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Enhancement of TiO2-photocatalyzed organic transformation by ZnO and ZnS. Oxidation of diphenylamine

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## a r t i c l e i n f o

*Article history:*

Received 4 September 2014 Received in revised form 22 October 2014

Accepted 3 December 2014

Available online 19 December 2014

*Keywords:* Photocatalysis Semiconductor Kinetic law

Interparticle charge transfer

## a b s t r a c t

TiO2 anatase photocatalyzes the oxidative transformation of diphenylamine (DPA) to N- phenyl-*p*-benzoquinonimine (PBQ) in ethanol. The PBQ formation increases with increase of [DPA], TiO2-loading, airflow rate and light intensity. The catalyzed formation of PBQ is larger with UV-C light illumination than with UV-A light illumination. The catalyst is recyclable. The photocatalytic reaction mechanism has been proposed and the kinetic parameters deduced. ZnO and ZnS enhance the TiO2-photocatalyzed DPA oxidation sug- gesting interparticle charge transfer in mixed semiconductors.

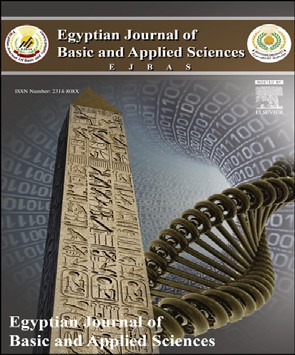
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# Introduction

Semiconductor-photocatalysis for environmental cleanup has been extensively studied [[1,2]](#_bookmark10) and reports on the application of this process for selective organic transformations are also available [[3](#_bookmark12)e[5]](#_bookmark12). The photocatalytic technology is benign and TiO2 is widely employed as a photocatalyst for both applica- tions [[2,3,5]](#_bookmark11). On band gap excitation, TiO2 produces electro- nehole pairs; electrons in the conduction band (CB) and holes in the valence band (VB) [[2]](#_bookmark11). In the presence of moisture and air, the photoproduced charge carriers generate reactive oxidizing species (ROS) such as hydroxyl radical, which mineralize the organic pollutants. The VB hole oxidizes the water molecule and hydroxide ion adsorbed on the TiO2

surface to produce hydroxyl radical. The oxygen molecule adsorbed on TiO2 picks up the CB electron to form superoxide radical, which through a series of reactions yield hydroxyl radical. But in non-aqueous media formation of hydroxyl radical is unlikely and the VB hole directly oxidizes the adsorbed substrate and hence photocatalyzed organic trans- formations are carried out in non-aqueous media. TiO2 selectively oxidizes alcohols to aldehydes or ketones and functionalized nitroarenes are selectively reduced by N-doped TiO2 [[4]](#_bookmark13). Propene and cyclopentene are transformed into the corresponding epoxide using TiO2eSiO2 as photocatalyst [[4]](#_bookmark13). TiO2 Degussa P25 selectively photocatalyzes the oxidation of benzyl amines to the corresponding imines [[5]](#_bookmark14). However, significant amounts of aldehydes are produced on the



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Peer review under responsibility of Mansoura University.

