied by compensation for the excess negative charge in the lattice of the semiconductor by the transition from Cr^{III} to Cr^{VI} and the release of molecular oxygen. Recombination of the charges at the anionic vacancies that arise here leads to a decrease in the activity of the system. In order to increase the stability of the semiconductors doped with Cr^{III} equimolar amounts of Ta^{5+} or Nb^{5+} are inserted into the lattice. An analogous effect of increase of the photocatalytic activity of a doped semiconductor in the reduction of water by compensation for the charge of the mixture was observed during the doping of TiO_2 and SrTiO_3 with mixtures of Ni^{2+} and Ta^{5+} [92] or Cr^{3+} and Sb^{5+} [93], during the insertion of a mixture of iridium and alkaline-earth or lanthanum cations into the compound NaMO_3 ($\text{M} = \text{Nb}, \text{Ta}$) [94], and also during the insertion of Cr^{3+} , Fe^{3+} , and Sb^{5+} compounds into layer perovskite $\text{La}_2\text{Ti}_2\text{O}_7$ [95, 96].

Photocatalytic activity in the reduction of water to hydrogen is also characteristic of ZnS and SrTiO₃ doped with La³⁺ ions [97]. In [98] it was proposed to use InTaO₄ and InNbO₄ as a photocatalyst for the release of hydrogen from water–methanol mixtures. By doping these materials with Ni²⁺ and depositing co-catalysts (Pt, RuO₂, NiO_x) on their surface it is possible to achieve a 0.66% quantum yield of hydrogen at wavelength 400 nm. Photocatalysts sensitive to visible light for the release of hydrogen from aqueous solutions of methanol and also of oxygen from silver nitrate solutions are produced by doping InTaO₄ not only with Ni²⁺ but also with Mn, Fe, Co, and Cu cations [99]. “Universal” photocatalysts capable of releasing hydrogen from solutions of methanol and pure water in the presence of Pt or Ni and producing oxygen from AgNO₃ solutions are formed by doping the heterostructures Ba₂In₂O₅/In₂O₃ with chromium [100].

In [101] a general approach was proposed for moving the threshold of the spectral light sensitivity of layer perovskite photocatalysts for the decomposition of water, e.g., CaBi₄Ti₄O₁₅, SrTi₂O₇, K_{0.5}La_{0.5}Ca_{1.5}Nb₃O₁₀, etc., into the visible region by doping with Pb²⁺ cations.

A wide range of dopants (Cr^{VI}, Fe^{III}, Co^{II}, Ni^{II}, Ru^{II}, and Pd^{II}) has been used to transform γ-Bi₂O₃ ($E_g = 2.8$ eV) into photocatalysts sensitive to visible light for the reduction of water [102]. The best of them was palladium(II), and this is probably due to its ability to be partly reduced and act as co-catalyst of the photoreaction.

In the overwhelming majority of such systems there is a specific optimum concentration of the dopant metal above which the activity is substantially reduced. Thus, for example, during the doping of TiO₂ with Ni²⁺ [103] or Bi³⁺ [89] ions the maximum activity in the release of hydrogen from water–alcohol media is achieved with a 1% content of the dopant metal [103]. This effect is presumably connected with the restricted free movement of the charges in the volume of the highly doped crystals on account of the presence of localized dopant levels, which can play the role of traps for electrons or holes. In certain cases there is mixing of the orbitals of the impurity and the semiconductor matrix close to the “ceiling” of the valence band, leading to narrowing of the forbidden band (and to increase of the sensitivity to visible light) without the creation of additional local states in it. Thus, on account of the mixing of the Ni3*d*, Cr3*d*, Ti3*d*/In5*sp*, and O2*p* orbitals a photocatalyst sensitive to visible light ($E_g = 2.14$ eV) for the release of hydrogen from solutions of methanol In₁₂NiCr₂Ti₁₀O₄₂ [104, 105], which considerably surpasses the compounds In₆NiTi₆O₂₂ ($E_g = 2.48$ eV) and In₃CrTi₂O₁₀ ($E_g = 2.00$ eV) synthesized with separate doping of the semiconductor with nickel or chromium cations in activity [104], was obtained during the doping of indium titanate with a mixture of nickel and chromium cations.

Tungsten oxide, which is sensitive to visible light and is also chemically and photochemically stable, has an insufficient potential for the reduction of water or protons to H₂. In order to overcome this restriction in [106] it was proposed to dope it with Mg²⁺ ions, which shifts the position of the forbidden bands by 2.25 eV without change in the width of the forbidden band (2.6 eV). Such a material exhibits activity in the release of hydrogen from aqueous solutions of EDTA under the influence of visible light.

In certain cases it is possible by varying the nature of the dopant metal to affect the ability of the semiconductor to act as photocatalyst both for the reduction branch and for the oxidation branch of the decomposition of water. Thus, the doping of SrTiO₃ with Mn²⁺ or Ru³⁺ cations gives rise to the oxidation of water to O₂ in solutions of silver nitrate during irradiation with visible light [107]. At the same time by doping strontium titanate with Ru, Rh, or Ir cations (1%) and depositing platinum (0.1%) on the surface of the semiconductor it is possible to obtain photocatalysts sensitive to visible light for the reduction of water on account of the oxidation of methanol, the effectiveness of which amounts to 5.2% at 420 nm [107].

In [108-114] it was proposed to use radio-frequency magnetron deposition for the production of TiO₂ films in which the sensitivity to visible light was due to the disruption of the stoichiometry – an O/Ti gradient from the surface into the volume of the film. By post-synthesis hydrothermal treatment of films produced in such a way it was possible to increase substantially their activity in the photoreduction of water on account of increase in the degree of crystallinity and specific surface area of the film [112]. In [115] samples in which the titanium dioxide had the form of “columns” arranged normally to the surface of the film, where the O/Ti ratio varied from 2.00 at the top of the “column” to 1.93 at the point of its contact with the substrate, were produced by such a method. In the presence of platinum such films were used as photocatalysts for the reduction of water in aqueous solutions of ethanol and for its oxidation in solutions containing AgNO₃ [108, 115]. The photoelectrocatalytic reduction of water was realized in systems based on films of α-Fe₂O₃ doped with platinum [116], silicon, titanium [117], chromium, and molybdenum [118].

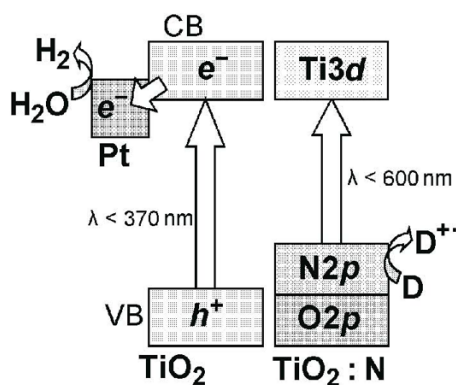


Fig. 4. Diagram of the operation of the photocatalytic system for the release of hydrogen from an aqueous solution of electron donor D with the participation of titanium dioxide doped with nitrogen ($\text{TiO}_2\text{:N}$).

4. PHOTOCATALYTIC SYSTEMS BASED ON SEMICONDUCTORS DOPED WITH METALLOIDS

Some of the most fruitful approaches to narrowing of the forbidden band in oxide semiconductors was partial substitution of the oxygen by other elements (nitrogen, carbon, and sulfur), which makes it possible to realize “band design,” i.e., intentional shift of the valence band of the photocatalyst [2, 79, 81-84] by virtue of the fact that the p orbitals of the impurity are situated in the valence band above the p orbitals of the oxygen, thereby narrowing the forbidden band without substantially moving the bottom of the conduction band (Fig. 4).

The introduction of nitrogen impurities into titanium dioxide during its synthesis by the hydrolysis of $\text{Ti}(\text{SO}_4)_2$ in the presence of ammonia [38] leads to retarded growth of the nanoparticles during calcination, reduction of their average size from 21 to 14 nm, shift of the intrinsic light sensitivity of the TiO_2 into the visible region of the spectrum, and the creation of oxygen vacancies on the surface of the semiconductor, thereby promoting the adsorption of the sensitizer (eosin). On the whole systems based on $\text{TiO}_2\text{:N}$ nanoparticles proved three times more active in the release of hydrogen from aqueous solutions of triethanolamine than the analogous systems based on undoped titanium dioxide.

Titanium dioxide doped with nitrogen, produced by the calcination of titanium dioxide with urea [119, 120], absorbs light up to 600 nm and is photocatalytically active in the release of hydrogen from aqueous solutions of Na_2SO_3 [119] and methanol [120]. Of the two forms of surface nitrogen (chemisorbed and substituting the oxygen in the lattice of the oxide) it is the last form that gives rise to the sensitivity to visible light and the activity. Moreover, it was found that during the doping of TiO_2 samples with nitrogen the mesoporous materials have higher activity in the reduction of water by the action of visible light [121]. It is possible to increase the photoactivity of $\text{TiO}_2\text{:N}$ samples in the release of hydrogen from water–methanol mixtures significantly by modifying their surface with platinum nanoparticles [122].

Tantalum oxynitride TaON, which absorbs visible light in the region of 400-500 nm, is obtained by heating tantalum oxide in a stream of ammonia and water vapor (to prevent the formation of tantalum nitride) [123, 124]. It exhibits high activity in the oxidation of water to O_2 . (The quantum yield at 420-500 nm amounts to 30%.) It is not, however, very active in the release of hydrogen even in the presence of platinum (quantum yield at 420-500 nm 0.2%). However, it was found that unlike the purely oxide materials, for which the best co-catalyst of the metals of the platinum group for the release of hydrogen is Pt, for the nitrogen-containing systems higher activities are obtained in the presence of Ru (0.8% with methanol and 2.1% with ethanol). The photocatalytic deposition of metal on the surface of TaON leads to the formation of a more active photocatalyst since it is accompanied by the formation of smaller particles of Ru (2-4 nm) compared with impregnation of the tantalum oxynitride and subsequent thermal reduction of the ruthenium compounds (20-50 nm) [123]. Full substitution of the oxygen by

nitrogen leads to the formation of the nitride Ta_3N_5 with $E_g = 2.1$ eV, which is also active in the decomposition of water in the presence of donor and acceptor components [124].

A similar approach – heating in a stream of ammonia – was used for the production of the oxynitride Zr_2ON_2 from zirconium dioxide [125]. Mixing of the $\text{N}2p$ and $\text{O}2p$ orbitals in the valence band of the oxynitride leads to narrowing of the forbidden band of the semiconductor to 2.6 eV. After the photocatalytic deposition of platinum (5 wt.%) Zr_2ON_2 exhibits activity in the release of hydrogen from an aqueous solution of silver nitrate under the influence of visible light. Nitrosation of the composite $\text{ZrO}_2/\text{Ta}_2\text{O}_5$ leads to the formation of photocatalysts sensitive to visible light for the reduction of water in solutions of methanol and its oxidation in solutions of AgNO_3 [126]. The optimum content of zirconium dioxide preventing the reduction of tantalum(V) during nitrosation in the photocatalytic reactions amounts to 10%. By the same method LaTaO_4 is converted into LaTaON_2 with retention of the layer structure of perovskite. Layer $\text{Y}_2\text{Ta}_2\text{O}_5\text{N}_2$ was obtained in a similar way [127]. In the presence of Pt and Ru these semiconductors exhibit photocatalytic activity in the release of hydrogen from aqueous solutions of ethanol [128, 129].

