Heteropoly Acid–Incorporated TiO2 Colloids as Novel Photocatalytic Systems Resembling the Photosynthetic Reaction Center

4 AUTHORS, INCLUDING:

Minjoong Yoon
Chungnam National University
87 PUBLICATIONS   1,527 CITATIONS

Heteropoly Acid-Incorporated TiO$_2$ Colloids as Novel Photocatalytic Systems Resembling the Photosynthetic Reaction Center

Minjoong Yoon,* Jeong Ah Chang, Yanghee Kim, and Jun Rye Choi

Department of Chemistry, Chungnam National University, Taejon, 305-764, Korea

Kwan Kim and Seung Joon Lee

Department of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul, 151-742, Korea

TiO$_2$ colloids are very useful photocatalytic systems, capable of converting solar energy to chemical or electrical energy and environmental cleaning. The key step in enhancing photocatalytic efficiency is improving photoinduced interfacial electron transfer like plant photosynthesis. It remains difficult to modify TiO$_2$ particles as a real analogue of the photosynthetic reaction centers of green plants. We attempted to incorporate a photoreactive heteropoly acid (HPA) such as H$_3$PW$_{12}$O$_{40}$ into TiO$_2$ colloids in aqueous polyvinyl alcohol (PVA) (0.1%) solution, and found that two light reactions appear to operate in a series. Upon illumination of the HPA/TiO$_2$ system with near-UV light (300−375 nm), interfacial electron transfer takes place from the conduction band of TiO$_2$ to the incorporated HPA, which is also excited to catalyze photoreduction of Methyl Orange. The extent of the photoinduced reduction of the HPA adsorbed on TiO$_2$ particles depends on the concentration ratio of the HPA and TiO$_2$ colloids, irradiation wavelength, and intensity of radiation. It is found that the interfacial electron-transfer mechanism of HPA/TiO$_2$ is quite analogous to the "Z-scheme" mechanism for plant photosynthetic systems. The photoinduced charge-carrier generation at the heterojunction is very efficient, and the photoreduction of Methyl Orange has been observed to be synergistically enhanced upon illumination of the HPA-incorporated TiO$_2$ with visible light as well as near-UV light.

Introduction

The photocatalytic reactions of inorganic and organic compounds have been important research topics in relation to solar energy conversion into chemical energy and environmental cleaning.[1−6] The most widely investigated route for photocatalytic reaction is interfacial electron transfer in semiconductors.[7−9] In view of the importance of the semiconductor as the photocatalyst, it is highly desirable to obtain efficient semiconductor materials which possess physical characteristics such as suitable band gap energies and stability toward photocorrosion. Among several semiconductors, TiO$_2$ has been shown to be the most suitable material with a relatively favorable band gap energy, offering the highest light energy conversion efficiency.[10−16]

In the past two decades a number of research groups have studied the electron-transfer reactions in TiO$_2$ colloids.[10−21] Their research results have shown that the TiO$_2$ colloids are useful for the photodissociation of water into H$_2$ and O$_2$[10−16] as well as the photodestruction of organic contaminants in water[17−19] or the photoreduction of nitrogen and carbon dioxide,[20,21] and the photoinduced electron-transfer reactions of the liquid-junction photovoltaic cells have shown a resemblance to the plant photosynthetic process.[10−16] However, in most cases the photon-to-electron conversion efficiency remained low, even though many research groups made many efforts to improve it through modification of the TiO$_2$ surface by adsorption of photosensitive dyes such as phthalocyanines,[15,16] Ru(bpy)$_3^{2+}$ and derivatives,[22] and 8-hydroxyquinoline complex.[23] Recently a

remarkable advance was made by Grätzel et al., who developed the dye-sensitized mesoporous TiO$_2$ solar cells with the highest photon-to-electron conversion quantum yield (33%).[11] However, efficient methods to decompose water without electricity have not been discovered yet. This is probably because most of the conventional systems use light absorbed by either TiO$_2$ or the sensitizer dye. Thus, it is worthwhile to attempt to make a novel photocatalytic system operated by the two photochemical reactions mimicking the plant photosynthetic process.

In this work, heteropoly acid (HPA), particularly H$_3$PW$_{12}$O$_{40}$, has been employed to modify the TiO$_2$ particle surface. The Keggin-type heteropoly acids, H$_{8−x}$XM$_{12}$O$_{40}$, where X is the central atom (P^{5+}, Si^{4+}, etc.), x is its oxidation state, and M is the metal ion (Mo^{6+}, W^{6+}, etc.), have received interesting attention as reagents or catalysts for redox processes involving organic substrates,[24] since they are well-known to be good electron acceptors which can store several electrons per molecule.[25−28] They have been also observed to be reduced in the presence of alcohol upon illumination of near-UV light producing the heteropoly blue as a reduced product which shows new absorption bands at 480 and 750 nm.[29] The blue components are known to be moderate reducing agents so that they can sensitize the photochemical reduction of oxygen and water.[28] Guendet and Grätzel have demonstrated that sodium metatungstate, Na$_6$[H$_2$W$_{12}$O$_{40}$], can act as a redox relay in the photoreduction of water by the photosynthetic membrane.[30] Thus, the HPA would be useful as an analogue of the plant photosystem I by incorporating with TiO$_2$. In fact, we have found a resemblance of the HPA-incorporated TiO$_2$ system to the plant photosynthetic reaction centers by observing the efficient

* To whom correspondence should be addressed. Telephone: 82-42-821-6546. FAX: 82-42-823-7008. E-mail: mjyoon@cnu.ac.kr.

photoinduced interfacial electron-transfer from TiO_2 colloids to heteropoly acids and the synergistic enhancement of the catalytic activity of photoreduction of Methyl Orange in aqueous solution.