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photooxidation of secondary benzyl amines on TiO2 [[5]](#_bookmark14). TiO2 is also useful for the photocatalytic oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline [[5]](#_bookmark14). Diphenylamine (DPA) is widely used in post-harvest treatment of apple and pear [[6]](#_bookmark15) and there is no study on the photocatalytic transformation of DPA. Photosensitized oxidation of DPA has been reported and cyanoanthracenes [[7]](#_bookmark16) and benzophenone [[8]](#_bookmark17) are some of the photosensitizers used. Photolysis of DPA solution in ethanol slowly yields N-phenyl-*p*-benzoquinonimine (PBQ) [[9]](#_bookmark18). Hence it is of interest to study the photocatalytic trans- formation of DPA with nanocrystalline TiO2 anatase. Gener- ally, the photocatalytic activity could be improved by enhancing the lifetime of the charge carriers in semi- conductor nanoparticles. This could be achieved through interparticle charge transfer (IPCT). When a mixture of two nanoparticulate semiconductors is used as a photocatalyst for mineralization of organics enhanced photocatalytic activity has been observed [[10,11]](#_bookmark19). This has been explained on the basis of IPCT. However, such enhancement is not realized in the photocatalytic oxidation of iodide ion suggesting the IPCT to be slower than hole-transfer to iodide ion [[12]](#_bookmark20). Hence it is of interest to study photocatalytic organic transformation using nanoparticulate semiconductor mixture as photocatalyst. Here we investigate the photocatalytic transformation of DPA on TiO2 and TiO2eZnO and TiO2eZnS mixtures; ZnO has also been employed as photocatalyst for organic transformation [[5]](#_bookmark14). Systematic study on TiO2-photocatalyzed transformation of DPA has been made to deduce the kinetic law of the reac- tion. TiO2 acts as a photocatalyst under natural sunlight uti- lizing the UV light (5%) present in the solar spectrum and hence the reaction has also been examined with natural sunlight.

# Experimental procedure

### *Materials and measurements*

TiO2, ZnS and ZnO (Merck) were used as supplied and their specific surface areas, obtained by BET method, are 14.7, 7.7

and 12.2 m2 g—1, respectively. The mean particle sizes (*t*) of TiO2, ZnS and ZnO, deduced using the relationship *t* = 6/r*S*, where r is the material density and *S* is the specific surface

area, are 104, 190 and 87 nm, respectively. The UVevisible diffuse reflectance spectra of the semiconductors were ob- tained using a Shimadzu UV-2600 spectrophotometer with an ISR-2600 integrating sphere attachment. The KubelkaeMunk plots provide the band gap energies of TiO2, ZnS and ZnO as 3.18, 3.57 and 3.15 eV, respectively. The recorded powder X-ray diffractograms of TiO2, ZnS and ZnO show the crystalline structures as anatase, zinc blende and wurtztie, respectively [[13]](#_bookmark21). Potassium tris(oxalato)ferrate(III), K3[Fe(C2O4)3].3H2O, was prepared following the reported procedure [[14]](#_bookmark22). DPA, AR (Merck) was used as received. Commercial ethanol was distilled with calcium oxide.

### *Photocatalysis with UV light*

Photocatalytic oxidation with UV light was performed in a multilamp photoreactor. The reactor was equipped with eight 8 W mercury UV lamps (Sankyo Denki, Japan) of wavelength 365 nm. The lamps were shielded by highly polished anodized aluminum reflector. Four cooling fans fixed at the bottom of the reactor dissipate the heat produced. A borosilicate glass tube of 15-mm inner diameter was used as the reaction vessel and was placed at the center of the photoreactor. The photo- reaction was also carried out in a micro photoreactor fixed with a 6 W 254 nm low-pressure mercury lamp and a 6 W 365 nm mercury lamp. Quartz and borosilicate glass tubes were employed as reaction vessels for 254 and 365 nm lamps, respectively. The light intensity (*I*) was determined using fer- rioxalate actinometer. The volume of the DPA solution was always maintained as 25 mL in the multilamp photoreactor and 10 mL in the micro-photoreactor. Air was bubbled through the DPA solution to keep the photocatalyst powder under suspension and at constant motion. The airflow rate was determined by soap bubble method. The UVevisible spectra were recorded using a Hitachi U-2001 UVevisible spectro- photometer, after diluting the solution 5-times to keep the