The compounds $\text{Sr}_2\text{Nb}_2\text{O}_{7-x}\text{N}_x$, which retain the layer structure and by virtue of the contribution of the $\text{N}2p$ orbitals to the top of the valence band are photocatalysts sensitive to the action of visible light for the release of hydrogen from solutions of methanol, were synthesized by doping the perovskite $\text{Sr}_2\text{Nb}_2\text{O}_7$ with nitrogen [129]. If $x > 2.8$ the orthorhombic perovskite structure is destroyed, and a cubic lattice is formed. This is accompanied by degradation of the photocatalytic properties of the semiconductor.

A solid solution of gallium and zinc oxides doped with nitrogen, which can be depicted by the formula $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with $x = 0.18$, in the presence of a mixed $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ co-catalyst was used as a photocatalyst for the reduction of water [130] with a quantum yield of about 6% at wavelength 420–440 nm. It should be noted that $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ was obtained by the photocatalytic reduction of KCrO_4 with the participation of the composite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)/\text{Rh}$, which in turn was synthesized by the photocatalytic deposition of rhodium nanoparticles on $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ [131]. The layer of chromium oxide on the surface of the metal prevents the occurrence of the reverse reaction between the oxygen and the hydrogen, making it possible to realize the stoichiometric photodecomposition of water using this composite. Active co-catalysts for this system were also obtained by impregnating ruthenium carbonyl $\text{Ru}_3(\text{CO})_{12}$ with a mixture of rhodium and chromium compounds followed by heat treatment [132–134]. Photocatalysts sensitive to visible light for the reduction of water with the composition $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$, where $x = 0.44$, were synthesized by the nitrosation of a mixture of germanium(IV) and zinc oxides [135].

Doping of indium oxide with nitrogen leads to narrowing of its forbidden band from 3.5 to 2.0 eV, which gives the material sensitivity to light with wavelengths $\lambda < 650$ nm [136]. During the action of visible light on $\text{In}_2\text{O}_3:\text{N}$ the density of the photocurrent, which is proportional to the rate of photoelectrochemical reduction of the water, is twice as high as in the case of undoped indium oxide and at least 50 times as high as the photocurrent for the system based on $\text{TiO}_2:\text{N}$.

High-temperature ammonolysis of $\text{Nb}_2\text{Zr}_6\text{O}_{17}$ gave compounds with the composition $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$ [137], which are active in the release of hydrogen from alkaline solutions of H_2S by the action of visible light. In the presence of co-catalysts (Pt or RuO_2) the quantum yield of the process reaches 13.5%.

In [138] a system was proposed for the photoelectrochemical production of hydrogen in which TiO_2 nanotubes with platinum nanoparticles incorporated into their volume are used as cathode while the role of anode is played by TiO_2 nanotubes doped with carbon. To produce such a photoanode, the effectiveness of which under the influence of visible light amounts to 8.5% with respect to current, sonoelectrochemical anodic oxidation of a titanium plate is realized in a mixture of NH_4F and ethylene glycol with subsequent calcination in an atmosphere of hydrogen.

By heating titanate nanotubes at 600 °C in a stream of CO it is possible to achieve the introduction of between 8 and 42% of carbon into the composition of the nanotubes without the formation of a separate titanium carbide phase [139]. The sensitivity of such materials to visible light is due to the narrowing of the forbidden band to 2.2 eV as a result of mixing of the $\text{O}2p$ and $\text{C}2p$ orbitals in the valence band of the semiconductor. By using TiO_2 nanotubes doped with carbon as anode and platinum as cathode it is possible to realize the splitting of water into H_2 and O_2 by the action of visible light [139, 140].

Another approach to the production of TiO_2 doped with carbon involves the combustion of titanium foil in a carbon-enriched flame [141, 142]. Doping leads to narrowing of the forbidden band of the semiconductor from 3.20 to 2.65 eV and also to the appearance of an additional sub-band at a distance of 1.6 eV from the ceiling of the valence band. This material was used as electrode in a system for the photoelectrochemical decomposition of water, taking place in a 5.0 M solution of

alkali with an efficiency amounting to 13% during irradiation of the electrode with “white” light. The authors of [141, 142] also point out that the doping of TiO_2 with carbon promotes increase in the porosity of the electrode surface and also renders assistance to the occurrence of the photoelectrochemical process.

Films of In_2O_3 doped with carbon, which are characterized by sensitivity to visible light ($\lambda < 500 \text{ nm}$) and improved photochemical (compared with the undoped oxide) characteristics (the density of the photocurrent and photocatalytic activity in the reduction of water), were produced by spray pyrolysis [143].

Nanocrystals of TiO_2 , obtained by mechanochemical treatment of titanium dioxide with elemental sulfur, are used in systems for the photoelectrochemical production of hydrogen from water by the action of visible light [144]. Photocatalytic reduction or oxidation of water (depending on the composition of the solution and the type of co-catalyst – Pt or IrO_2) during the action of visible light (420–480 nm) is observed with the participation of lanthanum and indium oxysulfides in whose lattice the oxygen is partly substituted by sulfur [145].

5. WAYS OF IMPROVING PHOTOCATALYTIC SYSTEMS BASED ON METAL–SULFIDE SEMICONDUCTORS

As mentioned, one of the approaches to the design of systems for the production of “solar” hydrogen involves the use of relatively narrow-band semiconductors. In this region the dominant role belongs to sulfide materials and mostly to cadmium sulfide [146], which is however photochemically unstable – it is susceptible to photocorrosion. Therefore, the improvement of the photocatalytic systems for the production of hydrogen based on sulfide semiconductors involves securing their photocorrosion resistance and also a change to materials not containing cadmium, lead, etc., the use of new co-catalysts not containing metals of the platinum group, and the search for methods of increasing the effectiveness of the photoprocesses through the creation of composite materials and the utilization of size effects.

Increase in the photocorrosion resistance of sulfide semiconductors is usually achieved by attaching them to supports. Thus, photocatalysts stable in water–alcohol mixtures for the release of molecular hydrogen are produced during the formation of CdS nanoparticles in the pores of zeolites [61, 147, 148]. The activity of such nanostructures depends substantially on the nature of the support and increases in the order $\text{L} < \text{SBA-15} < \text{zeolite Y}$ [147]. Fairly high activity in this reaction and photostability are exhibited by CdS nanoparticles stabilized with colloidal silica [149], formed on the surface of ZnS nanoparticles previously deposited on polymeric fibers [150] or attached to the surface of aluminum oxide [151], silica gel [152], glass [153], or polyethylene terephthalate [154], and also CdS nanoparticles produced by the thermal treatment of CdO in an atmosphere of hydrogen sulfide [155]. Cadmium sulfide nanoparticles incorporated into glass [153] are also characterized by high resistance to photocorrosion and are capable of releasing hydrogen from solutions of H_2S with quantum yields of 17–18% during irradiation with light of wavelength $\lambda = 470 \text{ nm}$.

The interaction of cadmium(II) salts with polyvinylene sulfide leads to the formation of a nanocomposite containing CdS nanoparticles measuring 6–30 nm attached to and uniformly distributed on the surface of the polymer [156]. Together with photochemical stability it also exhibits high quantum yields (up to 20%) in the release of hydrogen from aqueous solutions of hydrogen sulfide under the influence of visible light.

Photocatalysts based on bismuth, indium, ruthenium, and silver sulfides and their numerous solid solutions may become alternatives to cadmium sulfide. In particular, RuS_2 nanoparticles immobilized on the surface of capsules of polystyrene modified with thiols exhibit photocatalytic characteristics in the release of hydrogen from aqueous solutions of sodium sulfite or isopropyl alcohol [157]. In [158–161] it was established that the layer sulfide ZnIn_2S_4 ($E_g = 2.43 \text{ eV}$) and the nanocomposite $\text{ZnIn}_2\text{S}_4/\text{Pt}$, produced photocatalytically, are active in the release of hydrogen from aqueous solutions of Na_2S and Na_2SO_3 under the influence of visible light. A relationship was found between the conditions of synthesis of the ZnIn_2S_4 samples and their photoactivity – the less prolonged their hydrothermal treatment and the higher the concentration of the template (cetyltrimethylammonium bromide), the higher the rate of formation of hydrogen. The reason for this is presumably deformation of the crystal lattice of the ZnIn_2S_4 formed under the indicated conditions. This leads to the appearance of a dipole moment in the interlayer space of the sulfide, which promotes separation of the photogenerated charges and the occurrence of the reaction. By doping the sulfide ZnIn_2S_4 with copper(II) it is possible to shift its light sensitivity threshold to 800 nm (at a Cu^{II} content of 2.5%). The maximum activity for such a material in the photocatalytic formation of hydrogen is reached at 0.5%

doping [162]. It should be noted that thin films of ZnIn_2S_4 on conducting glass (ITO), produced by spray pyrolysis of a solution of thiourea and a mixture of metal salts [163], can be used for photoelectrocatalytic reduction of water.

Photocatalytic characteristics in the release of hydrogen from solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ by the action of light with wavelength $\lambda > 420$ nm are exhibited by porous agglomerates of CuInS_2 nanoparticles ($E_g = 1.53$ eV) modified with Pt nanoparticles [164].

More complex sulfides in the form of solid solutions with composition $(\text{CuAg})_x\text{In}_{2-x}\text{Zn}_{2(1-2x)}\text{S}_2$ with deposited platinum also exhibit fairly high photocatalytic activity in the release of hydrogen from aqueous solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$, and this is highest in the region of $x = 0.05$ - 0.10 ($E_g = 2.24$ - 2.05 eV) [165, 166]. The sensitivity of these materials to visible light is due to the contribution from the $\text{Cu}3d$ and $\text{S}3p$ orbitals in the valence band and the $\text{In}5s5p$ and $\text{Zn}4s4p$ orbitals in the conduction band of the mixed sulfide. The nanoporous solid solution $\text{ZnS-In}_2\text{S}_3\text{-Ag}_2\text{S}$ has activity in the reduction of water during the action of visible light in the absence of additional co-catalysts [167].

It was established that the triple sulfide $\text{AgInZn}_7\text{S}_9$ ($E_g = 2.3$ eV) is capable of releasing hydrogen from water even in the absence of donors and co-catalysts [168]. In the presence of Pt the quantum yield for the formation of hydrogen from solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ with this photocatalyst amounts to 15% at wavelength $\lambda = 420$ nm. Nanotubes of CdIn_2S_4 are active in the reduction of water in the presence of donor compounds, giving quantum yields up to 17% [169]. The mixed sulfide AgIn_5S_8 ($E_g = 1.77$ eV) in the presence of platinum exhibits fairly high activity in the release of hydrogen from sulfide/sulfite solutions during the action of light with wavelength $\lambda > 420$ nm. The quantum yield of this process amounts to 5.3% at 410 nm [170].

Layer NaInS_2 ($E_g = 2.3$ eV) is an active photocatalyst for the reduction of water by the action of visible light on account of the oxidation of Na_2SO_3 [171]. In the presence of platinum its activity increases and amounts to 6% at 400 nm. Normal indium sulfide, which does not have a layer structure, proved inactive in this reaction [171]. At the same time, the nanoparticles of In_2S_3 , measuring 2.5 nm, formed by ion exchange followed by sulfidization in the pores of the titanium-containing zeolite Ti-MCM-41, proved active in the reduction of water [172] due to the photoinduced transfer of an electron from the indium sulfide nanoparticle to the zeolite and suppression of the electron-hole recombination process.

Films of Bi_2S_3 with $E_g = 1.28$ eV on platinum and bismuth, which are active in the release of hydrogen from solutions of Na_2S by the action of visible light, were obtained by electrodeposition [173].