Experimental Section

Titanium(VI) tetraisopropoxide (97%) and polyvinyl alcohol (average M_w 31,000−50,000) were purchased from Aldrich Chemical Co. Heteropoly acid [HPA; phosphotungstic acid hydrate ($H_3PW_{12}O_{40}$)] and Methyl Orange (ACS reagent) were purchased from Fluka and Aldrich Chemical Co., respectively. They were purified by repetitive recrystallization with water. 2-Propanol was purchased from Merck Chemical Co. as spectroscopic grade and used without further purification. Four absorption bands at 1072, 976, 880, and 792 cm^{-1} are typical of the Keggin unit.[31] The lines at 1072 and 976 are assigned to P−O and W=O groupings, while the two others are due to W−O−W vibrations.

Colloidal TiO_2 was prepared by the method described by Grätzel.[4] One gram of titanium(VI) tetraisopropoxide Ti(OCH-(CH_3)$_2$)$_4$ was dissolved in 20 mL of 2-propanol. A 10 mL sample of this solution was slowly dropped into 100 mL of acidified water (pH 1.5, adjusted with HCl). This mixture was stirred until it was virtually clear. After vacuum evaporation of the solvent, a transparent solution of colloidal TiO_2 particles (0.5 g/L) was obtained. Particle sizes and crystallinity were established via EF-TEM (energy filtering transmission electron microscopy) on EM912-OMEGA. TEM samples were prepared in which a colloid drop flowed across an amorphous carbon substrate. This procedure minimizes particle aggregation on the substrate, if the crystallites are initially well dispersed in the colloid. TEM demonstrated that the colloidal particles are spherical with a mean particle radius of 200. The number of TiO_2 molecules per colloidal particle were 8.4×10^5 as calculated by[32]

$$N = (4\pi r^3/3)(\rho A/M) \qquad (1)$$

where r is the radius of a colloidal particle, M is the molecular weight, ρ is the density, and A is Avogadro's number.

Infrared spectra of aqueous HPA and HPA/TiO_2 solutions were obtained using a Bruker IFS 113v spectrometer equipped with a Harrick 9-reflection ZnSe prism liquid cell and a wide-band, liquid N_2 cooled cadmium mercury telluride detector. A Harrick diffuse reflectance optical unit was employed when obtaining the diffuse reflectance infrared Fourier transform (DRIFT) spectrum of powdered HPA.

The absorption spectra were measured on a Cary 3E UV−vis spectrophotometer. A high-pressure Hg Arc lamp in conjunction with a monochromator (1350 grooves/mm, Bausch & Lomb) or 450 W Xe lamp with cutoff filters ($\lambda \geq 320$ nm) were used as the light source. Light intensities were measured using potassium ferrioxalate actinometry as developed by Hatchard and Parker.[33] Sample solutions in a Pyrex tube (transmittance 22.7%) with a Pyrex cutoff ($\lambda \geq 320$ nm) or band-pass filter (270−390 nm) were degassed with nitrogen gas. In our experiments the concentration of heteropoly acids must be selected over 5×10^{-5} M. The extinction values were determined immediately on diluting a stock solution in order to eliminate errors from the slow dissociation of anion noticeable at concentration less than about 5×10^{-5} M. The photoreduction of HPA or Methyl Orange was monitored by analysis of absorption spectra in the prescence of colloidal TiO_2 or TiO_2/HPA.

Transient absorption spectra were obtained by a Q-switched nanosecond Nd:YAG laser (10 Hz, pulse width 7 ns) with 355 nm excitation light and a 250 W tungsten lamp as the monitoring light source. The monitoring light was oriented perpendicularly to the exciting laser beam, passed through a grating monochromator, and detected with a photomultiplier (Hamamatsu R-928) and a storage oscilloscope (LeCroy 9310A, 400 MHz).

Results and Discussion

1. FT-IR Spectral Characteristics of HPA/TiO_2. Most of the infrared spectra of HPA previously reported were taken in a solid state after pressing into a disk with dried KBr. However, Herring and McCormick[34] recently found that the infrared spectrum of the KBr pellet of HPA resembles, under any hydration condition, the spectrum of the potassium salt (KPA) of HPA. This implies that any exposure of HPA to metal cations results in formation of the corresponding metal salt. The same authors also found that the infrared peaks of HPA are dependent on the extent of water present. Edwards et al.[31] performed ^{31}P and ^{1}H magic angle spinning (MAS) NMR and FT-IR experiments to investigate the surface structure of HPA supported on extruded, pressed, and powdered TiO_2. They concluded that HPA should present in at least five forms on the titania surface. However, to obtain infrared spectra, samples were prepared in 10 wt %, and it is not certain whether the IR peak shifts observed are intrinsic to HPA/TiO_2 or they are due to the formation of the potassium salt of HPA.