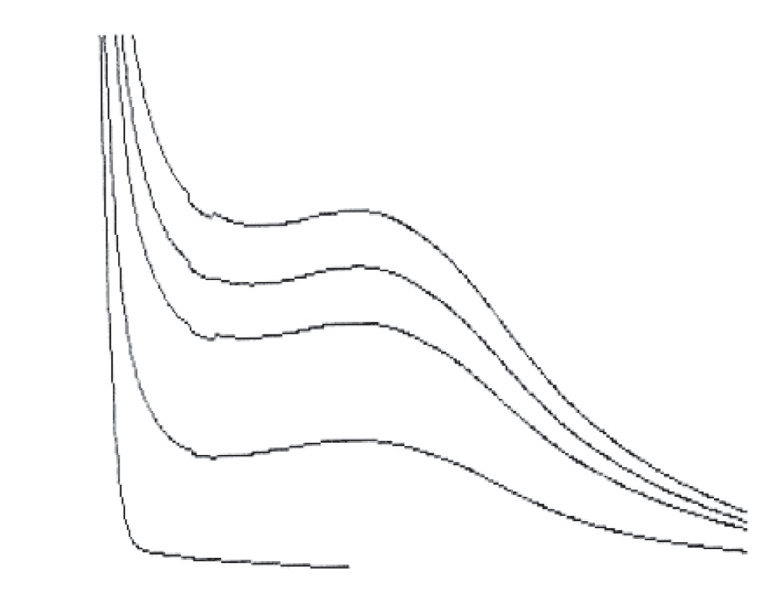




Fig. 1 e (a) PBQ formation in presence of TiO2 under UV light in ethanol: the UVevisible spectra of reaction solution (5-times diluted) at 0, 30, 60, 90 and 120 min (↑) ([DPA] ¼ 20 mM, TiO2-loading ¼ 1.0 g, airflow rate ¼ 7.8 mL s¡1,

*I* ¼ 25.2 meinstein L¡1 s¡1, volume of reaction solution ¼ 25 mL), (b) Linear increase of PBQ formed with illumination time.

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absorbance within the BeereLambert law limit. The formed PBQ was estimated from its absorbance at 450 nm.



### *Photocatalysis with sunlight*

The photocatalytic transformation with natural sunlight was made in summer (MarcheJuly) under clear sky at 11.30 am e

12.30 pm. The intensity of sunlight (W m—2) was determined

Bombay. The solar irradiance (Einstein L—1 s—1) was also with a Global pyranometer, supplied by Industrial Meters, 440 W m—2 corresponds to 22 mEinstein L—1 s—1. For each set of measured by ferrioxalate actinometry. The measured experiment, solution of DPA of desired concentration in

ethanol was prepared afresh and taken in wide cylindrical glass vessels of uniform diameter. The entire bottom of the vessel was covered by the catalyst powder. Air was bubbled using a micro pump without disturbing the catalyst bed. The volume of DPA solution was 25 mL and the loss of solvent due to evaporation was compensated periodically. The formed PBQ was estimated spectrophotometrically.

# Results and discussion

### *TiO2-catalyzed DPA oxidation with UV light*

The TiO2-photocatalyzed oxidation of DPA in ethanol was carried out in the presence of air with a multilamp photo- reactor fixed with UV lamps of wavelength 365 nm. The UVevisible spectra of the illuminated solution, recorded at different reaction time, reveal the formation of PBQ

(lmax = 450 nm). [Fig. 1](#_bookmark1) (a) displays the time scan. The illumi-

nated solution is EPR silent indicating absence of formation of

diphenylnitroxide. In addition, thin layer chromatographic analysis shows the formation of a single product. The illu- minated DPA solution was evaporated after the separation of TiO2 powder and the solid was dissolved in chloroform to develop the chromatogram on a silica gel G-coated plate using benzene as eluant. The PBQ formed was estimated from the measured absorbance at 450 nm using its molar extinction coefficient [[15,16]](#_bookmark23). The linear increase of [PBQ] with illumina- tion time, displayed in [Fig. 1](#_bookmark1) (b), provides the initial rate of PBQ formation and the rates are reproducible to ±6%. The direct