The cadmium content of the photocatalyst for the release of hydrogen can be reduced by using mixed sulfides $\text{Cd}_x\text{Zn}_{1-x}\text{S}$. A characteristic feature of compounds of this family is their capacity for photocatalytic reduction of water in the absence of additional co-catalysts [174, 175]. As a rule a “bell-shaped” relationship between the composition of the photocatalyst (the quantity x) and the activity is observed in such systems. The question of the position of the maximum on this relationship remains debatable, due most likely to the differences in the methods of synthesis of the mixed sulfides $\text{Cd}_x\text{Zn}_{1-x}\text{S}$, which have a substantial effect on their photochemical behavior. Thus, in [174] the attainment of a maximum quantum of 10.2% yield during the release of hydrogen from aqueous sulfide/sulfite solutions at wavelength 420 nm with $x = 0.8$ was reported. According to data in [175] the highest quantum yields for the release of hydrogen are observed in the region of $x = 0.25$ - 0.30 . At the same time in [176] two extrema (at $x = 0.5$ and 0.2) were observed on the relationship between the composition and the activity in this reaction during investigation of cadmium and zinc sulfides deposited on paper. The maximum activity for $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ microspheres produced by hydrothermal synthesis [177] appears at $x = 0.1$. The quantum yield for the release of hydrogen in this system increases to 16% at wavelength 420 nm after doping the semiconductor with Ni^{2+} (0.1 wt.%). Finally, according to data in [178] the maximum photoactivity for the cadmium and zinc sulfides in the release of hydrogen is found at $x = 0.7$.

In [28] it was shown by laser photolysis that the dependence of the ability of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles to accumulate under the conditions of pulse photoexcitation of the excess negative charge (photoinduced polarization of the semiconductor nanoparticles) on their composition is also described by a bell-shaped curve, and the position of the maximum corresponds to the position of the maximum on the dependence of the quantum yield for the release of hydrogen on x (Fig. 5). There is evidently a direct relationship between the photocatalytic activity of the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles in the reaction and their electric capacity. The latter depends on the structure of the nanoparticles and on the state of their surface, which is largely determined by the conditions used for the production of the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles.

The effectiveness of the photocatalytic systems for the production of hydrogen based on sulfide semiconductors can be improved in several ways: by using mesoporous materials; by photochemical treatment of nanodisperse metal sulfides with a

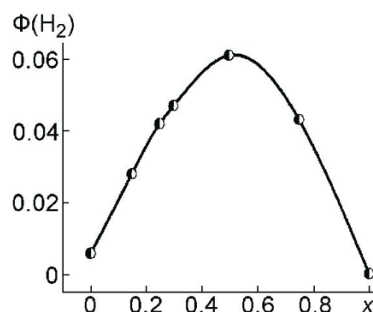


Fig. 5. The dependence of the quantum yield for the photocatalytic release of hydrogen from an aqueous solution of Na_2SO_3 on the composition of the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles stabilized with sodium polyphosphate (SPP) for $[\text{Cd}_x\text{Zn}_{1-x}\text{S}] = [\text{SPP}] = 5 \cdot 10^{-3} \text{ M}$, $[\text{Na}_2\text{SO}_3] = 1 \cdot 10^{-2} \text{ M}$, 20°C , and light intensity $I = 2.3 \cdot 10^{15} \text{ quanta/s}$, $\lambda_{\text{irr}} = 310\text{-}370 \text{ nm}$ [28].

view to removing the surface defects by etching; by creating composites in which the cathodic and anodic decomposition of water are spatially separated.

Ultrasonic treatment of the reaction mixtures during the deposition of cadmium sulfide on the surface of aluminum and magnesium oxides promotes the formation of mesoporous CdS with average pore diameter of 5.4 nm and particle size of 4-6 nm [179]. Such materials have high photoactivity in the release of hydrogen from aqueous solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ in the presence of metals of the platinum group, which can be arranged in the order $\text{Pt} > \text{Pd} > \text{Rh}$ according to their activity as catalysts of the process. In [180] an analogous series was obtained for the activity of metals of the platinum group as co-catalysts for the reduction of water in the presence of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and CdS nanoparticles, and it was shown that it corresponds to the decrease of the redox potential of the metal in the same order and also to the increase of the energy of the metal–hydrogen bond.

The authors of [181] proposed a photochemical treatment of nanocrystalline CdS in order to improve its photocatalytic activity in the release of hydrogen from solutions of formic acid. The treatment involves irradiation of the CdS nanoparticles in solutions saturated with air, during which the size of the nanoparticles decreases as a result of destruction of their surface layer in the oxidative photocorrosion reaction. Here the activity is almost doubled as a result of the increase in the specific surface area of the sulfide and the disappearance of surface defects, which can take part in the recombination processes as traps for the charges [181].

A number of examples of the creation of effective composite photocatalysts involving metal sulfides such as $\text{CdS}/\text{TiO}_2/\text{Pt}$ were examined above during discussion of the properties of semiconductor heterostructures (section 2). We note that the $\text{CdS}/\text{CdO}/\text{ZnO}/\text{Pt}$ (Ru) composites also have higher photocatalytic activity than cadmium sulfide in the release of hydrogen from aqueous solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ on account of the spatial separation of the charges between the components [182].

An interesting example of a composite photocatalyst is the system consisting only of cadmium sulfide in which nanodimensional crystals of CdS with cubic structure ($E_g = 2.6 \text{ eV}$) are deposited on the surface of hexagonal microcrystalline cadmium sulfide with $E_g = 2.3 \text{ eV}$ [183]. The spatial separation of the charges, which occurs in such a composite on account of the difference in the position of the conduction band of the components, gives it good photocatalytic characteristics in the release of hydrogen from aqueous solutions of sodium sulfite. As in the system based on $\text{CdS}/\text{TiO}_2/\text{Pt}$ nanostructures examined above [67], the positioning of the co-catalyst is important in the composition of the nanohetero structure. The highest activity is found in the nanocomposite in which the photocatalytic deposition of platinum nanoparticles on the surface of microcrystalline CdS occurs before the layer of more wide-band nanoparticles of cadmium sulfide is formed on it.

The photocatalytic activity of the nanocomposite CdS/LaMnO₃, produced in reverse micellar media, during the release of water from aqueous sulfide/sulfite solutions by the action of visible light ($\lambda > 420$ nm) is six times higher than the activity of the original CdS, whereas the individual lanthanum manganate is inactive in this reaction [184]. The high activity of this nanohetero structure is due to the phase transfer of the photogenerated hole from CdS to LaMnO₃, where it interacts with the electron donor. In [185] it was proposed to use this heterostructure for the photocatalytic release of hydrogen from the biomass. The rate of formation of hydrogen in such a system with irradiation by polychromatic light is commensurable with the effectiveness of systems based on a sulfide/sulfite donor, and this is due to the presence of methanol and formic acid in the partly fermented biomass [186].

The nanocomposites InP/CdS and InP/ZnTe are effective photoelectro catalysts for the production of hydrogen [186].

An improvement of the photocatalytic activity in the reduction of water can be achieved with the use of semiconductor crystals of anisotropic (nonspherical) form in which movement of charges at unequal rates occurs along the various axes of the crystal. A typical example of this approach is the use of CdS nanofibers 3–4 μm in length and 50 nm in diameter, produced by solvothermal synthesis in the presence of ethylenediamine. They are more active photocatalysts for the release of hydrogen from solutions of Na₂S/Na₂SO₃ than the usual polycrystalline cadmium sulfide [187].

One approach to improving the commercial appeal of photocatalytic systems for the release of hydrogen based on narrow-band semiconductors may lie in reduction of the cost of their electron-donor components as, for example, in the case examined above of systems involving CdS/LaMnO₃ nanocomposites, the effective functioning of which for use in the biomass is comparable with model systems based on a sulfide/sulfite donor [185]. Of special interest also are attempts to use the components of various industrial wastes as electron donors in the reduction of water. A significant example is the systems proposed in [188] for the production of hydrogen based on CdS/Pt, in which solutions of hydrogen sulfide in ethanolamines (from mono- to trisubstituted) – industrial wastes from the coal-chemical industry, natural gas processing, and hydrodesulfurization of petroleum raw materials – are used as donor. Hydrogen sulfide dissolves extremely well in such amines, which favor its dissociation with the release of protons that are reduced to hydrogen during the reaction. The high solubility of polysulfide anions, formed during the oxidation of HS[–] by the photogenerated holes of the valence band of CdS, in the ethanolamines promotes the desorption of S_x^{2–} from the surface of the photocatalyst and makes it possible to prevent their undesirable side reaction with electrons of the conducting band of the CdS.

6. PHOTOCATALYTIC SYSTEMS BASED ON OTHER TYPES OF SEMICONDUCTORS

A new type of photocatalyst for the reduction of water is provided by the spinels CuGa₂O₄ and CuGa_{2–x}Fe_xO₄ ($x = 0.6$), which are capable in the presence of NiO/RuO₂ as co-catalyst of accelerating the release of hydrogen from alkaline solutions of hydrogen sulfide during the action of visible light ($\lambda > 420$ nm) [146]. Photocatalytic activity during the release of hydrogen from sulfide/sulfite solutions is characteristic of CuLaO₂ ($E_g = 2.33$ eV) on the surface of which platinum has been deposited photocatalytically [189] and also of the structurally similar compounds CuLaO_{2.62} [190] and CuAlO₂ [191]. Nanocrystals of CuFe₂O₄ can also be used as photocatalyst for the release of hydrogen from solutions of oxalic acid by the action of visible light [192].

In [193] a family of new photocatalysts was proposed for the reduction of water by the action of visible light: InVO₄ ($E_g = 1.9$ eV), InNbO₄ ($E_g = 2.5$ eV), and InTaO₄ ($E_g = 2.6$ eV). The differences in E_g for these compounds are due to the position of the forbidden band, formed respectively by the V3*d*, Nb4*d*, and Ta5*d* orbitals. The activity of the indicated metallates in the photocatalytic reduction of water in the absence of donor additions can be increased substantially by using nickel oxide as co-catalyst [193, 194]. Mesoporous InVO₄, which has higher photocatalytic activity than nonporous nanocrystalline indium vanadate in the release of hydrogen, is produced by template synthesis [195]. Photocatalytic properties during the reduction of water by the action of visible light are also exhibited by BiVO₄/Ag nanohetero structures [196].

Nanocrystalline films of WO₃ were used as electrodes for the photoelectrochemical reduction of water in water–methanol solutions [197]. Electrodes of Cu₂O ($E_g = 2.0$ – 2.2 eV), synthesized by electrodeposition followed by the

photocatalytic deposition of nickel, were used as photocatalysts sensitive to visible light for the release of hydrogen from aqueous solutions of hydroquinone [198].

In [199] the activity of CdSe nanoribbons in the release of hydrogen from aqueous sulfide/sulfite solutions during the action of visible light was reported. This is one of the few instances of the display of photocatalytic characteristics by cadmium selenide and the first evidence of the ability of CdSe to induce the reduction of water. The series of fairly exotic photocatalysts for the release of hydrogen can be extended to silicon carbide, which is capable of reducing water during exposure to visible light even in the absence of electron-donating compounds [200]. There is also gallium nitride, the conduction band potential of which is 0.5 V higher than the reduction potential of water, which is sufficient to overcome the overpotential for the release of hydrogen from solutions of methanol and mixtures of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ during the action of visible light in the absence of additional co-catalysts [201]. In earlier investigations it was established that a photocatalyst for the release of hydrogen from aqueous solutions of formic acid can be produced by reducing chloroplatinic acid on the surface of crystalline silicon [202].