Considering all the reported infrared data, we attempted to record the infrared spectra of HPA and its mixture with TiO_2 in the aqueous phase. Before taking the solution spectra, we obtained the DRIFT spectrum for the purified, neat HPA powder without mixing with KBr. In fact, the Keggin ion bands of the powdered HPA were identified at 1155 and 1099 cm^{-1} for $\nu_{as}(PO)$, 1020 cm^{-1} for $\nu_{as}(WO_tH)$, 920 cm^{-1} for $\nu_{as}(WO_c)$, and 866 cm^{-1} for $\nu_{as}(WO_e)$. Recalling the reports of Herring and McCormick,[34] the present HPA powder is neither in fully hydrated nor in hexahydrated state; both species seem to be co-present in the ambient condition. When taking the infrared spectra of aqueous solutions, D_2O was used as the reference material, but the Keggin ion bands were barely identifiable due to the stronger H_2O absorption. Hence, the H_2O absorption was subtracted from the measured spectra of HPA and HPA + TiO_2 solutions. Curves a and b in Figure 1 are the infrared spectra thus obtained in the 1200−750 cm^{-1} region for the aqueous solutions of 5×10^{-3} M HPA and 5×10^{-4} M HPA + 5×10^{-2} M TiO_2, respectively; even by a computer subtraction method, however, the O−H stretching and bending regions were not resolved clearly. As can be seen in Figure 1a, for free HPA the Keggin ion bands are observed at 1080 cm^{-1} for $\nu_{as}(PO)$, 984 cm^{-1} for $\nu_{as}(WO_tH)$, 903 cm^{-1} for $\nu_{as}(WO_c)$, and 818 cm^{-1} for $\nu_{as}(WO_e)$. In the presence of TiO_2 colloids (Figure 1b), the corresponding bands are identified at 1080 cm^{-1} for $\nu_{as}(PO)$, 979 cm^{-1} for $\nu_{as}(WO_tH)$, 895 cm^{-1} for $\nu_{as}(WO_c)$, and 810 cm^{-1} for $\nu_{as}(WO_e)$. The peak positions of HPA in the dissolved state are substantially different from those in the powdered state. Rather they are close to those observed for the potassium salt of HPA. In the presence of TiO_2, the P−O stretching band is barely affected, but the W−O stretching bands are all red shifted by 5−8 cm^{-1}.

In fact, the observation made on the $\nu_{as}(PO)$ is consistent with the report that the vibrational motion of the phosphate group is independent of the remaining cage of the anion; the equivalent mode in free PO_4^{3-} is also observed at 1080 cm^{-1}. On the other hand, the red shift of the $\nu(WO)$ modes in Figure

HPA-Incorporated TiO$_2$ Colloids

*J. Phys. Chem. B, Vol. 105, No. 13, 2001* **2541**
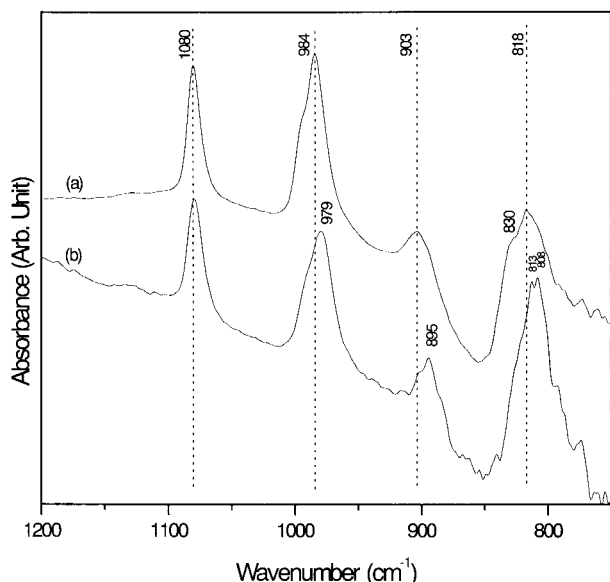
Figure 1. Infrared spectra of aqueous solutions of (a) 5×10^{-3} M HPA and (b) 5×10^{-4} M HPA + 5×10^{-2} M TiO$_2$.
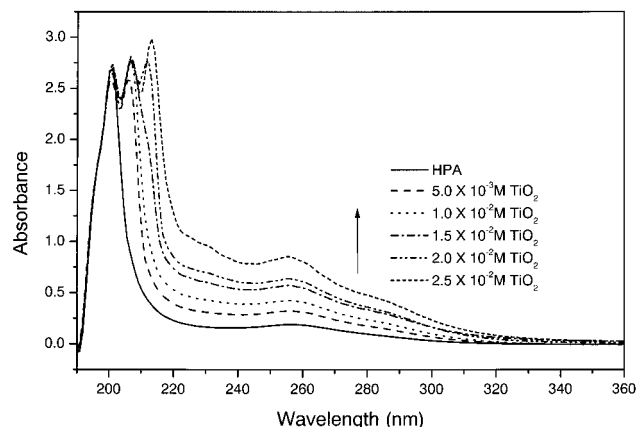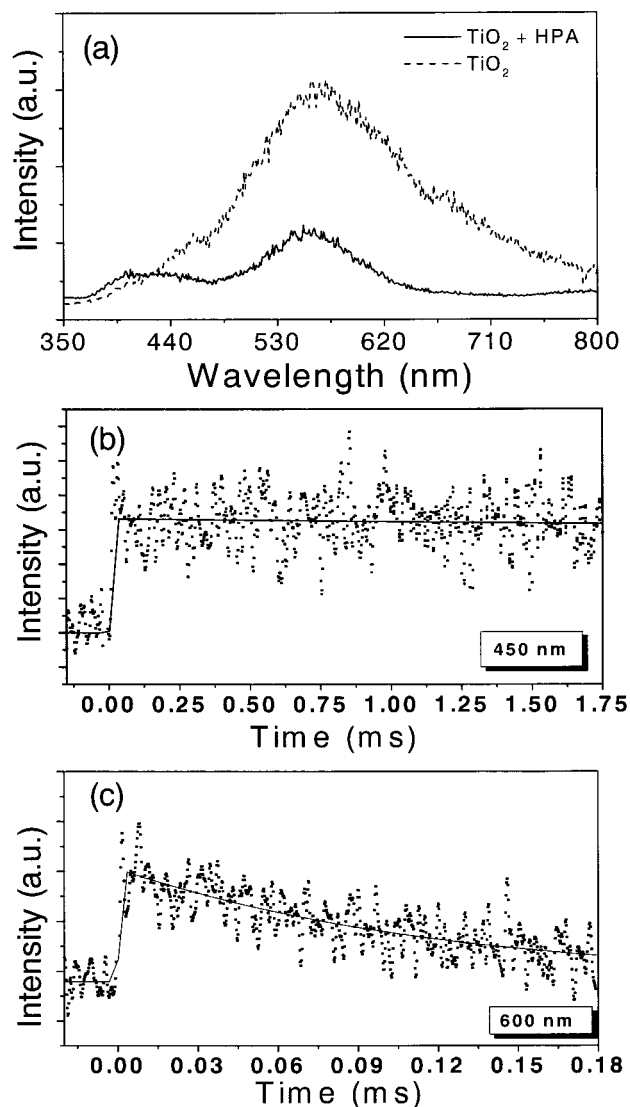

