

Review Article

Development of Visible Light-Responsive Sensitized Photocatalysts

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The paper presents a review of studies about the visible-light-promoted photodegradation of the contaminants and energy conversion with sensitized photocatalysts. Herein we studied mechanism, physical properties, and synergism effect of the sensitized photocatalysts as well as the method for enhancing the photosensitized effect. According to the reported studies in the literature, inorganic sensitizers, organic dyes, and coordination metal complexes were very effective sensitizers that were studied mostly, of which organic dyes photosensitization is the most widely studied modified method. Photosensitization is an important way to extend the excitation wavelength to the visible range, and therefore sensitized photocatalysts play an important role in the development of visible light-responsive photocatalysts for future industrialized applications. This paper mainly describes the types, modification, photocatalytic performance, application, and the developments of photosensitization for environmental application.

1. Introduction

Fujishima and Honda reported the first example for water splitting into hydrogen and oxygen with TiO_2 as catalyst under UV illumination in 1972 [1], and subsequently photocatalysis has been a hot topic in many research fields, and more efficient photocatalysts and photoelectrodes have been reported in the past years. A number of semiconductors such as TiO_2 , ZnO , Fe_2O_3 , CdS , and ZnS have exhibited excellent photocatalytic performance [2–6]. Among the common semiconductor photocatalysts, TiO_2 has been used for energy conversion and photodegradation of many contaminants. However, solar energy reaching the surface of the earth and the available solar energy for exciting TiO_2 ($\lambda \leq 387 \text{ nm}$) are relatively small which only occupy less than 5% of the whole sunlight. The low solar energy conversion efficiency and the high charge recombination rate of the photogenerated electrons and holes are often two major limiting factors for its widely practical applications [2]. In order to utilize the cheaper visible light from solar energy and enhance the energy conversion efficiency during the photocatalytic reactions, efforts have been focused on exploring novel methods to modify TiO_2 , of which photosensitization is an

important way to excite TiO_2 to the wavelength of visible light.

Photosensitization can be achieved by a photosensitizer which absorbs light energy, transforms the light energy into chemical energy, and transfers it under favorable conditions to otherwise photochemically unreactive substrates [7]. Under appropriate circumstances, photosensitizer can be adsorbed at the semiconductor surface by an electrostatic, hydrophobic, or chemical interaction that, upon excitation, injects an electron into its conduction band [8]. Based on the reported studies in the literatures, inorganic sensitizers [9], organic dyes, and coordination metal complexes [10] are very effective sensitizers that are studied mostly, of which organic dyes photosensitization is the most widely studied modified method.

It is well known that the organic dyes have prominent photophysical properties [11]. What is more, the structures of the organic dyes can be changed according to what they are required by low cost, low toxicity, and easy handling approaches [12–14]. In the past years, plentiful organic dyes got particular attention and had been tested as photosensitizers, such as eosin Y [15–23], riboflavin [24–28], rose bengal [24, 26], cyanine [11, 29], cresyl violet [30], hemicyanine

[12], and merocyanine [31–33]. However, the stability of pure organic dyes is a notable problem which should be solved emergently [34, 35].

Semiconductors with narrow band gaps which can adsorb visible light have also been exploited as sensitizers. Compared with pure organic dyes, semiconductors show greater stability, adjustable band gap which can tailor optical absorption over a wider wavelength range, and the possibility of exploiting multiple exciton generation to obtain high efficiencies [36]. There are two prerequisites for such heterogeneous semiconductor systems to function efficiently: (i) the band gap of the sensitizer should be near the appropriate value for optimum utilization of solar radiant energy and (ii) its conduction band edge should be higher than that of TiO_2 to allow electrons transferring from the sensitizers to TiO_2 [9]. However, because of the limit in the light absorption range, the energy conversion efficiency with the semiconductor sensitizers is much lower than that with the dyes sensitizers. Thus efforts have been made to find new narrow band gap semiconductor with ideal optical properties, enough stability, and low toxicity.

In addition to organic dyes and inorganic sensitizers, dyes and coordination metal complexes are efficient photosensitizers which have been receiving increasing research attentions, of which ruthenium complexes have been widely used to extend the photoresponse of TiO_2 into the visible region [37–39]. Surface photosensitization by organic dyes and coordination metal complexes via photoinduced sensitizer-to- TiO_2 charge transfer shows attractive features, such as regenerative sensitization and the ability for mediating the degradation of nonvisible absorbing substrates [40]. But the general difficulty in establishing stable surface anchorage of the charge-transfer photosensitizers is an important problem which requires further solution.