7. NEW CO-CATALYSTS OF PROCESSES FOR THE PRODUCTION OF HYDROGEN

Co-catalysts of the photoreduction of water based on platinum, palladium, and rhodium, the function of which is to lower the overpotential of the process, have been used in most of the investigated photocatalytic systems for the production of hydrogen. As demonstrated above for a series of examples, these traditional co-catalysts can be replaced by the nanoparticles of nickel and its oxide, the mixed oxides of rhodium and chromium, and also the no less active materials, tungsten carbide [203] and MoS_2 [204]. In particular, in systems based on CdS and molybdenum disulfide, deposited on the surface of cadmium sulfide by impregnation with $(\text{NH}_4)_2\text{MoS}_4$ followed by thermal treatment in a stream of hydrogen sulfide, even with a 0.2% content of the co-catalyst there is a 36-fold increase in the photocatalytic activity of CdS in the release of hydrogen from aqueous solutions of lactic acid [204]. At the same time mechanical mixing of the separately synthesized CdS and MoS_2 gives only a small increase in the photoactivity of cadmium sulfide in this reaction. Among the reasons giving rise to the ability of molybdenum disulfide to act as co-catalyst for the reduction of water the authors of the paper name the effective separation of the photogenerated charges in the CdS/ MoS_2 heterostructure and also the ability of molybdenum disulfide to activate the hydrogen, due to which it is widely used as catalyst for many hydrogenation/dehydrogenation reactions.

Enzymes and hydrogenase in particular evidently have good prospects of being used as co-catalysts for the photocatalytic release of hydrogen in systems based on semiconductor materials [43, 205].

8. SEMICONDUCTOR PHOTOCATALYTIC SYSTEMS FOR THE TOTAL DECOMPOSITION OF WATER BY THE ACTION OF VISIBLE LIGHT

One of the requirements for effective realization of the stoichiometric decomposition of water into oxygen and hydrogen is the spatial separation of the reduction of water to hydrogen and its oxidation to oxygen in order to prevent the reverse reaction between the products of these reactions [2]. As a consequence of this two separate electrode cells connected by a membrane are usually employed for the photodecomposition of water involving semiconductor materials. In one of the cells the water is reduced at the expense of the oxidation of a mediating substance, the oxidized form of which regenerates its original state by diffusing into the other cell and acts as electron acceptor at the stage of oxidation of the water to oxygen (Fig. 6).

Such a dual system has often been compared with the Z scheme for the photosynthesis process [2, 81-84, 206, 207]. This scheme is very convenient since it makes it possible to use an independent design for the cathode and anode parts of the cell and then to combine them by means of a mediating substance such as the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ or I^-/IO_3^- pairs.

Thus, in [208, 209] a system was proposed for the decomposition of water by the action of visible light, in which the hydrogen is released at the surface of the SrTiO_3/Pt electrode doped with the $\text{Cr}^{3+}/\text{Ta}^{5+}$ pair on account of oxidation of the iodide ions to IO_3^- , while the oxygen is released with the regeneration of the I^- involving a WO_3/Pt electrode. The quantum

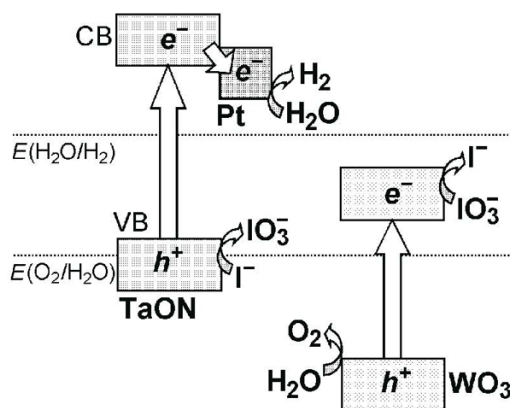


Fig. 6. Diagram of the photocatalytic system for the stoichiometric splitting of water into H₂ and O₂ based on tantalum(V) oxynitride and tungsten(VI) oxide and also the I⁻/IO₃⁻ pair as mediator.

yield of the decomposition of water in such a system amounts to 0.1% at a wavelength of 420 nm. A cell for the release of hydrogen based on the GaInP₂/Pt composite sensitive to visible light was linked in a similar way to a cell based on AgCl sensitized with silver bromide, which is photocatalytically active in the oxidation of water [210].

A series of other cathode–anode pairs linked by an iodide/iodate mediator have been proposed, in particular: TiO₂ (anatase)/Pt (release of H₂)–TiO₂ (rutile)/Pt (release of O₂) [211]; TaON/Pt (release of H₂)–WO₃/Pt (release of O₂) [212]; ATaO₂N/Pt, where A = Ca, Sr, Ba (release of H₂)–WO₃/Pt (release of O₂) [213]; TaON/Pt (release of H₂)–TaON/RuO₂ (release of O₂) [214]; TaON/ZrO₂/Pt(Ru) (release of H₂)–WO₃/Pt (release of O₂) [126]. We note that in the majority of such systems as a result of the effective adsorption of IO₃⁻ on the electrode surface selective oxidation of water occurs in the presence of a significant amount of I⁻ [211].

In the Z scheme, which combines the reduction of water on the surface of an electrode of rhodium-doped SrTiO₃/Pt with the oxidation of water involving BiVO₄, the Fe^{III}/Fe^{II} pair is used as mediator [215, 216]. Such a system functions during the action of visible light with $\lambda < 500$ nm with 0.3% effectiveness (at 440 nm). The Fe^{III}/Fe^{II} pair fulfills the role of electron transfer agent in a dual system for the total photocatalytic decomposition of water based on SrTiO₃ doped with rhodium and WO₃ [217].

If semiconductor nanomaterials formed in a specific way, e.g., nanorods, nanotubes, layer materials, etc., are used it is possible to achieve spatial separation of the reduction and oxidation of water within the limits of one photocatalyst, i.e., to create a short-circuited electrochemical cell. Thus, in systems based on composites of TiO₂ nanotubes with Pt nanoparticles [218, 219] on account of the reduction and oxidation of water at different components of the heterostructure (at platinum and titanium dioxide respectively) the conversion of light amounts to 0.6% [218]. In the heterostructure Ni/NiO_x/In_{0.9}Ni_{0.1}TaO₄ the particles of the co-catalyst (Ni/NiO_x) act as cathode for the release of hydrogen while the surface of the doped tantalate acts as anode for the oxidation of water to oxygen [220]. The effectiveness of such a photocatalytic system amounts to 0.66%. The separation of the cathodic and anodic processes in the decomposition of water is also realized by the use of a composite photocatalyst produced by the intercalation of Fe₂O₃ particles into the interlayer space of HTiNb(Ta)O₅ [221].

The processes leading to the formation of hydrogen and oxygen are separated in space during the photodecomposition of water with bilateral nanocrystalline magnetron-deposited films of TiO₂ on one side of which platinum is deposited. During exposure to visible light in such a system on one side of the film on the TiO₂ nanoparticles hydrogen is released from an aqueous solution of H₂SO₄ while on the opposite side water is oxidized in a solution of NaOH [111].

The authors of [85] proposed a photoelectrochemical cell for the total decomposition of water in which oxygen is produced at an electrode of polycrystalline silicon to the surface of which TiO₂ nanoparticles are attached while hydrogen is produced at a carbon electrode doped with nanoparticles of platinum. With such a cell it is possible to obtain 10% conversion of

solar energy into the chemical form. The oxidation of a titanium plate in the presence of water vapor and NaF gave thin films of fluorine-doped titanium dioxide on which the photoelectrochemical splitting of water was realized by the action of visible light [222]. After etching in a solution of HF nanocrystalline films of TiO_2 have photocatalytic properties in the total decomposition of water by the action of visible light [223]; this is obviously due to the formation of titanium oxyfluorides in the surface layer of the films.

In addition to the complex systems described above, in which conditions for the spatial separation of the cathodic and anodic processes in the decomposition of water are created, substances capable of realizing both these processes simultaneously under the influence of visible light are also being developed. One of the first photocatalysts of such a type is a solid solution of gallium nitride and zinc oxide, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, with E_g in the range of 2.58-2.76 eV. This has high photostability and can secure the total decomposition of the water during the action of visible light [224]. A solid solution of bismuth and yttrium tungstates, BiYWO_6 ($E_g = 2.71$ eV), in the presence of RuO_2 or $\text{Pt/Cr}_2\text{O}_3$ can also act as photocatalyst for the total decomposition of water with 0.17% effectiveness at a wavelength of 420 nm [225]. Porous electrodes of BiVO_4 , synthesized by the thermal decomposition of vanadium hydroxyacetylacetonate, are capable of decomposing water stoichiometrically during the action of visible light and an externally applied potential [226]. Photoelectrochemical decomposition of water can be realized at the surface of nanocrystalline films of silicon-doped hematite $\alpha\text{-Fe}_2\text{O}_3$ produced by the thermal decomposition of ferrocene or iron pentacarbonyl [227, 228].

In [229] a photoelectrochemical cell sensitive to visible light was proposed for the total decomposition of water; the water is oxidized on a polycrystalline film of TiO_2 sensitized with bipyridyl complexes of Ru^{II} , and the water is reduced to H_2 at a platinum cathode. In this system the ruthenium complex serves not only as an “antenna” sensitive to visible light but also acts at the same time as a bridge connecting to the TiO_2 nanoparticles through the phosphate groups on one side and to the IrO_2 nanoparticles on the other through the carboxy groups. During the photoexcitation of such a system electron transfer occurs along a chain consisting of a water molecule (release of O_2) \rightarrow IrO_2 nanoparticles \rightarrow sensitizer \rightarrow TiO_2 nanoparticles \rightarrow platinum cathode \rightarrow water molecule (release of H_2).

Substitution of the Ca^{II} in calcium niobate or tantalate $\text{Ca}_2\text{Ta}_2\text{O}_7$ ($E_g = 4.8$ eV) by tin(II) ions gave the compounds $\text{Sn}_2\text{Ta}_2\text{O}_7$ ($E_g = 3.0$ eV) and $\text{Sn}_2\text{Nb}_2\text{O}_7$ ($E_g = 2.3$ eV), which are sensitive to visible light due to the contribution from the $\text{Sn}5s$ orbitals to the valence band. These compounds exhibit photoactivity in the release of hydrogen from aqueous solutions of methanol and also oxygen from solutions of silver nitrate in the presence of IrO_2 as co-catalyst [230].

In [231-233] three types of new photocatalysts were proposed for the decomposition of water by the action of UV and partly visible light: BiMnNbO_7 ($M = \text{Al}^{\text{III}}, \text{Ga}^{\text{III}}, \text{In}^{\text{III}}$), InMO_4 ($M = \text{Nb}^{\text{V}}, \text{Ta}^{\text{V}}$), and BiMO_4 ($M = \text{Nb}^{\text{V}}$ or Ta^{V}) with E_g in the range of 2.4-2.7 eV. The activity of these compounds is increased substantially in the presence of co-catalysts – NiO and Pt . More sensitive to visible light are the compounds NiNb_2O_6 ($E_g = 2.2$ eV) and NiTa_2O_6 ($E_g = 2.3$ eV), capable of the photocatalytic reduction of water to hydrogen in the absence of co-catalysts [234].

Compounds with the composition $\text{K}_4\text{Ce}_2\text{M}_{10}\text{O}_{30}$ ($M = \text{Nb}, \text{Ta}$) with forbidden band width in the range of 1.8-2.3 eV are active photocatalysts for the reduction of water in solutions of Na_2SO_3 and its oxidation in solutions of AgNO_3 [235]. The co-catalysts Pt , RuO_2 , and NiO_x accelerate these reactions substantially. A series of other photocatalysts active in the release of hydrogen and oxygen from water in the presence of electron-donor and electron-acceptor additives was described above during examination of the systems based on semiconductors doped with metals and metalloids (sections 3 and 4).