Figure 2. Absorption spectra of 5×10^{-5} M H$_3$PW$_{12}$O$_{40}$ in the absence and presence of TiO$_2$ at different concentrations in aqueous solution.

1 is indicative of the direct interaction of HPA with TiO$_2$ in H$_2$O. The amount of red shift observed herein in the aqueous phase is 2−3 times larger than that by observed Edwards et al. in the powdered state of HPA/TiO$_2$. This indicates that much stronger hydrogen bonds are formed in the solution phase than in the dried state between the oxygen atoms of Keggin ion and the hydroxyl groups of titania. The W=O$_t$⋯HO−Ti type hydrogen bond is supposed to be dominant in the aqueous solution of HPA and TiO$_2$. Since the ν_{as}(WO$_c$) and ν_{as}(WO$_e$) modes are more red shifted than the ν_{as}(WO$_t$) mode upon interacting with TiO$_2$, other types of hydrogen bonding, i.e., W−O$_c$⋯HO−Ti and W−O$_e$⋯HO−Ti, may also contribute to the final distribution of interaction species. Although Edwards et al.[31] concluded that HPA is present in least five forms on the powdered HPA/TiO$_2$ surface (a bulk salt phase, two weakly bound intact Keggin species, and partially and fully fragmented clusters), we presume that three different hydrogen bonds are involved when Keggin ions interact in the solution phase with the hydroxylated colloidal TiO$_2$ surface.

2. Interfacial Electron Transfer at Heterojunction of HPA/ TiO$_2$. Figure 2 shows the absorption spectrum of 5×10^{-5} M H$_3$PW$_{12}$O$_{40}$ (HPA) in the presence of various concentrations of colloidal TiO$_2$ (0.05 g/L). In the absence of TiO$_2$, the HPA shows dominant peaks at 223 and 256 nm due to oxygen-to-
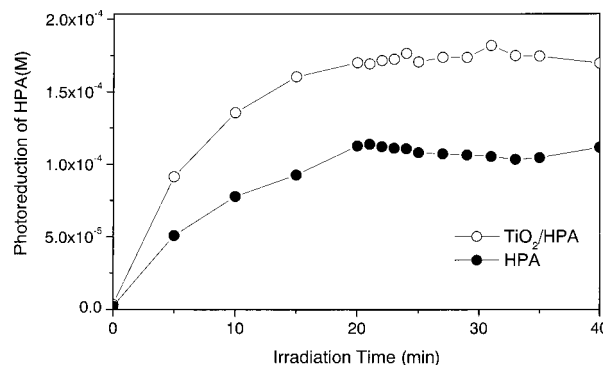

Figure 3. Photoreduction of HPA in 0.1% PVA aqueous solution in the absence and presence of TiO$_2$ colloids (0.5 g/L), as monitored by the absorbance increase at 748 nm as a function of irradiation time.

Figure 4. Transient absorption spectra of 5×10^{-3} M HPA with colloidal TiO$_2$ (5 g/L) in 0.1% PVA aqueous solution (a) and time profile of the absorption at 450 (b) and 600 nm (c).

tungsten charge transfer.[35] Adding colloidal TiO$_2$ to the HPA aqueous solution, the absorbance at 223 or 256 nm gradually increases, indicating that the HPA is adsorbed on TiO$_2$ colloidal surface. According to the measurement of solid state ^{31}P and ^{1}H MAS NMR by Knifton et al., the chemical nature of the HPA adsorbed on powdered TiO$_2$ was reported to be changed.[31] When HPAs in aqueous polyvinyl alcohol (PVA) solution are

SCHEME 1:   Energy Diagram: (A) Photosynthesis in Green Plants; (B) Photoinduced Electron Transfer at the Heterojunction of HPA/TiO$_2$ Colloids in the Presence of 0.1% PVA as an Electron Donor

(A)