photooxidation of DPA, the photoformation of PBQ in the

absence of TiO2, is not negligible [[9]](#_bookmark18) and the rate of TiO2- photocatalyzed PBQ formation was obtained by measuring the rates of PBQ formation in the presence and absence of TiO2. [Fig. 2](#_bookmark2) displays the increase of rate of TiO2-photocatalyzed PBQ formation with [DPA]. The results are characteristic of Lang- muireHinshelwood kinetics with respect to [DPA]. The in- crease of the amount of TiO2 suspended in the DPA solution results in increased PBQ formation and the rate reaches a limit at high TiO2-loading; [Fig. 3](#_bookmark3) presents the results. Determina- tion TiO2-photocatalyzed reaction rate at different airflow rates shows enhancement of TiO2-photocatalyzed trans- formation by oxygen and the dependence of the reaction rate on the airflow rate conforms to the LangmuireHinshelwood kinetic law. The results are displayed in [Fig. 4](#_bookmark4). PBQ formation was also measured without bubbling air but the solution was not deoxygenated.

Fig. 2 e Dependence of TiO2-photocatalyzed PBQ formation rate in ethanol on [DPA] (TiO2-loading ¼ 1.0 g, volume of reaction solution ¼ 25 mL; UV: l ¼ 365 nm,

*I* ¼ 25.2 meinstein L¡1 s¡1, airflow rate ¼ 7.8 mL s¡1; Solar: bed area ¼ 11.36 cm2, airflow rate ¼ 4.6 mL s¡1).

The dissolved oxygen itself brings out the photocatalysis but the PBQ formation is slow. The TiO2-catalyzed PBQ for- mation was examined at different light intensities. The reac- tion was carried out with two, four and eight lamps; the angles

sustained by the adjacent lamps are 180◦, 90◦ and 45◦,

respectively. [Fig. 5](#_bookmark5) shows the variation of the catalyzed reac-

tion rate with the light intensity. PBQ is not formed in the dark. Investigation of the TiO2-catalyzed PBQ formation with UV-A and UV-C light, using a 6 W 365 nm mercury lamp

(*I* = 18.1 meinstein L—1 s—1) and a 6 W 254 nm low-pressure mercury lamp (*I* = 5.22 meinstein L—1 s—1), separately in the micro-photoreactor under identical conditions reveals that

UV-C light is more efficient than UV-A light in bringing out the organic transformation. PBQ formation with UV-A and UV-C

light are 12.8 and 51.7 nmol L—1 s—1, respectively. TiO2 does

not lose its photocatalytic activity on usage. Reuse of TiO2

quencher azide ion (5 mmol L—1) fails to suppress the forma- shows sustainable photocatalytic activity. Singlet oxygen tion of PBQ indicating the absence of involvement of singlet

oxygen in the photocatalytic transformation. This is in agreement with an earlier report; Fox and Chen [[17]](#_bookmark24) excluded



Fig. 3 e Variation of TiO2-photocatalyzed PBQ formation rate in ethanol with TiO2-loading ([PBQ] ¼ 5.0 mM, airflow rate ¼ 7.8 mL s¡1, l ¼ 365 nm, *I* ¼ 25.2 meinstein L¡1 s¡1,

volume of reaction solution ¼ 25 mL).

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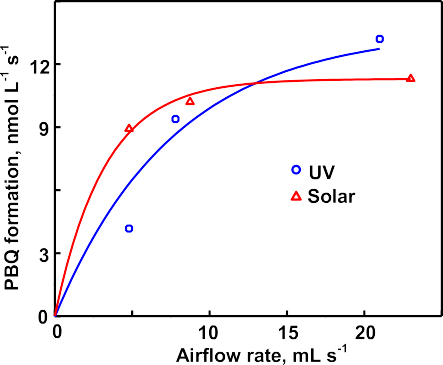


Fig. 4 e Influence of airflow rate on TiO2-photocatalyzed PBQ formation rate ([DPA] ¼ 5.0 mM, TiO2-loading ¼ 1.0 g, volume of reaction solution ¼ 25 mL; UV: l ¼ 365 nm,

*I* ¼ 25.2 meinstein L¡1 s¡1; Solar: bed area ¼ 11.36 cm2).