The possibility of photocatalytic decomposition of water contained in the inner volume of single-walled carbon nanotubes synthesized by arc discharge was demonstrated in [236]. Irradiation of the nanotubes leads to the formation of a mixture of gases, 80% of which consists of hydrogen while the remainder is a mixture of carbon oxides, methane, and trace quantities of other substances.

Researches are being carried out on fundamentally new semiconductor materials capable of acting as photocatalysts for the reduction and oxidation of water. Thus, in [237] systems are described for the release of H_2 and O_2 from solutions containing donor and acceptor additives in the presence of carbon nitride C_3N_4 , which has a graphite-like structure.

CONCLUSION

In the conclusion of this discussion of the conversion of solar energy by the photocatalytic production of hydrogen from water it seemed appropriate to sum up the information presented above, to analyze the principal directions in the

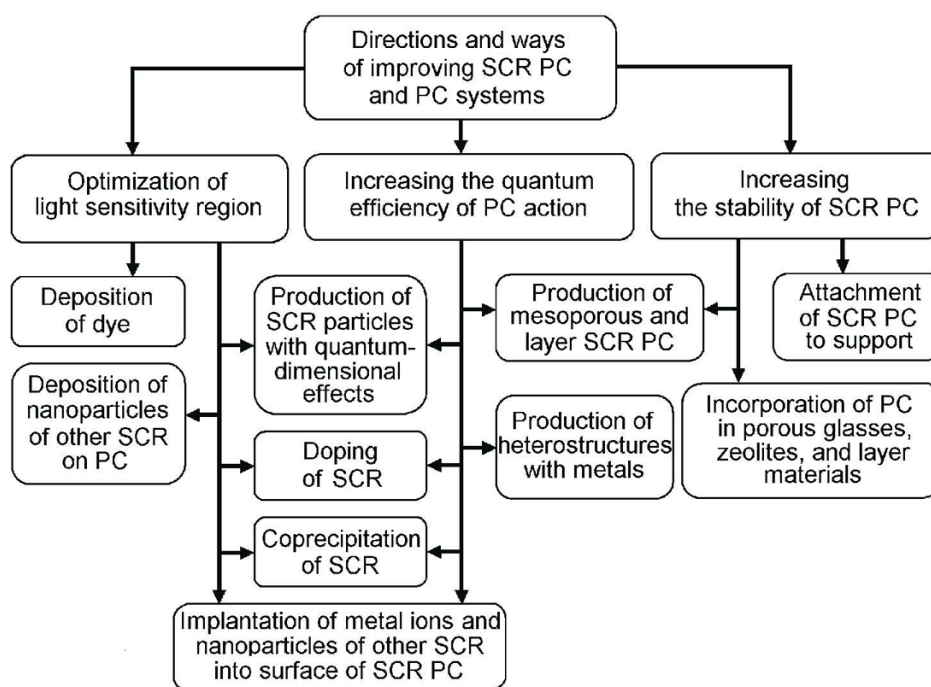


Fig. 7. Diagram illustrating the ways of improving semiconductor photocatalysts (PC) and photocatalytic (PC) systems sensitive to visible light for the production of hydrogen from water.

development of the process and the physicochemical approaches to the attainment of its goal, to correlate the results, and to analyze recently outlined trends.

Photocatalytic systems intended for the production of hydrogen from water by the action of sunlight must meet a series of requirements, the most important of which are sensitivity to visible light over a wide range of wavelengths, high quantum yields for the photodecomposition of water under such irradiation conditions, and chemical and photochemical stability during prolonged use. As shown by analysis of the data presented above, these requirements formed the basis of three directions of work aimed at improvement of the photocatalysts and photocatalytic systems. These directions and also the ways of achieving the desired results and their interdependence can, in our opinion, be represented by the scheme presented in Fig. 7.

As seen from the scheme, the physicochemical aspects of the design of effective photocatalysts are extremely diverse. The whole arsenal of the influences leading to the formation of high-performance photocatalysts can be divided into those that are realized during the production of the respective semiconductors and those realized during their post-synthesis treatment. As demonstrated by many investigations, it is possible to achieve a number of fundamentally differing results by changing the conditions of the synthesis. They include: the production of semiconductor materials with quantum-dimensional effects – spherical nanoparticles, nanorods, nanotubes, etc.; the production of semiconductors with unusual geometrical structure for a given chemical composition – mesoporous and layer materials; the production of semiconductor particles with modified electronic structure – with electron-donor or electron-acceptor levels in the forbidden band arising as a result of doping the semiconductors with metals or nonmetals in the course of their synthesis; the products from the joint production of two semiconductors – heterostructures SCR(1)/SCR(2) or the new substances SCR(3) formed during their interaction.

The physicochemical approaches to conferring improved photocatalytic properties onto the semiconductors after completion of their syntheses are also extremely diverse. To judge from the results examined above the following items must be included among the most important forms of post-synthesis treatment: the deposition of nanoparticles of another semiconductor on the semiconductor; the implantation of metal ions and the nanoparticles formed by them into the surface of the semiconductor; the production of heterostructures of the semiconductor with metals; the deposition (adsorption) of a sensitizer dye on the semiconductor.

During analysis of the results from improvement of the photocatalysts attention is drawn to the complexity of the changes in the characteristics brought about by some of the influences on the semiconductor shown in the scheme. Thus, the implantation of nanoparticles of another semiconductor into the surface of the photocatalyst can in isolated cases lead not only to increase in the quantum effectiveness of the action of light but also to a bathochromic shift of the boundary of light sensitivity. The same dual positive effect has been obtained many times as a result of “co-precipitation,” i.e., the joint synthesis of two semiconductors.

In the case of the production of semiconductor nanoparticles with quantum-dimensional effects the significant increase in the photocatalytic activity is accompanied by a hypsochromic shift of the light sensitivity, which is extremely undesirable for photocatalysts used for the conversion of solar energy sensitive to visible light. The design of photocatalytic systems based on semiconductors with quantum-dimensional effects must therefore in our opinion be undertaken after evaluating the possibility of an energy gain, made by comparing the spectrum of the solar radiation reaching the earth's surface. We note, finally, that as a result of doping not only is there a shift of the absorption toward lower energy, on which authors usually concentrate attention, but as shown in the case of other redox reactions the photocatalytic activity also changes, and this must be taken into account.

Together with the ways of solving the problem of increasing the photochemical activity and extending the light sensitivity of photocatalysts examined here, as already mentioned above, there is also a need to secure their long-term operation. Here it should be noted that in a series of investigations devoted to the question of increasing the quantum effectiveness of the photocatalytic processes such approaches to increasing the stability as the attachment of the photocatalysts to a support or their incorporation into the intergallery space of layer materials and also into zeolites and porous glasses have been found. Of particular interest, in our view, are the data on the enhanced stability of the recently developed mesoporous and layer semiconductor photocatalysts, which frequently have higher activity than substances with the same chemical composition but having the ordinary structures.

While analyzing the state of developments in the photocatalytic production of hydrogen by the decomposition of water under the influence of sunlight it is possible in our view to mark the following achievements.

The problem of managing the photodecomposition of water with the simultaneous production of hydrogen and oxygen in two linked cells has in principle been solved. Further developments in this direction will probably involve the search for effectively functioning components for such systems – photocatalysts, sensitizers, mediators.

New substances with semiconductor characteristics are being synthesized and tested with encouraging results.

Increased activity has been established in semiconductors with known photocatalytic function distinguished by an atypical structures (porous and layer materials, nanotubes, nanorods, etc.).

Semiconductor nanoparticles with quantum-dimensional effects attached to various supports and having on this account greater stability have found widespread usage.

In general it can be concluded quite confidently that considerable progress has recently been made in the development of “solar” hydrogen production from water.

REFERENCES

1. J. Calvert and J. Pitts, *Photochemistry* [Russian translation], Mir, Moscow (1968).
2. K. Maeda and K. Domen, *J. Phys. Chem. C*, **111**, No. 22, 7851-7861 (2007).
3. R. van de Krol, Y. Liang, and J. J. Schoonman, *Mater. Chem.*, **18**, No. 20, 2311-2320 (2008).
4. A. I. Kryukov, S. Ya. Kuchmii, A. V. Korzhak, and S. V. Kulik, *Teor. Éksp. Khim.*, **25**, No. 4, 452-459 (1989). [*Theor. Experim. Chem.*, **25**, No. 4, 420-425 (1989).]
5. S. Ya. Kuchmii, Yu. V. Kholodenko, and A. I. Kryukov, *Ukr. Khim. Zh.*, **55**, No. 11, 1157-1161 (1989).
6. V. D. Pokhodenko, A. I. Kryukov, S. Ya. Kuchmii, et al., *Teor. Éksp. Khim.*, **28**, Nos. 5/6, 407-410 (1992). [*Theor. Experim. Chem.*, **28**, Nos. 5/6, 312-314 (1992).]
7. V. D. Pokhodenko, V. G. Koshechko, S. Ya. Kuchmii, et al., *Teor. Éksp. Khim.*, **28**, Nos. 5/6, 411-415 (1992). [*Theor. Experim. Chem.*, **28**, Nos. 5/6, 315-318 (1992).]
8. A. I. Kryukov, S. Ya. Kuchmii, A. V. Korzhak, et al., *Teor. Éksp. Khim.*, **29**, No. 3, 270-274 (1993). [*Theor. Experim. Chem.*, **29**, No. 3, 182-184 (1993).]