(B)
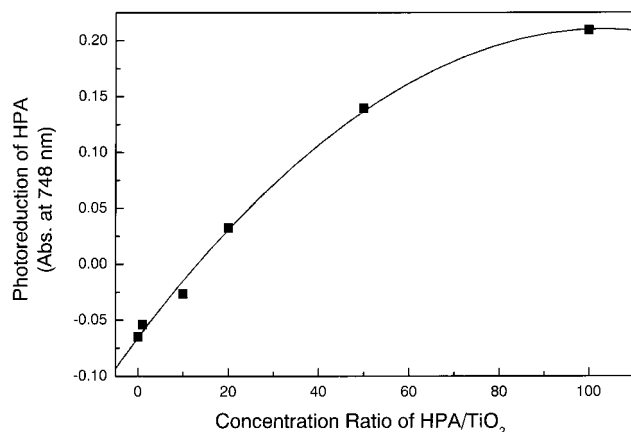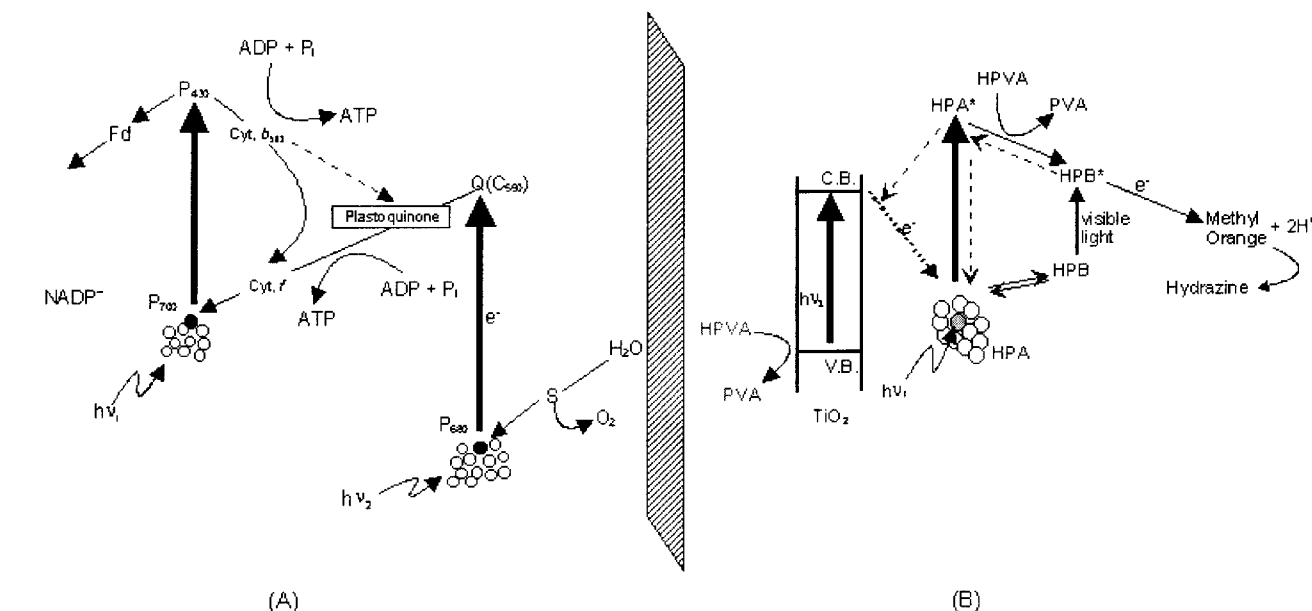
Figure 5. Photoreduction of HPA as monitored by the absorption at 748 nm after 60 min irradiation in the presence of various concentration ratios of HPA and TiO$_2$.

illuminated at 310 nm, they are reduced to so-called heteropoly blues, showing new absorption bands at 480 nm ($\epsilon = 1000$ L·mol^{-1}·cm^{-1}) and 750 nm ($\epsilon = 2000$ L·mol^{-1}·cm^{-1}), due to the d–d or intervalence charge transfer (W(VI) → W(V)).[29] The absence of PVA resulted in no steady-state photoreduction of HPA. The illumination wavelength is effective only in the range between 300 and 350 nm, assigned as a charge transfer from the π-character bridging oxygen to metal. These results indicate that the photoreduction of HPA in the PVA aqueous solution proceeds via UV-induced charge transfer from the π-character bridging oxygen to W(VI) at the W^{VI}=O bond with an accompanying transfer of a PVA proton to a second bridging oxygen at the WO$_6$ octahedral site, as in the case of photoreduction of H$_6$BW$_{12}$O$_{40}$ in the presence of methanol.[36]

Figure 3 shows the initial rate of photoreduction of HPA is linearly proportional to the number of photons absorbed by the HPA. It is also interesting to note that the initial rate of the photoreduction is greatly enhanced in the presence of TiO$_2$ (Figure 3), implying that interfacial electron transfer takes place from the TiO$_2$ conduction band to HPA. In fact, nanosecond-laser flash photolysis of deaerated TiO$_2$ solution in the presence of PVA shows a transient trapped conduction electron (120 μs)

at 600 nm as observed by Bahnemann et al.,[37] while in the presence of HPA it is quenched by generating a longer lived transient with maximum adsorption around 450 nm (ca. 40 ms) instead of the trapped electron (Figure 4). The 450 nm transient species are attributed to the trapped hole due to the effective electron transfer to HPA. Such an effective electron transfer can remove the fast electron–hole recombination on TiO$_2$, and the trapped holes have sufficient time to allow their transient absorption spectrum to be recorded.

The photoreduction yield also increases linearly as the concentration of TiO$_2$ colloid or HPA increases as shown in Figure 5, implying dependence of the photoreduction on the relative mixing ratio of TiO$_2$/HPA. The highest efficiency was achieved under the concentrations of mixing ratio of TiO$_2$/HPA = 100 with 0.1% PVA. These results indicate that the HPA photoreduction is synergistically enhanced by TiO$_2$. The enhancement results can be best explained if one were to assume that the electron transfer proceeds via two photochemical reactions as the "Z-scheme" for the plant photosynthesis (see Scheme 1). The near-UV illumination of HPA/TiO$_2$ in the presence of PVA results in charge separation of TiO$_2$ as well as excitation of HPA. Thus, the formation of heteropoly blue (HPB) is produced by direct electron transfer from the TiO$_2$ conduction band to the ground-state HPA in addition to photoreduction through the excited state of HPA.