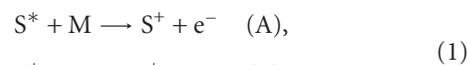
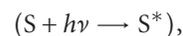
The photosensitization method has been applied to many fields in recent years, including the visible-light-promoted photodegradation of the contaminants [24–29], the dye-sensitized solar cell (DSSC) [41, 42], the semiconductor-sensitized solar cells (SSSC) [36], and visible-induced hydrogen evolution from water [16–23]. The sensitized photodegradation process was found to be an effective way to accelerate the photodecay of contaminants compared with the direct photolytic process (i.e., no sensitizer involved) [27]. Compared with the conventional photovoltaic solar cell, the DDSC possessing easy and low-cost fabrication technology achieved high photon-electron conversion efficiency because the dye on the semiconductor electrode (mostly TiO_2) absorbed more wide-range light than TiO_2 , and the photons were converted to electrons [41]. Thus it is meaningful to carry on further research in visible-induced photosensitization method.

In this paper, we will describe the mechanism of sensitized photocatalysts and various methods for enhancing the photosensitized effects detailedly. Furthermore, the synergism effect among the participants during the process of photosensitization is an important factor which affects the energy conversion efficiency. The characteristics and performance of the photosensitizer under visible light irradiation are quantitatively contrasted. The regenerative

photosensitization system utilizing electron donors is also discussed.

2. The Photosensitization Mechanism

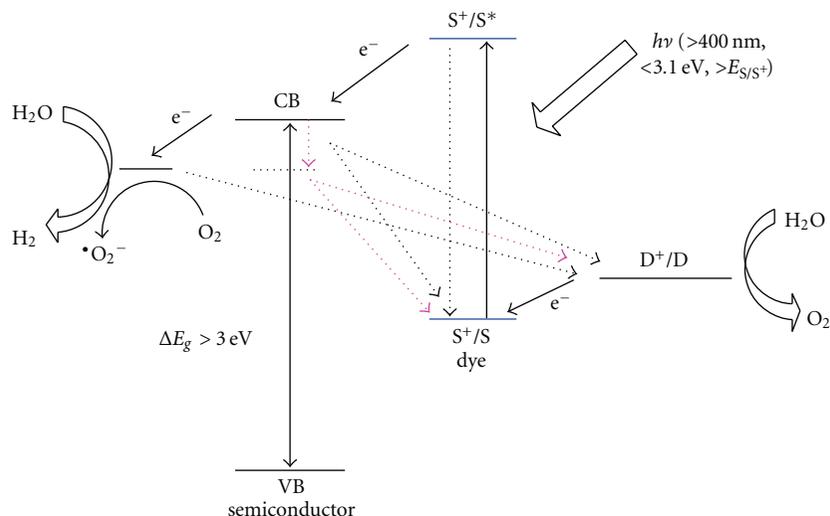
Redox processes are possible mechanisms for photoinduced energy transfer, which can be illustrated primitively by the following formula:



A photochemically excited molecule may donate an electron to the medium (M, reaction A) or another molecule which acts as an acceptor (X, reaction B), or it may act as an electron acceptor when a suitable electron donor is present (Z, reaction C) [7].

The proposed mechanism of the primary electron pathways over dye-sensitized semiconductor photocatalyst is illustrated in Scheme 1. In the photosensitization system, dye S serves as both a sensitizer component and a molecular bridge to connect electron donor D to a metal oxide semiconductor [38, 43]. The visible light (>400 nm) with the energy which is lower than the band gap of the semiconductor photocatalyst but higher than the band gap of the sensitizer molecules (S) which are adsorbed on the photocatalyst excites the sensitizer, and subsequently the electrons are injected to the conduction band (CB) of the photocatalyst, leading to the efficient charge separation at the interface between the photocatalyst and the sensitizer and producing the oxidized form of the dye (S^+). Subsequently the electrons can reduce water to H_2 on the reduction site (Pt mostly) over the photocatalyst in the process of water splitting. Similarly, if this process happens at or near the catalyst surface, a set of reactions in presence of water molecules and dissolved oxygen will result in the formation of several active oxygen species such as superoxide anion, singlet oxygen, and hydroperoxyl radical which will participate in the degradation reactions during the process of pollutants' degradation [15, 44]. The original form of the sensitizer is reformed by accepting an electron from the electron donor such as ethylenediaminetetraacetic acid (EDTA) in the solution, which irreversibly donates electrons and then decomposes [31].