9. A. I. Kryukov, S. Ya. Kuchmii, and V. D. Pokhodenko, *Teor. Éksp. Khim.*, **30**, No. 4, 175-191 (1994). [*Theor. Experim. Chem.*, **30**, No. 4, 141-157 (1994).]
10. A. I. Kryukov, S. Ya. Kuchmii, S. V. Kulik, et al., *Teor. Éksp. Khim.*, **30**, No. 4, 197-201 (1994). [*Theor. Experim. Chem.*, **30**, No. 4, 163-166 (1994).]
11. S. Ya. Kuchmii, S. V. Kulik, A. V. Korzhak, and A. I. Kryukov, *Teor. Éksp. Khim.*, **30**, No. 4, 231-235 (1994). [*Theor. Experim. Chem.*, **30**, No. 4, 195-199 (1994).]
12. A. I. Kryukov, A. V. Korzhak, S. V. Kulik, et al., *Ukr. Khim. Zh.*, **60**, No. 12, 833-838 (1994).
13. S. Ya. Kuchmii, A. V. Korzhak, N. F. Guba, et al., *Teor. Éksp. Khim.*, **31**, No. 6, 370-374 (1995). [*Theor. Experim. Chem.*, **31**, No. 6, 309-313 (1995).]
14. A. I. Kryukov, N. P. Smirnova, A. V. Korzhak, et al., *Teor. Éksp. Khim.*, **33**, No. 1, 32-35 (1997). [*Theor. Experim. Chem.*, **33**, No. 1, 30-33 (1997).]
15. N. P. Smirnova, A. I. Kryukov, A. V. Korzhak, et al., *J. Mol. Struct.*, **408/409**, 563-567 (1997).
16. A. I. Kryukov, S. Ya. Kuchmii, and V. D. Pokhodenko, *Teor. Éksp. Khim.*, **33**, No. 5, 306-321 (1997). [*Theor. Experim. Chem.*, **33**, No. 5, 272-287 (1997).]
17. V. Pokhodenko, N. Guba, A. Kryukov, et al., *Functional Materials*, **5**, No. 3, 387-390 (1998).
18. A. I. Kryukov, N. P. Smirnova, A. V. Korzhak, et al., *Teor. Éksp. Khim.*, **34**, No. 6, 360-365 (1998). [*Theor. Experim. Chem.*, **34**, No. 6, 332-337 (1998).]
19. A. I. Kryukov, S. Ya. Kuchmii, and V. D. Pokhodenko, *Teor. Éksp. Khim.*, **36**, No. 2, 69-89 (2000). [*Theor. Experim. Chem.*, **36**, No. 2, 63-81 (2000).]
20. A. S. Kovalenko, S. Ya. Kuchmii, T. F. Makovskaya, et al., *Teor. Éksp. Khim.*, **39**, No. 2, 111-117 (2003). [*Theor. Experim. Chem.*, **39**, No. 2, 119-125 (2003).]
21. V. I. Yats'kiv, A. V. Korzhak, V. M. Granchak, et al., *Teor. Éksp. Khim.*, **39**, No. 3, 167-171 (2003). [*Theor. Experim. Chem.*, **39**, No. 3, 172-176 (2003).]
22. A. L. Stroyuk, A. V. Korzhak, A. E. Raevskaya, et al., *Nanosyst., Nanomater., Nanotekhnol.*, **1**, No. 2, 565-590 (2003).
23. A. L. Stroyuk, A. V. Korzhak, A. E. Raevskaya, and S. Ya. Kuchmii, *Teor. Éksp. Khim.*, **40**, No. 1, 1-6 (2004). [*Theor. Experim. Chem.*, **40**, No. 1, 1-6 (2004).]
24. N. I. Ermokhina, V. I. Yatskiv, A. V. Korzhak, et al., *Nanosyst., Nanomater., Nanotekhnol.*, **2**, No. 4, 1281-1285 (2004).
25. A. V. Korzhak, N. I. Ermokhina, A. L. Stroyuk, et al., *Teor. Éksp. Khim.*, **41**, No. 1, 24-29 (2005). [*Theor. Experim. Chem.*, **41**, No. 1, 26-31 (2005).]
26. A. E. Raevskaya, A. V. Korzhak, A. L. Stroyuk, and S. Y. Kuchmii, *Proc. of the Intern. Hydrogen Energy Congr. and Exhibition, IHEC 2005*, July 13-15, Istanbul, Turkey (2005).
27. A. V. Korzhak, A. E. Raevskaya, A. L. Stroyuk, et al., *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Springer, Netherlands (2007), pp. 587-597.
28. A. L. Stroyuk, A. E. Raevskaya, A. V. Korzhak, et al., *Teor. Éksp. Khim.*, **45**, No. 1, 8-16 (2009). [*Theor. Experim. Chem.*, **45**, No. 1, 12-22 (2009).]
29. M. L. Ghirardi, A. Dubini, J. Yu, and P.-C. Maness, *Chem. Soc. Rev.*, **38**, No. 1, 52-61 (2009).
30. K. Szacilowski, W. Macyk, A. Drzewiecka-Matuszek, et al., *Chem. Rev.*, **105**, No. 6, 2647-2694 (2005).
31. S. I. Allakhverdiev, V. D. Kreslavski, V. Thavasi, et al., *Photochem. Photobiol. Sci.*, **8**, No. 2, 148-156 (2009).
32. Jie Zhang, Pingwu Du, J. Schneider, et al., *J. Am. Chem. Soc.*, **129**, No. 25, 7726-7727 (2007).
33. A. A. Nada, H. A. Hamed, M. H. Barakat, et al., *Int. J. Hydrogen Energy*, **33**, No. 13, 3264-3269 (2008).
34. Z. Jin, X. Zhang, G. Lu, and S. Li, *J. Mol. Catal. A*, **259**, Nos. 1/2, 275-280 (2006).
35. Y. Astuti, E. Palomares, S. A. Haque, and J. R. Durrant, *J. Am. Chem. Soc.*, **127**, No. 43, 15120-15126 (2005).
36. Qiuye Li, Zhiliang Jin, Zhiguang Peng, et al., *J. Phys. Chem. C*, **111**, No. 23, 8237-8241 (2007).
37. Qiuye Li and Gongxuan Lu, *J. Mol. Catal. A*, **266**, Nos. 1/2, 75-79 (2007).
38. Yuexiang Li, Chengfu Xie, Shaoqin Peng, et al., *J. Mol. Catal. A*, **282**, Nos. 1/2, 117-123 (2008).
39. R. Abe, K. Sayama, and H. Arakawa, *J. Photochem. Photobiol. A*, **166**, Nos. 1-3, 115-122 (2004).
40. S. Ikeda, C. Abe, T. Torimoto, and B. Ohtani, *J. Photochem. Photobiol. A*, **160**, Nos. 1/2, 61-67 (2003).
41. N. Fu and G. Lu, *Catal. Lett.*, **127**, Nos. 3/4, 319-322 (2009).

42. N. Fu and G. Lu, *Appl. Surface Sci.*, **255**, No. 9, 4378-4383 (2009).
43. E. Reisner, J. C. Fontecilla-Camps, and F. A. Armstrong, *Chem. Commun.*, No. 5, 550-552 (2009).
44. Tianyou Peng, Dingning Ke, Ping Cai, et al., *J. Power Sources*, **180**, No. 1, 498-505 (2008).
45. N. Lakshminarasimhan, Eunyoung Bae, and Wonyong Choi, *J. Phys. Chem. C*, **111**, No. 42, 15244-15250 (2007).
46. K. Maeda, M. Eguchi, W. J. Youngblood, and T. E. Mallouk, *Chem. Mater.*, **20**, No. 21, 6770-6778 (2008).
47. K. Maeda, M. Eguchi, S.-H. A. Lee, et al., *J. Phys. Chem. C*, **113**, No. 18, 7962-7969 (2009).
48. Tianyou Peng, Ke Dai, Huabing Yi, et al., *Chem. Phys. Lett.*, **460**, Nos. 1-3, 216-219 (2008).
49. B. I. Fedoseev, E. N. Savinov, and V. N. Parmon, *Kinet. Katal.*, **28**, No. 5, 1111-1115 (1987).
50. Dengwei Jing and Liejin Guo, *Catal. Commun.*, **8**, No. 5, 795-799 (2007).
51. K. Ogisu, K. Takanabe, D. Lu, et al., *Bull. Chem. Soc. Jpn.*, **82**, No. 4, 528-535 (2009).
52. T. Hirai, K. Suzuki, and I. Komasaawa, *J. Colloid Interface Sci.*, **244**, No. 2, 262-265 (2001).
53. A. L. Stroyuk, A. I. Kryukov, S. Ya. Kuchmii, and V. D. Pokhodenko, *Teor. Éksp. Khim.*, **41**, No. 2, 67-87 (2005).
[*Theor. Experim. Chem.*, **41**, No. 2, 67-91 (2005).]
54. A. L. Stroyuk, A. I. Kryukov, S. Ya. Kuchmii, and V. D. Pokhodenko, *Teor. Éksp. Khim.*, **41**, No. 4, 199-218 (2005).
[*Theor. Experim. Chem.*, **41**, No. 4, 207-228 (2005).]
55. Shaohua Shen and Liejin Guo, *Mater. Res. Bull.*, **43**, No. 2, 437-446 (2008).
56. Yao Jun Zhang, Wei Yan, Yan Pei Wu, and Zhen Huan Wang, *Mater. Lett.*, **62**, No. 23, 3846-3848 (2008).
57. Chanjuan Xing, Dengwei Jing, Maochang Liu, and Liejin Guo, *Mater. Res. Bull.*, **44**, No. 2, 442-445 (2009).
58. J. C. Kim, J. Choi, Y. B. Lee, et al., *Chem. Commun.*, No. 48, 5024-5026 (2006).
59. W. Shangguan and A. Yoshida, *Solar Energy Mater. Solar Cells*, **69**, No. 2, 189-194 (2001).
60. W. Shangguan and A. Yoshida, *J. Phys. Chem. B*, **106**, No. 47, 12227-12230 (2002).
61. Su Young Ryu, J. Choi, W. Balcerski, et al., *Ind. Eng. Chem. Res.*, **46**, No. 23, 7476-7488 (2007).
62. Wenfeng Shangguan, *Sci. Technol. Adv. Mater.*, **8**, Nos. 1/2, 76-81 (2007).
63. Jihuai Wu, Jianming Lin, Shu Yin, and T. Sato, *J. Mater. Chem.*, **11**, No. 12, 3343-3347 (2001).
64. J. Choi, Y. Ryu, W. Balcerski, et al., *J. Mater. Chem.*, **18**, No. 20, 2371-2378 (2008).
65. Won-Wook So, Kwang-Je Kim, and Sang-Jin Moon, *Int. J. Hydrogen Energy*, **29**, No. 3, 229-234 (2004).
66. Sang Min Ji, Hwichan Jun, Jum Suk Jang, et al., *J. Photochem. Photobiol. A*, **189**, No. 1, 141-144 (2007).
67. H. Park, W. Choi, and M. R. Hoffmann, *J. Mater. Chem.*, **18**, No. 20, 2379-2385 (2008).
68. Jum Suk Jang, Sun Hee Choi, Hyun Gyu Kim, and Jae Sung Lee, *J. Phys. Chem.*, **112**, No. 44, 17200-17205 (2008).
69. Jum Suk Jang, Sang Min Ji, Sang Won Bae, et al., *J. Photochem. Photobiol. A*, **188**, No. 1, 112-119 (2007).
70. Jum Suk Jang, Hyun Gyu Kim, P. H. Borse, and Jae Sung Lee, *Int. J. Hydrogen Energy*, **32**, No. 18, 4786-4791 (2007).
71. G. Guan, T. Kida, K. Kusakabe, et al., *Appl. Catal. A*, **295**, No. 1, 71-78 (2005).
72. J. S. Jang, H. G. Kim, U. A. Joshi, et al., *Int. J. Hydrogen Energy*, **33**, No. 21, 5975-5980 (2008).
73. R. Brahimi, Y. Bessekhoud, A. Bouguelia, and M. Trari, **122**, Nos. 1/2, 62-65 (2007).
74. N. K. I. Senevirathna, P. K. D. D. P. Pitigaka, and K. Tennakone, *J. Photochem. Photobiol. A*, **171**, No. 3, 257-259 (2005).
75. J. Bandara, C. K. Udawatta, and C. S. K. Rajapakse, *Photochem. Photobiol. Sci.*, **4**, No. 11, 857-861 (2005).
76. A. Derbal, S. Omeiri, A. Bouguelia, and M. Trari, *Int. J. Hydrogen Energy*, **33**, No. 18, 4274-4282 (2008).
77. R. Brahimi, Y. Bessekhoud, A. Bouguelia, and M. Trari, *J. Photochem. Photobiol. A*, **186**, Nos. 2/3, 242-247 (2007).
78. Y. Ou, J. Lin, S. Fang, and D. Liao, *Chem. Phys. Lett.*, **429**, Nos. 1-3, 199-203 (2006).
79. A. Kudo, *Int. J. Hydrogen Energy*, **32**, No. 14, 2673-2678 (2007).
80. Meng Ni, M. K. H. Leung, D. Y. C. Leung, and K. Sumathy, *Renew. Sustain Energy Rev.*, **11**, No. 3, 401-425 (2007).
81. M. Matsuoka, M. Kitano, M. Takeuchi, et al., *Catal. Today*, **122**, Nos. 1/2, 51-61 (2007).
82. J. S. Lee, *Catal. Surv. Asia*, **9**, No. 4, 217-227 (2005).
83. A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, **38**, No. 1, 253-278 (2009).
84. A. Kudo, *Catal. Surv. Asia*, **7**, No. 1, 31-38 (2003).
85. I. Tsuji and A. Kudo, *J. Photochem. Photobiol. A*, **156**, Nos. 1-3, 249-252 (2003).
86. A. Kudo and M. Sekizawa, *Chem. Commun.*, No. 15, 1371-1372 (2000).
87. A. Kudo and M. Sekizawa, *Catal. Lett.*, **58**, 241-243 (1999).