out the given set of experiments simultaneously and the re- sults presented in each figure represent identical solar irra- diance. The PBQ formation rates were obtained by illuminating the DPA solutions on TiO2 bed for 1 h. The vari- ation of PBQ formation rate with [DPA] is displayed in [Fig. 2](#_bookmark2). The observed increase of PBQ formation with [DPA] is char- acteristic of LangmuireHinshelwood kinetic law. The double reciprocal plot of PBQ formation rate versus [DPA] is linear with a positive *y*-intercept (figure not given) confirming the LangmuireHinshelwood kinetics. [Fig. 4](#_bookmark4) displays the TiO2- photocatalyzed PBQ formation rate at different airflow rates. The observed enhancement of the reaction by oxygen reveals that the organic transformation conforms to Lang- muireHinshelwood kinetics with respect to oxygen also. The double reciprocal plot of reaction rate versus airflow rate is a straight line with a finite *y*-intercept (figure not given). The TiO2-photocatalyzed PBQ formation was studied without

bubbling air but the solution was not deoxygenated. The dis-

the possibility of singlet oxygen in the TiO2-photocatalyzed olefin-to-carbonyl oxidative cleavage.

### *TiO2-catalyzed DPA oxidation with sunlight*

TiO2 also photocatalyzes the oxidation of DPA to PBQ under natural sunlight in ethanol in the presence of air. The UVevisible spectrum of sunlight illuminated DPA solution in

UV light (lmax = 450 nm). Furthermore, the irradiated solution ethanol, in the presence of TiO2 and air, is similar to that with is EPR silent revealing the absence of diphenylnitroxide. In

uct. Measurement of solar irradiance (W m—2) shows fluctua- addition, TLC analysis shows the formation of a single prod- tion of sunlight intensity during the course of the experiment

even under clear sky. Hence, the solar experiments at different reaction conditions were carried out in a set so that the quantity of sunlight incident on unit area remains the same. This makes possible comparison of the solar results. A pair of solar experiments carried out simultaneously under

identical conditions yield results within ±6% and this is so no different days. The effect of operational parameters on the solar photocatalytic transformation was studied by carrying

solved oxygen itself brings in the photocatalytic trans- formation. However, the reaction is slow. The TiO2- photocatalyzed reaction enhances linearly with the apparent area of TiO2-bed. [Fig. 6](#_bookmark6) presents the results. PBQ is not formed in the dark. TiO2 does not lose its photocatalytic efficiency on usage. Reuse of the catalyst shows sustainable photocatalytic activity.

### *Mechanism*

Band gap illumination of TiO2 generates electronehole pairseelectrons in the conduction band (CB) and holes in the valence band (VB). The recombination of the electronehole pairs in semiconductor is so fast (occurring in a picoseconds time scale) and for an effective photocatalysis the reactants are to be adsorbed on the surface of TiO2 [[2]](#_bookmark11). The hole is likely

form diphenylamine radical-cation (Ph2NH●+). The oxygen to take up an electron from the adsorbed DPA molecule to molecule adsorbed on the TiO2 surface picks up the CB elec-

tron. The formed superoxide radical-anion is likely to react with diphenylamine radical-cation yielding PBQ.

TiO2 + *h*n / *h*+ + e‒



(VB) (CB)

Fig. 5 e Effect of photon flux on TiO2-photocatalyzed PBQ formation rate ([DPA] ¼ 5.0 mM, TiO2-loading ¼ 1.0 g, airflow rate ¼ 7.8 mL s¡1, l ¼ 365 nm, volume of reaction solution ¼ 25 mL).

Fig. 6 e TiO2-photocatalyzed PBQ formation as a function of catalyst-bed area ([DPA] ¼ 5.0 mM, TiO2-loading ¼ 1.0 g, airflow rate ¼ 4.6 mL s¡1, volume of reaction

solution ¼ 25 mL).