Scheme 1 also illustrates the possible recombination pathways and fluorescence decay of excited sensitizer. Back electron transfer between the photo injected electron and the oxidized sensitizer plays an important role for controlling the efficiency of net electron transfer [30]. At each branch point in the chain, a high quantum yield can be obtained only if the forward electron transfer rate (solid arrows) is faster than the sum of all the reverse rates from the same point in the system. For example, in Scheme 1, the forward electron transfer from the semiconductor to the hydrogen evolving catalyst must compete effectively with back transfer



SCHEME 1: Proposed mechanism of dye-sensitized photocatalysis under visible light irradiation, including forward electron transfer (solid lines) and possible recombination pathways (dotted lines). Reproduced with a perfect scheme copy from [41]. Copyright 2009 American Chemical Society.

to the oxidized dyes, and also with electron transfer to the catalyst for water oxidation. In general, the reverse pathways have much greater driving forces than the forward ones, and this makes the reverse reactions faster [41]. However, due to the existence of the interface between the dyes and the photocatalyst, the separated electrons and holes have little possibility to recombine again, regardless of the existence of the charge-capturing species which are mentioned above. This ensures higher charge separation efficiency and better photooxidation capacity for the composite [45]. While the CB acts as a mediator for transferring electrons from the sensitizer to substrate electron acceptors on the photocatalyst surface, the VB remains unaffected in a typical photosensitization [41, 46].

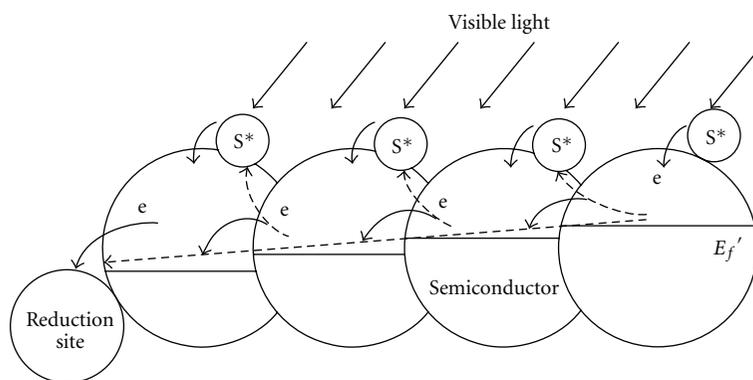
The transport of injected charge across sensitized-semiconductor nanocrystallites under visible light irradiation is illustrated vividly in Scheme 2. As shown in Scheme 1, during the injected charge's transit to the collecting surface of the reduction site, there is a significant amount of electrons which are lost as they recombine with excited sensitizers at the grain boundaries. The driving force for the electron transport within the nanocrystalline semiconductor film is created from the varying degree of the electron accumulation. As more electrons accumulate away from the surface of the reduction site, the quasi-Fermi level is altered in such a way that a potential gradient is created within the thin film [30].

The study of the interfacial electron transfer between molecular adsorbates and semiconductor nanoparticles is presently under intense investigation [47]. It is desirable to have a mechanistic understanding of the molecular factors that influence the quantum yield for excited-state electron transfer to the semiconductor which is a critical parameter for the production of electrical power.

3. Methods for Enhancing the Photosensitized Effects

Though many research papers about visible-light photosensitization have been reported, there are still many exigent problems which should be solved. Most of sensitizers suffer from a stability problem such as dissolution and the photocatalytic degradation, an increase of carrier recombination centers, or the requirement of an expensive facility and relatively long reaction time. In addition, several drawbacks such as deactivation and separation of fine catalyst powders from the aqueous phase after utilization prevent the large-scale applications of this promising method [2].