88. E. Ekambaram, Y. Iikubo, and A. Kudo, *J. Alloys Compounds*, **433**, Nos. 1/2, 237-240 (2007).
89. Y. Wu, G. Lu, and S. Li, *J. Phys. Chem. C*, **113**, No. 22, 9950-9955 (2009).
90. T. Ishii, H. Kato, and A. Kudo, *J. Photochem. Photobiol. A*, **163**, Nos. 1/2, 181-186 (2004).
91. D. Wang, J. Ye, T. Kako, and T. Kimura, *J. Phys. Chem. B*, **110**, No. 32, 15823-15830 (2006).
92. R. Niishiro, H. Kato, and A. Kudo, *Phys. Chem. Chem. Phys.*, **7**, No. 10, 2241-2245 (2005).
93. H. Kato and A. Kudo, *J. Phys. Chem. B*, **106**, No. 19, 5029-5034 (2002).
94. A. Iwase, K. Saito, and A. Kudo, *Bull. Chem. Soc. Jpn.*, **82**, No. 4, 514-518 (2009).
95. Dong Won Hwang, Hyun Gyu Kim, Jae Sung Lee, et al., *J. Phys. Chem. B*, **109**, No. 6, 2093-2102 (2005).
96. D. W. Hwang, H. G. Kim, J. S. Jang, et al., *Catal. Today*, **93-95**, 845-850 (2004).
97. A. Kudo, R. Niishiro, A. Iwase, and H. Kato, *Chem. Phys.*, **339**, Nos. 1-3, 104-110 (2007).
98. Zhigang Zou and H. Arakawa, *J. Photochem. Photobiol. A*, **158**, Nos. 2/3, 145-162 (2003).
99. Zh. Zou, J. Ye, K. Sayama, and H. Arakawa, *J. Photochem. Photobiol. A*, **148**, Nos. 1-3, 65-69 (2002).
100. D. Wang, Z. Zou, and J. Ye, *Chem. Mater.*, **17**, No. 12, 3255-3261 (2005).
101. S. Yin, J. Wu, D. Ito, et al., *Composite Interfaces*, **11**, No. 2, 195-204 (2004).
102. K. Gurunathan, *Int. J. Hydrogen Energy*, **29**, No. 9, 933-940 (2004).
103. D. Jing, Y. Zhang, and L. Guo, *Chem. Phys. Lett.*, **415**, Nos. 1-3, 74-78 (2005).
104. D. Wang, J. Ye, H. Kitazawa, and T. Kimura, *J. Phys. Chem. C*, **111**, No. 34, 12848-12854 (2007).
105. D. Wang, Z. Zou, and J. Ye, *Chem. Phys. Lett.*, **411**, Nos. 4-6, 285-290 (2005).
106. D. W. Hwang, J. Kim, T. J. Park, and J. S. Lee, *Catal. Lett.*, **80**, Nos. 1/2, 53-57 (2002).
107. R. Konta, T. Ishii, H. Kato, and A. Kudo, *J. Phys. Chem. B*, **108**, No. 26, 8992-8995 (2004).
108. M. Kitano, M. Takeuchi, M. Matsuoka, et al., *Catal. Today*, **120**, No. 2, 133-138 (2007).
109. S. Fukumoto, M. Kitano, M. Takeuchi, et al., *Catal. Lett.*, **127**, Nos. 1/2, 39-43 (2009).
110. M. Kitano, K. Tsujimaru, and M. Anpo, *Top. Catal.*, **49**, Nos. 1/2, 4-17 (2008).
111. E. Selli, G. L. Chiarello, E. Quartarone, et al., *Chem. Commun.*, No. 47, 5022-5024 (2007).
112. M. Matsuoka, M. Kitano, S. Fukumoto, et al., *Catal. Today*, **132**, Nos. 1-4, 159-164 (2008).
113. M. Kitano, M. Takeuchi, M. Matsuoka, et al., *Chem. Lett.*, **34**, No. 4, 616-617 (2005).
114. R. Dholam, N. Patel, M. Adami, and A. Miotello, *Int. J. Hydrogen Energy*, **33**, No. 23, 6896-6903 (2008).
115. M. Matsuoka, M. Kitano, M. Takeuchi, et al., *Top. Catal.*, **35**, Nos. 3/4, 305-310 (2005).
116. Yong-Sheng Hu, A. Kleiman-Shwarsstein, A. J. Forman, et al., *Chem. Mater.*, **20**, No. 12, 3803-3805 (2008).
117. J. A. Glasscock, P. R. F. Barnes, I. C. Plumb, and N. Savvides, *J. Phys. Chem. C*, **111**, No. 47, 16477-16488 (2007).
118. A. Kleiman-Shwarsstein, Yong-Sheng Hu, A. J. Forman, et al., *J. Phys. Chem. C*, **112**, No. 40, 15900-15907 (2008).
119. Jian Yuan, Mingxia Chen, Jianwei Shi, and Wenfeng Shanguang, *Int. J. Hydrogen Energy*, **31**, No. 10, 1326-1331 (2006).
120. T. Sreethawong, S. Laehsatee, and S. Chavadej, *Catal. Commun.*, **10**, No. 5, 538-543 (2009).
121. T. Sreethawong, S. Laehsatee, and S. Chavadej, *Int. J. Hydrogen Energy*, **33**, No. 21, 5947-5957 (2008).
122. W.-C. Lin, W.-D. Yang, I.-L. Huang, et al., *Energy Fuels*, **23**, No. 4, 2192-2196 (2009).
123. M. Hara, J. Nunoshige, T. Takata, et al., *Chem. Commun.*, No. 24, 3000-3001 (2003).
124. M. Hara, G. Hitoki, T. Takata, et al., *Catal. Today*, **78**, Nos. 1-4, 555-560 (2003).
125. T. Mishima, M. Matsuda, and M. Miyake, *Appl. Catal. A*, **324**, 77-82 (2007).
126. K. Maeda, H. Terashima, K. Kase, et al., *Bull. Chem. Soc. Jpn.*, **81**, No. 8, 927-937 (2008).
127. M. Liu, W. You, Zh. Lei, et al., *Chem. Commun.*, No. 19, 2192-2193 (2004).
128. M. Liu, W. You, Zh. Lei, et al., *Chin. J. Catal.*, **27**, No. 7, 556-558 (2006).
129. S. M. Ji, P. H. Borse, H. G. Kim, et al., *Phys. Chem. Chem. Phys.*, **7**, No. 8, 1315-1321 (2005).
130. K. Maeda, K. Teramura, and K. Domen, *J. Catal.*, **254**, No. 2, 198-204 (2008).
131. K. Maeda, K. Teramura, D. Lu, et al., *J. Phys. Chem. C*, **111**, No. 20, 7554-7560 (2007).
132. K. Maeda, K. Teramura, D. Lu, et al., *J. Phys. Chem. B*, **110**, No. 28, 13753-13758 (2006).
133. K. Teramura, K. Maeda, T. Saito, et al., *J. Phys. Chem.*, **109**, No. 46, 21915-21921 (2005).
134. K. Maeda, K. Teramura, T. Takata, et al., *J. Phys. Chem.*, **109**, No. 43, 20504-20510 (2005).
135. Y. Lee, H. Terashima, Y. Shimodaira, et al., *J. Phys. Chem.*, **111**, No. 2, 1042-1048 (2007).

136. K. R. Reyes-Gil, E. A. Reyes-Garcia, and D. Raftery, *J. Phys. Chem.*, **111**, No. 39, 14579-14588 (2007).
137. K. G. Kanade, J.-O. Baeg, B. B. Kale, et al., *Int. J. Hydrogen Energy*, **32**, No. 18, 4678-4684 (2007).
138. S. K. Mohapatra, M. Misra, V. K. Mahajan, and K. S. Raja, *J. Phys. Chem.*, **111**, No. 24, 8677-8685 (2007).
139. J. H. Park, S. Kim, and A. J. Bard, *Nano Lett.*, **6**, No. 1, 24-28 (2006).
140. Z. Liu, B. Pesic, K. S. Raja, et al., *Int. J. Hydrogen Energy*, **34**, No. 8, 3250-3257 (2009).
141. Y. A. Shaban and S. U. M. Khan, *Int. J. Hydrogen Energy*, **33**, No. 4, 1118-1126 (2008).
142. Y. A. Shaban and S. U. M. Khan, *J. Solid State Electrochem.*, **13**, No. 7, 1025-1036 (2009).
143. Y. Sun, C. J. Murphy, K. R. Reyes-Gil, et al., *Int. J. Hydrogen Energy*, **33**, No. 21, 5967-5974 (2008).
144. L. K. Randeniya, A. B. Murphy, and I. C. Plumb, *J. Mater. Sci.*, **43**, No. 4, 1389-1399 (2008).
145. K. Ogisu, A. Ishikawa, K. Teramura, et al., *Chem. Lett.*, **36**, No. 7, 854-855 (2007).
146. K. Gurunathan, J.-O. Baeg, Sang Mi Lee, et al., *Int. J. Hydrogen Energy*, **33**, No. 11, 2646-2652 (2008).
147. Su Young Ryu, W. Balcerski, T. K. Lee, and M. R. Hoffmann, *J. Phys. Chem. C*, **111**, No. 49, 18195-18203 (2007).
148. T. Hirai, M. Nanba, and I. Komasaawa, *J. Colloid Interface Sci.*, **268**, No. 2, 394-399 (2003).
149. A. Henglein and M. Gutierrez, *Ber. Bunsenges. Phys. Chem.*, **87**, No. 2, 852-858 (1983).
150. A. Deshpande, P. Shah, R. S. Gholap, and N. M. Gupta, *J. Colloid Interface Sci.*, **333**, No. 1, 263-268 (2009).
151. T. Hirai, Y. Bando, and I. Komasaawa, *J. Phys. Chem. B*, **106**, No. 35, 8967-8970 (2002).
152. T. Hirai, M. Nanba, and I. Komasaawa, *J. Colloid Interface Sci.*, **252**, No. 1, 89-92 (2002).
153. B. B. Kale, J.-O. Baeg, S. K. Apte, et al., *J. Mater. Chem.*, **17**, No. 40, 4297-4303 (2007).
154. P. S. Lunawat, S. Senapati, R. Kumar, and N. M. Gupta, *Int. J. Hydrogen Energy*, **32**, No. 14, 2784-2790 (2007).
155. D. Jing and L. Guo, *J. Phys. Chem. B*, **110**, No. 23, 11139-11145 (2006).
156. K. G. Kanade, J.-O. Baeg, U. P. Mulik, et al., *Mater. Res. Bull.*, **41**, No. 12, 2219-2225 (2006).
157. T. Hirai, Y. Nomura, and I. Komasaawa, *J. Nanoparticle Res.*, **5**, No. 1, 61-67 (2003).
158. Shaohua Shen, Liang Zhao, and Liejin Guo, *Int. J. Hydrogen Energy*, **33**, No. 17, 4501-4510 (2008).
159. Zh. Lei, W. You, M. Liu, et al., *Chem. Commun.*, No. 17, 2142-2143 (2003).
160. Ma Guijun, Yan Hongjian, Zong Xu, et al., *Chin. J. Catal.*, **29**, No. 4, 313-315 (2008).
161. Shaohua Shen, Liang Zhao, and Liejin Guo, *Mater. Res. Bull.*, **44**, No. 1, 100-105 (2009).
162. S. Shen, L. Zhao, Z. Zhou, and L. Guo, *J. Phys. Chem.*, **112**, No. 41, 16148-16155 (2008).
163. Mingtao Li, Jinzhan Su, and Liejin Guo, *Int. J. Hydrogen Energy*, **33**, No. 12, 2891-2896 (2008).
164. L. Zheng, Y. Xu, Y. Song, et al., *Inorg. Chem.*, **48**, No. 9, 4003-4009 (2009).
165. I. Tsuji, H. Kato, and A. Kudo, *Chem. Mater.*, **18**, No. 7, 1969-1975 (2006).
166. I. Tsuji, H. Kato, H. Kobayashi, and A. Kudo, *J. Phys. Chem. B*, **109**, No. 15, 7323-7329 (2005).
167. Y. Li, G. Chen, C. Zhou, and J. Sun, *Chem. Commun.*, No. 15, 2020-2022 (2009).
168. A. Kudo, I. Tsuji, and H. Kato, *Chem. Commun.*, No. 17, 1958-1959 (2002).
169. B. B. Kale, J.-O. Baeg, S. M. Lee, et al., *Adv. Funct. Mater.*, **16**, No. 10, 1349-1354 (2006).
170. Di Chen and Jinhua Ye, *J. Phys. Chem. Solids*, **68**, 2317-2320 (2007).
171. A. Kudo, A. Nagane, I. Tsuji, and H. Kato, *Chem. Lett.*, No. 9, 882-883 (2002).
172. S. Shen and L. Guo, *J. Solid State Chem.*, **179**, No. 8, 2629-2635 (2006).
173. Y. Bessekhoud, M. Mohammedi, and M. Trari, *Solar Energy Mater. Solar Cells*, **73**, No. 3, 339-350 (2002).
174. Kai Zhang, Dengwei Jing, Chanjuan Xing, and Liejin Guo, *Int. J. Hydrogen Energy*, **32**, No. 18, 4685-4691 (2007).
175. F. del Valle, A. Ishikawa, K. Domen, et al., *Catal. Today*, **143**, Nos. 1/2, 51-56 (2009).
176. A. M. Roy and G. C. De, *J. Photochem. Photobiol. A.*, **157**, No. 1, 87-92 (2003).
177. X. Zhang, D. Jing, M. Liu, and L. Guo, *Catal. Commun.*, **9**, No. 8, 1720-1724 (2008).
178. A. Koca and M. Şanin, *Int. J. Hydrogen Energy*, **27**, No. 4, 363-367 (2002).
179. M. Sathish and R. P. Viswanath, *Catal. Today*, **129**, Nos. 3/4, 421-427 (2007).
180. M. Sathish, B. Viswanathan, and R. P. Viswanath, *Int. J. Hydrogen Energy*, **31**, No. 7, 891-898 (2006).
181. Y. Li, Y. Du, S. Peng, et al., *Int. J. Hydrogen Energy*, **33**, No. 8, 2007-2013 (2008).
182. R. M. Navarro, F. del Valle, and J. L. G. Fierro, *Int. J. Hydrogen Energy*, **33**, No. 16, 4265-4273 (2008).
183. L. A. Silva, Su Young Ryu, J. Choi, et al., *J. Phys. Chem. C*, **112**, No. 32, 12069-12073 (2008).
184. T. Kida, G. Guan, Y. Minami, et al., *J. Mater. Chem.*, **13**, No. 5, 1186-1191 (2003).