It is also noteworthy that the ground-state HPB formed by illumination of near-UV light can be recovered photochemically as well as thermally. Figure 6 shows the recovery from exhaustively reduced PW$_{12}$O$_{40}{}^{4-}$ to the reoxidized HPA (PW$_{12}$O$_{40}{}^{3-}$) as a function of time under the condition of visible light (>600 nm) irradiation or in the dark. Nearly complete recovery of the original spectrum is observed after 30 min irradiation. This recovery is accompanied by a total disappearance of the intense blue color. In the absence of TiO$_2$, the rate of reoxidation of the HPB is the same for both irradiated and dark conditions, indicating that HPA itself is in quick thermal equilibrium state with HPB produced from the excited-state of HPA (see Scheme 1). However, in the presence of TiO$_2$, the reoxidation rate in the dark condition is rather faster than in the light condition. At present the reason for this difference is
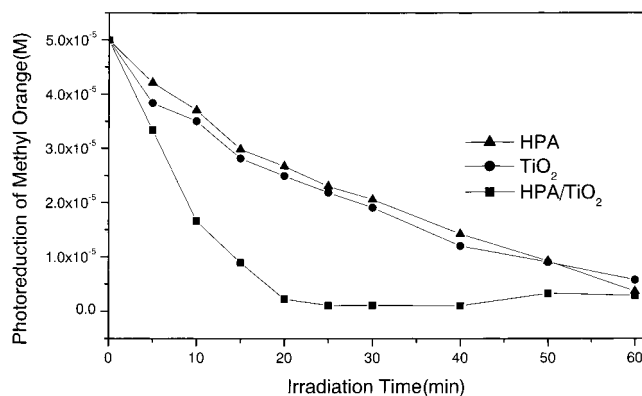
HPA-Incorporated TiO₂ Colloids

J. Phys. Chem. B, Vol. 105, No. 13, 2001 **2543**
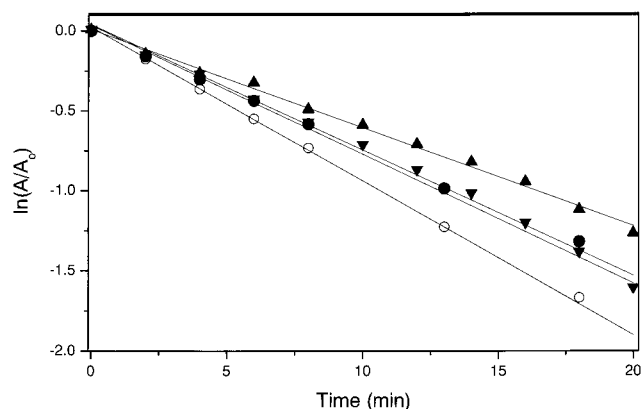
Figure 6. Recovery of HPA from HPB ($PW_{12}O_{40}^{4-}$) upon illumination with visible light (>600 nm) in the absence (▼, $k = -0.078$ min^{-1}) and presence of TiO₂ colloids (▲, $k = -0.065$ min^{-1}), and in the dark in the absence (●, $k = -0.081$ min^{-1}) and presence of TiO₂ colloids (○, $k = -0.096$ min^{-1}).
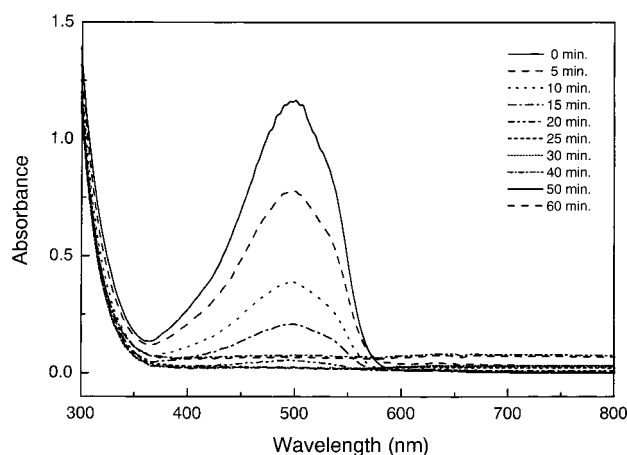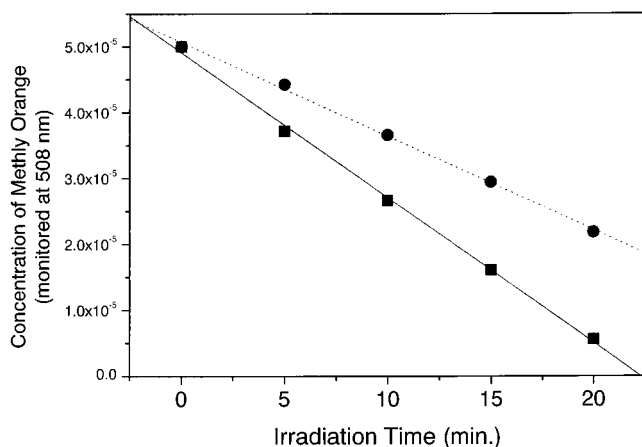

Figure 7. Absorption spectral changes of Methyl Orange (5×10^{-4} M) in the presence of HPA/TiO₂ colloids upon illumination by Xe lamp ($\lambda \geq 320$ nm).

Figure 8. Photoreduction of Methyl Orange in the presence of HPA, naked TiO₂, or HPA/TiO₂ in 0.1% PVA aqueous solutions as a function of irradiation time by Xe lamp ($\lambda \geq 320$ nm). [TiO₂] = 5×10^{-3} M, [HPA] = 5×10^{-5} M.