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Fig. 7 e Enhanced PBQ formation on mixing TiO2 with ZnO or ZnS.

computer program [[18]](#_bookmark25), confirms the rate law ([Figs. 2 and 4](#_bookmark2)). The linear double reciprocal plots of TiO2 formation rate versus [DPA] and airflow rate confirm the kinetic law. The

56 L mol—1 and 0.010 mL—1 s, respectively, and the specific data-fit provides the adsorption coefficients *K*1 and *K*2 as reaction rate *k* as 110 mmol L m—2 einstein—1. However, the

TiO2-photocatalyzed PBQ formation rate fails to increase lin-

early with the amount of TiO2 suspended. This is because of the high catalyst loading. At high catalyst loading, the surface area of the catalyst exposed to light does not commensurate with the weight of the catalyst. The amount of TiO2 employed is beyond the critical amount corresponding to the volume of the reaction solution and reaction vessel; the whole amount of TiO2 is not exposed to illumination. The photocatalytic reac- tion lacks linear dependence on illumination intensity; less

than first power dependence of surface-photocatalysis rate on

light intensity at high photon flux is well known [[19]](#_bookmark26).

Ph2NH(ads) + *h*+ / Ph2NH●+

(VB)

2

### *3.5. Enhancement of photooxidation by ZnS and ZnO*

O2(ads) + e‒

(CB)

/ O ●—



Vectorial transfer of photoformed charge carriers from one

semiconductor to another is possible in coupled semi- conductors. This separation of charges leads to improved photocatalytic efficiency and examples of coupled semi- conductors are many [[20]](#_bookmark27). In coupled semiconductors, both the semiconductors exist in the same particle and the charge separation takes place within the particle. But what we observe here is enhanced photocatalytic transformation of DPA to PBQ on mixing ZnO or ZnS powder with TiO2 powder.

### *Kinetic law*

Kinetic treatment could be made using the results obtained with artificial UV light. The heterogeneous photocatalytic re- action taking place in a continuously stirred tank reactor (CSTR) is governed by the kinetic law [[18]](#_bookmark25):

TiO2-photocatalyzed PBQ formation rate = *kK*1*K*2*SIC*[DPA]g/ (1 + *K*1[DPA]) (1 + *K*2g) (1)

where *K*1 and *K*2 are the adsorption coefficients of DPA and O2 on illuminated TiO2 surface, *k* is the specific rate of oxidation of DPA on TiO2 surface, g is the airflow rate, *S* is the specific surface area of TiO2, *C* is the amount of TiO2 sus- pended per liter and *I* is the photon flux. The data-fit to the LangmuireHinshelwood kinetic curve, drawn using a

[Fig. 7](#_bookmark7) presents the enhancement of photocatalytic formation of PBQ under UV light on mixing ZnO or ZnS with TiO2; the two particulate semiconductors are in suspension and at constant motion. This observed enhanced photocatalytic trans- formation is because of interparticle charge transfer [[10,11]](#_bookmark19). Nanoparticles in suspension aggregate [[21]](#_bookmark28). [Fig. 8](#_bookmark8) presents the particle size distributions of TiO2, ZnS and ZnO in suspension. Examination of [Fig. 8](#_bookmark8) in conjunction with the determined particle sizes shows aggregation of the particles. As observed in individual semiconductor suspension, aggregation is likely in particulate semiconductor mixtures under suspension and both the semiconductor particles are likely to be present in the aggregates. Charge transfer between TiO2 and ZnS or ZnO particles is likely to take place when both the semiconductors are under band gap-illumination and in contact with each other; electron from CB of a semiconductor may move to another if the latter is of lower energy and so is the hole from



Fig. 8 e Aggregation of nanoparticles.