185. T. Kida, G. Guan, N. Yamada, et al., *Int. J. Hydrogen Energy*, **29**, No. 3, 269-274 (2004).
186. Z. G. Yu, C. E. Pryor, W. H. Lau, et al., *J. Phys. Chem. B*, **109**, No. 48, 22913-22919 (2005).
187. Jum Suk Jang, U. A. Joshi, and Jae Sung Lee, *J. Phys. Chem.*, **111**, No. 35, 13280-13287 (2007).
188. G. Ma, H. Yan, J. Shi, et al., *J. Catal.*, **260**, No. 1, 134-140 (2008).
189. S. Saadi, A. Bouguelia, A. Derbal, and M. Trari, *J. Photochem. Photobiol. A*, **187**, No. 1, 97-104 (2007).
190. N. Koriche, A. Bouguelia, and M. Trari, *Int. J. Hydrogen Energy*, **31**, No. 9, 1196-1203 (2006).
191. N. Koriche, A. Bouguelia, A. Aider, and M. Trari, *Int. J. Hydrogen Energy*, **30**, No. 7, 693-699 (2005).
192. H. Yang, J. Yan, Z. Lu, et al., *J. Alloys Compounds*, **476**, Nos. 1/2, 715-719 (2009).
193. J. Ye, Z. Zou, H. Arakawa, et al., *J. Photochem. Photobiol. A*, **148**, Nos. 1-3, 79-83 (2002).
194. J. Ye, Zh. Zou, M. Oshikiri, et al., *Chem. Phys. Lett.*, **356**, Nos. 3/4, 221-226 (2002).
195. L. Xu, L. Sang, C. Ma, et al., *Chin. J. Catal.*, **27**, No. 2, 100-102 (2006).
196. Z. Shan, J. Wu, F. Xu, et al., *J. Phys. Chem. C*, **112**, No. 40, 15423-15428 (2008).
197. B. Yang, P. R. F. Barnes, Y. Zhang, and V. Luca, *Catal. Lett.*, **118**, 280-284 (2007).
198. S. Somasundaram, C. R. N. Chenthamarakshan, N. R. de Tacconi, and K. Rajeshwar, *Int. J. Hydrogen Energy*, **32**, No. 18, 4661-4669 (2007).
199. F. A. Frame, E. C. Carroll, D. S. Larsen, et al., *Chem. Commun.*, No. 19, 2206-2208 (2008).
200. Y. Gao, Y. Wang, and Y. Wang, *React. Kinet. Catal. Lett.*, **91**, No. 1, 13-19 (2007).
201. T. Kida, Y. Minami, G. Guan, et al., *J. Mater. Sci.*, **41**, No. 11, 3527-3534 (2006).
202. H. Yoneyama, N. Matsumoto, and H. Tamura, *Bull. Chem. Soc. Jpn.*, **59**, No. 10, 3302-3304 (1986).
203. Jum Suk Yang, Dong Jim Ham, N. Lakshminarasimhan, et al., *Appl. Catal. A*, **346**, Nos. 1/2, 149-154 (2008).
204. X. Zong, H. Yan, G. Wu, et al., *J. Am. Chem. Soc.*, **130**, No. 23, 7176-7177 (2008).
205. J. P. Yasomanee and J. Bandara, *Solar Energy Mater. Solar Cells*, **92**, No. 3, 348-352 (2008).
206. B. D. Alexander, P. J. Kulesza, I. Rutkowska, et al., *J. Mater. Chem.*, **18**, No. 20, 2298-2303 (2008).
207. A. Kudo, H. Kato, and I. Tsuji, *Chem. Lett.*, **33**, No. 12, 1534-1539 (2004).
208. K. Sayama, K. Mukasa, R. Abe, et al., *J. Photochem. Photobiol. A*, **148**, Nos. 1-3, 71-77 (2002).
209. K. Sayama, K. Mukasa, R. Abe, et al., *Chem. Commun.*, No. 23, 2416-2417 (2001).
210. D. Schürch, A. Currao, S. Sarkar, et al., *J. Phys. Chem. B*, **106**, No. 49, 12764-12775 (2002).
211. R. Abe, K. Sayama, and H. Sugihara, *J. Phys. Chem. B*, **109**, No. 33, 16052-16061 (2005).
212. R. Abe, T. Takata, H. Sugihara, and K. Domen, *Chem. Commun.*, No. 30, 3829-3831 (2005).
213. M. Higashi, R. Abe, T. Takata, and K. Domen, *Chem. Mater.*, **21**, No. 8, 1543-1549 (2009).
214. M. Higashi, R. Abe, A. Ishikawa, et al., *Chem. Lett.*, **37**, No. 2, 138-139 (2008).
215. H. Kato, M. Hori, R. Kenta, et al., *Chem. Lett.*, **33**, No. 10, 1348-1349 (2004).
216. H. Kato, Y. Sasaki, A. Iwase, and A. Kudo, *Bull. Chem. Soc. Jpn.*, **80**, No. 12, 2457-2464 (2007).
217. S. W. Bae, S. M. Ji, S. J. Hong, et al., *Int. J. Hydrogen Energy*, **34**, No. 8, 3243-3249 (2009).
218. M. Paulose, G. K. Mor, O. K. Varghese, et al., *J. Photochem. Photobiol. A*, **178**, No. 1, 8-15 (2006).
219. M. Alam Khan, M. Shaheer Akhtar, Seong Ihl Woo, and O-Bong Yang, *Catal. Commun.*, **10**, No. 1, 1-5 (2008).
220. Z. Zou, J. Ye, and H. Arakawa, *J. Phys. Chem. B*, **106**, No. 51, 13098-13101 (2002).
221. J. S. Jang, H. G. Kim, V. R. Reddy, et al., *J. Catal.*, **231**, No. 1, 213-222 (2005).
222. Guosheng Wu and Aicheng Chen, *J. Photochem. Photobiol. A*, **195**, No. 1, 47-53 (2008).
223. M. Kitano, K. Iyatani, K. Tsujimaru, et al., *Top. Catal.*, **49**, Nos. 1/2, 24-31 (2008).
224. K. Maeda, T. Takata, M. Hara, et al., *J. Am. Chem. Soc.*, **127**, No. 23, 8286-8287 (2005).
225. Hui Liu, Jian Yuan, Wenfeng Shangguang, and Y. Teraoka, *J. Phys. Chem.*, **112**, No. 23, 8521-8523 (2008).
226. K. Sayama, A. Nomura, T. Arai, et al., *J. Phys. Chem. B*, **110**, No. 23, 11352-11360 (2006).
227. S. Saremi-Yarahmadi, K. G. Upul Wijayantha, A. A. Tahir, and B. Vaidhyanathan, *J. Phys. Chem. C*, **113**, No. 12, 4768-4778 (2009).
228. S. Saremi-Yarahmadi, A. A. Tahir, B. Vaidhyanathan, and K. G. Upul Wijayantha, *Mater. Lett.*, **63**, No. 5, 523-526 (2009).
229. W. J. Youngblood, S.-H. A. Lee, Y. Kobayashi, et al., *J. Am. Chem. Soc.*, **131**, No. 3, 926-927 (2009).
230. Y. Hosogi, Y. Shimodaira, H. Kato, et al., *Chem. Mater.*, **20**, No. 4, 1299-1307 (2008).

- 231. Z. Zou, J. Ye, and H. Arakawa, *Int. J. Hydrogen Energy*, **28**, No. 6, 663-669 (2003).
- 232. M. Oshikiri, M. Boero, J. Ye, et al., *J. Chem. Phys.*, **117**, No. 15, 7313-7318 (2002).
- 233. Z. Zou, J. Ye, and H. Arakawa, *Mater. Res. Bull.*, **36**, Nos. 7/8, 1185-1193 (2001).
- 234. J. Ye, Z. Zou, and A. Matsushita, *Int. J. Hydrogen Energy*, **28**, No. 6, 651-655 (2003).
- 235. M. Tian, W. Shangguan, J. Yuan, et al., *Appl. Catal. A*, **309**, No. 1, 76-84 (2006).
- 236. D.-Z. Guo, G.-M. Zhang, Z.-X. Zhang, et al., *J. Phys. Chem. B*, **110**, No. 4, 1571-1575 (2006).
- 237. K. Maeda, X. Wang, Y. Nishihara, et al., *J. Phys. Chem. C*, **113**, No. 12, 4940-4947 (2009).