Figure 9. Photoreduction of Methyl Orange in HPA/TiO₂ in 0.1% PVA aqueous solutions upon illumination with near-UV (320−390 nm) lights only (●, $k = -1.42 \times 10^{-6}$ M/min), and near-UV plus visible lights (>320 nm) (■, $k = -2.20 \times 10^{-6}$ M/min).

not quite clear, but it is probably because the HPB molecules are in the vicinity on the TiO₂ surface so that thermal activation of HPB molecules is facilitated. On the other hand, in the light condition, the HPB is excited and goes back to the excited HPA, which subsequently returns to the ground-state HPA. Thus, the reoxidation rate should be slowest under the visible light condition in the presence of TiO₂. If there is another electron acceptor nearby, the excited HPB can donate electrons to it so that photoreduction is facilitated.

3. Catalytic Activity of HPA/TiO₂ in Photoreduction of Methyl Orange. If the electron-transfer mechanism of HPA/TiO₂ system is valid as discussed above, photodecomposition of some organic substrate would be catalyzed by the HPA/TiO₂ colloids by using visible light in addition to near-UV light. Thus, the catalytic activity of HPA/TiO₂ colloids has been assessed by carrying out the photoreduction of Methyl Orange in aqueous medium. When anaerobic aqueous solutions of Methyl Orange (5×10^{-5} M) in the presence of naked HPA, TiO₂, or HPA/TiO₂ colloids were illuminated with near-UV radiation (cutoff ≥ 320 nm), the visible absorption band of Methyl Orange at 502 nm starts to disappear without a wavelength shift (Figure 7), while no bleaching is observed in the absence of the colloids or HPA. No HPB absorption peak is observed until bleaching of Methyl Orange is finished. This indicates that the bleaching is due to photoreduction catalyzed by the TiO₂ colloidal systems or HPA itself by electron transfer from the TiO₂ conduction

band or the excited HPB. However, the photoreduction rate or yield is quite different depending on the catalytic systems and the illumination wavelength. Figure 8 shows the comparison of the photoreduction rate of Methyl Orange in the presence of naked TiO₂ and colloidal HPA/TiO₂ colloids. From these data, the catalytic activity of HPA/TiO₂ colloids (100% bleaching within 20 min) is tremendously increased as compared to that of the naked TiO₂ or HPA itself (only 60% bleaching within 60 min). Based on these catalytic effects on photoreduction of Methyl Orange, the photon-to-electron conversion yield in the presence of HPA/TiO₂ is almost 34% with 320 nm monochromatic light. Furthermore, it is found that upon additional illumination with visible light (400−600 nm), the photocatalytic reduction of Methyl Orange by HPA/TiO₂ is much faster as compared to the result obtained by near-UV light only (320−390 nm). Concomitantly, the rate of Methyl Orange reduction in the presence of HPA/TiO₂ is of zero order over most of its course as shown in Figure 9. The rate constant is significantly bigger when visible light is additionally used for illumination than when UV light only is used. These results are quite different from the electrocatalytic activity of diruthenated complex combined with cobalt porphyrin derivative.[38] This complex has sequential four-electron reduction steps, whereas in the TiO₂/HPA complex system, TiO₂/HPA and HPB play as separate reaction centers like PS I and PS II in plant photosynthetic system, responsible for absorbing different energies of light, such as UV light and visible light, respectively. To establish
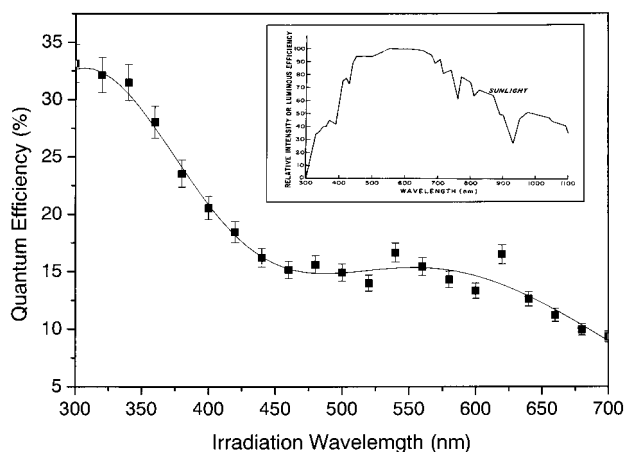
Figure 10. Photocatalytic action spectrum of HPA/TiO$_2$ in 0.1% PVA aqueous solutions upon two-beam irradiation. One beam is 300 nm and the other is a variable from 300 to 700 nm. Inset shows the spectrum of sunlight from the zenith at the surface of Earth.[38]

the photon-to-electron conversion efficiency in reliable manner, we have attempted the photocatalytic action spectrum of HPA/TiO$_2$ systems, which is monitored by photoreduction of Methyl Orange with two-beam irradiation; one is fixed at 300 nm and the other perpendicular to the 300 nm beam is variable from 300 to 700 nm. The quantum efficiency was calculated by using the Planck relation as follows:

$$E_i = n_i h \nu_i = \frac{n_i h c}{\lambda_i} \quad (2)$$

$$n_i = \frac{E \lambda_i}{hc} \quad (3)$$

quantum efficiency (%) =

$$\frac{\text{no. of photoreduced Methyl Orange}}{\text{total no. of absorbed photons}} \times 100 \quad (4)$$

where E is a light intensity of selected wavelength, h is the Planck constant (6.626×10^{-34} J·s), and c is the velocity of light (3.0×10^8 m/s). The intensity of the 300 nm fixed beam is very weak compared with the intensity of variable beam, because the 300 nm fixed beam is just an initiator for the photoreduction of HPA. As shown in Figure 10, the action spectrum shows two maximum efficiencies at 320 and 570 nm, implying that Methyl Orange can be reduced by visible light irradiation after UV irradiation, and the additional use of visible light also plays an important role in the photocatalytic reaction of HPA/TiO$_2$ systems. This broad irradiation range is overlapped with the sun spectrum from the zenith at the surface of the Earth (inset of Figure 10).[39] This is consistent with the synergistic effect of HPA/TiO$_2$ on the photon-to-electron conversion efficiency due to the two photochemical pathways as described in Scheme 1. This result indicates that the direct reducing agent is the excited-state HPB (HPB*), it is rapidly restored by additional visible light, the reduction rate should be synergistically enhanced, and this system should be useful under natural sunlight.