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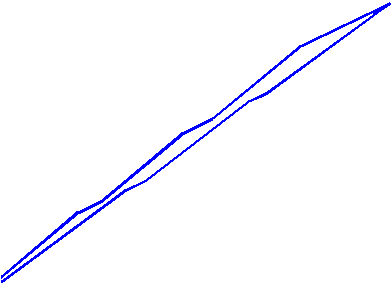
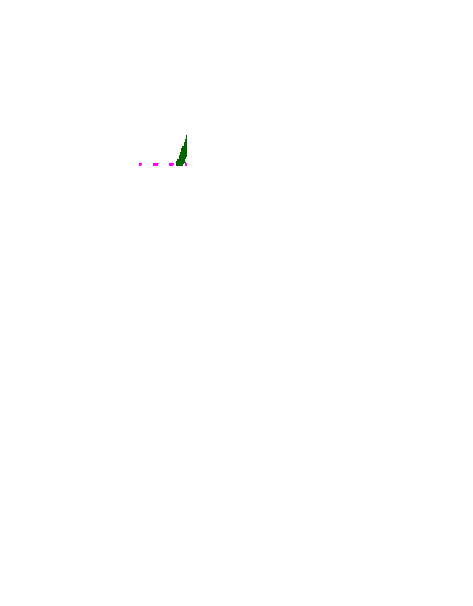
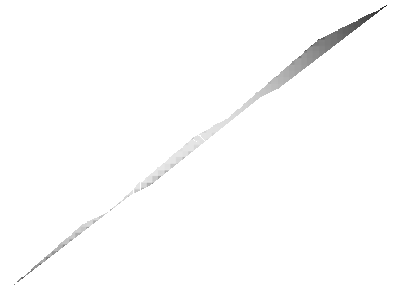
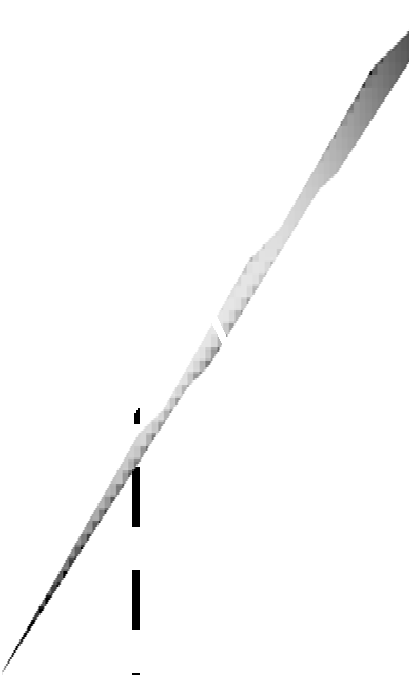
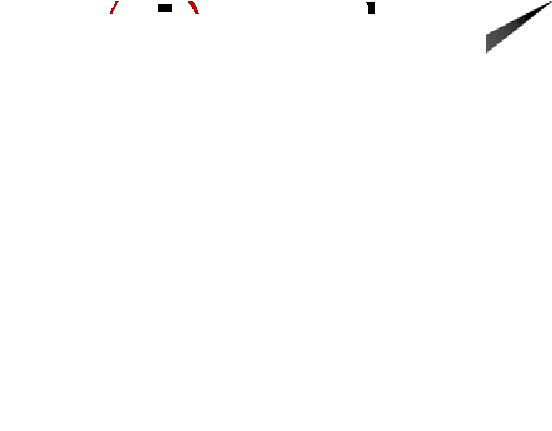
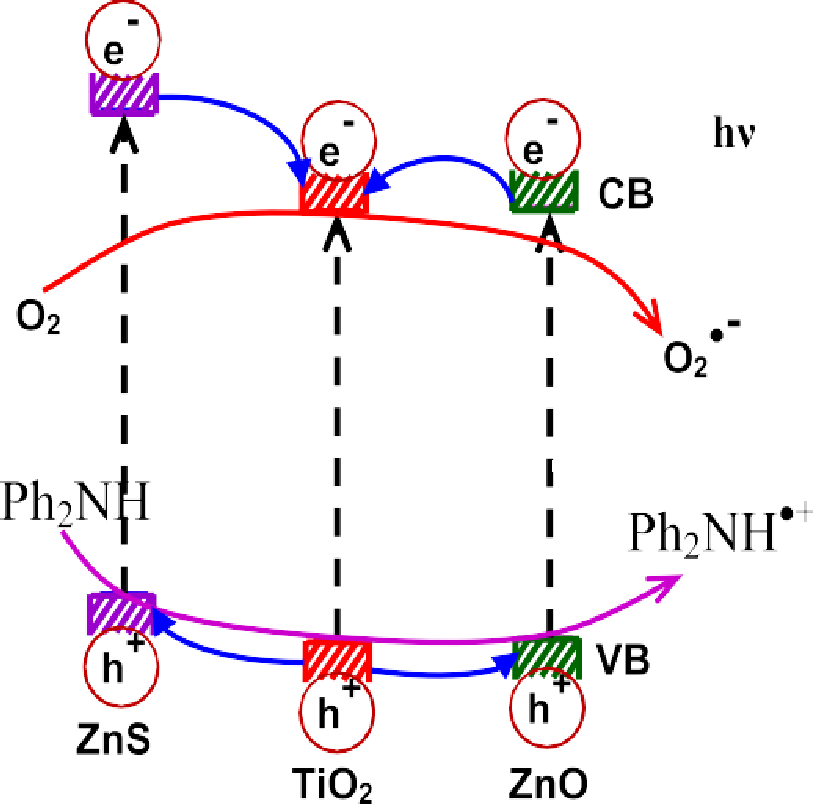


Fig. 9 e Mechanism of enhanced photooxidation.

VB. The charge transfer between the particulate semi- conductors is governed by the CB and VB energy levels. The CB electron of TiO2 is less cathodic than those of ZnO [[22]](#_bookmark29) and ZnS [[23]](#_bookmark30). This enables transfer of electron from the CB of ZnO or ZnS to the CB of TiO2 in TiO2eZnO or TiO2eZnS mixtures ([Fig. 9](#_bookmark9)). The VB hole of TiO2 is more anodic than those of ZnO and ZnS. This favors transfer of hole from the VB of TiO2 to that of ZnO or ZnS. This interparticle charge transfer en- hances the photocatalytic process. The energy difference be- tween the CB electrons or VB holes of the two semiconductors

the free energy change is given by eD*G* = *e*(*E*(CBSC1) e *E*(CBSC2) or is the driving force for the interparticle charge separation and *e*(*E*(VBSC1) e *E*(VBSC2)) [[24]](#_bookmark31). In terms of redox chemistry, the CB

and VB refer to the reduced and oxidized states in the semi-

reduced forms of Ti4+ (*i.e*., Ti3+) and Zn2+ (*i.e*., Zn+), respec- conductor. In TiO2 and ZnO or ZnS the CB electrons refer to the forms of the respective O2— (*i.e*., O—) or S2— (*i.e*., S—). The tively. Similarly, the VB hole corresponds to the oxidized interparticle charge-transfer, the transfer of electron from the

from Zn+ to Ti4+. The hole-transfer from the VB of TiO2 to CB of ZnS or ZnO to that of TiO2 refers to the electron jump O2— of ZnO or S2— of ZnS to O— of TiO2. The possibility of cross- those of ZnO and ZnS corresponds to the electron-jump from electronehole combination, the transfer of electron from the

CB of one semiconductor (SC1) to the VB of the other (SC2) is very remote; the very low population of the excited states makes the electron transfer between two excited states highly improbable. A possible reason for not observing the maximum photocatalytic transformation at 50% wt. composition for the semiconductor mixtures is the densities and particle sizes of the semiconductors and also the aggregation.

# Conclusions

TiO2 photocatalyzes the oxidative transformation of DPA to BPQ. The BPQ formation enhances with [DPA] and airflow rate and follows the LangmuireHinshelwood kinetic law. TiO2

mixed with ZnO or ZnS produces more PBQ than by the indi- vidual semiconductor and this is likely because of interpar- ticle charge separation.

# Acknowledgments

Prof. C. Karunakaran is thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi for the Emeritus Scientist Scheme [21(0887)/12/EMR-II].

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