Conclusions

Illumination of HPA results in the characteristic spectra of "heteropoly blue (HPB)" products in 0.1% PVA aqueous solution via one-electron transfer through hydrogen abstraction of excited-state HPA from PVA. The photoreduction of HPA

is synergistically enhanced by coupling with TiO$_2$ which transfers electrons directly to interfacial HPA. HPB subsequently absorbs visible light to form excited-state HPB, and it consequently catalyzes the reduction of Methyl Orange synergistically. Such an electron-transfer mechanism of HPA/TiO$_2$ is very similar to the "Z-scheme" of the plant photosynthetic system, and HPA/TiO$_2$ should be a quite efficient artificial photosynthetic reaction center for water photolysis to get H$_2$ and O$_2$ without electricity by using visible light as well as near-UV light which includes the whole spectrum of sunlight on Earth. This possibility is under scrutiny in our laboratory at present.

References and Notes

(1) Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 6547−6555.
(2) Navio, J. A.; Marchena, F. J. *J. Photochem. Photobiol. A: Chem.* **1991**, *55*, 319−322.
(3) Wang, Y.; Wan, C. *J. Photochem. Photobiol. A: Chem.* **1994**, *84*, 195−202.
(4) Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977−2985.
(5) Muzyka, J. L.; Fox, M. A. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 27−39.
(6) Pichat, P.; Mozzanega, M.; Courbon, H. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 697−704.
(7) Karakitsou, K. E.; Verykios, X. E. *J Phys. Chem.* **1993**, *97*, 1184−1189.
(8) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69−96.
(9) Duonghong, D.; Borgarello, E.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 4685−4690.
(10) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49−68.
(11) Bach, U.; Lupo, D.; Comte, P.; Mpser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer H.; Grätzel, M. *Nature* **1998**, *395*, 583−585.
(12) Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* **1984**, *106*, 6557−6564.
(13) Kalyanasundaram, K.; Vlachopoulos, N.; Krishnan, V.; Monnier, A.; Grätzel, M. *J. Phys. Chem.* **1987**, *91*, 2342−2347.
(14) Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. *J. Am. Chem. Soc.* **1988**, *110*, 1216−1220.
(15) Fan, F. F.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 6139−6140.
(16) Giraudeau, A.; Fan, F. F.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 5138−5142.
(17) Tennakone, K.; Tilakaratune, C. T. K.; Kottegoda, I. R. M. *J. Photochem. Photobiol. A: Chem.* **1995**, *87*, 177−179.
(18) Cermenati, L.; Pichat, P.; Guillard, C.; Albini, A. *J. Phys. Chem. B* **1997**, *101*, 2650−2658.
(19) Mills, A.; Davies, R. *J. Photochem. Photobiol. A: Chem.* **1995**, *85*, 173−178.
(20) Hidaka, H.; Horikoshi, S.; Ajisaka, K.; Zhao, J.; Serpone, N. *J. Photochem. Photobiol. A: Chem.* **1997**, *108*, 197−205.
(21) Mills, A.; Hunte, S. L. *J. Photochem. Photobiol. A: Chem.* **1997**, *108*, 1−35.
(22) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988−2990
(23) Houlding, V. H.; Grätzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 5695−5696.
(24) Török, B.; Molnör, A.; Balogh, N.; Kiricsi, I. P.; Linko, I.; Horvath, L. *Appl. Catal., A: Gen.* **1997**, *158*, L17−L25.
(25) Lim, K. R.; Yoon, M.; So, H. *J. Korean Chem. Soc.* **1975**, *19*, 16−20.
(26) Na, K.; Okuhara, T.; Misono, M. *J. Catal.* **1997**, *170*, 96−107.
(27) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148−5157.
(28) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1985**, 395−399.
(29) Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, 793−799.
(30) Cuendet, P.; Grätzel, M. *Photochem. Photobiol.* **1982**, *36*, 203−210.
(31) Edward, J.; Thiel, C. Y.; Benac, B.; Knifton, J. F. *Catal. Lett.* **1998**, *51*, 77−83.

HPA-Incorporated TiO$_2$ Colloids

J. Phys. Chem. B, Vol. 105, No. 13, 2001 **2545**

(32) Choi, J.; Yeo, K.; Yoon, M.; Lee, S. J.; Kim, K. *J. Photochem. Photobiol. A: Chem.* **2000**, *132*, 105−114.

(33) Vincze, L.; Kemp, T. J.; Unwin, P. R. *J. Photochem. Photobiol. A: Chem.* **1999**, *123*, 7−13.

(34) Herring, A. M.; McCormick, R. L. *J. Phys. Chem. B* **1998**, *102*, 3175−3184.

(35) Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1988**, *110*, 5461−5470.

(36) Yamase, T.; Watanabe, R. *J. Chem. Soc., Dalton Trans.* **1968**, 1669−1675.

(37) Bahnemann, D.; Henglein, A.; Lillie, J.; Soankel, L. *J. Phys. Chem.* **1984**, *88*, 709−711.

(38) Singer, B.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 5767−5779.

(39) Smith K. C. *The Science of Photobiology*; Plenum Press: New York, 1977; chapter 1.