According to the reports from the literatures, the photosensitization effect not only depended on their chemical structure and the employed sensitizer, but also depended on the experimental conditions such as the concentrations of the dissolved oxygen and contaminants [24]. It was possible to improve the efficiency of photosensitization if the life time of the sensitizers in the solvent could be increased by suitable methods such as changing solution pH value, adding metal ions as complex agents, and derivatizing the functional group of the sensitizer [25]. It had been well recognized that the electron injection efficiencies of the sensitizers upon nanocrystalline wide band-gap semiconductors were determinant in photosensitization systems, which not only depended on their respective intrinsic properties such as energy levels [48] and excited state lifetimes, but also depended on the manner in which they were connected [49], such as physically or chemically adsorbed manner, the nature of anchoring groups, and the distance of the dye skeleton from the nanocrystalline surface [12, 50]. We will present the methods to enhance the photosensitization effect from several aspects below.



SCHEME 2: Transport of injected charge across sensitized semiconductor nanocrystallites under visible light irradiation. E_f' refers to the quasi-Fermi level of the semiconductor nanocluster. Reproduced with a perfect scheme copy from [30]. Copyright 1997 American Chemical Society.

3.1. Sensitizer

3.1.1. Novel Photosensitizers. Some researchers developed some novel photosensitizers which exhibited high photocatalytic activity. Min et al. [2] found that the conjugated polymers (CP's) with extended p-conjugated electron systems showed the relatively high photoelectric conversion efficiency and charge transfer due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, and good stability. The conjugated polymers could be separated from the aqueous phase by using simple gravity settling and be recycled easily. For example, thiophene oligomer could photosensitize TiO_2 to catalyze the degradation of phenol under visible light irradiation [51], and Eu^{3+} - β -diketonate complexes with a remarkable quantum yield of 43% were excited under visible light irradiation at 440 nm [52], and so on. As the conjugated polymers, TiO_2 /polyaniline composite nanoparticles also showed good sedimentation ability and could decant from the suspension in about 5 min, while the pure TiO_2 nanoparticles did not decant after 2 h [53].

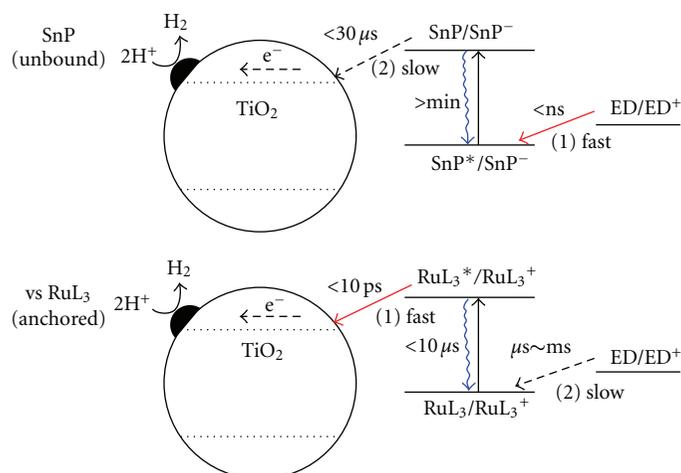
Besides Ru complexes, Os complexes were also effective for sensitizing TiO_2 because electron injection into nanocrystalline TiO_2 was thought to occur on a subpicosecond time scale which restrained the back electron transfer and thus enhanced the sensitization effect although the excited-state lifetimes for Os complexes were typically shorter than those for the analogous Ru complexes. Sauvé et al. speculated that the more important reason for this was that the ground-state potentials of the Os complexes could be readily tuned to less positive potentials by using stronger donor ligands [10].

Many sensitizers such as Ru complexes [54], Os porphyrins [10], and Pt complexes [55] had been fixed on the surface of TiO_2 through chemical anchoring groups (e.g., carboxylate, phosphonate, and catechol linkage). However, such chemical anchoring bond could be made only in a specific pH value range and was not inherently stable in an aquatic environment. Kim et al. [56] investigated the metalloporphyrins (especially tin(IV)-porphyrin (SnP)) for their photochemical activity in various applications, because

the lifetime of photogenerated SnPc* was long enough to survive the slow diffusion from the solution bulk to the TiO_2 surface, which made the adsorption of SnP on TiO_2 not to be required and the H_2 production was active over a wide pH value range (pH 3–11), while the dye anchoring onto the surface of TiO_2 was an essential requirement for the visible light sensitization with Ru complexes. Scheme 3 illustrates the electron transfer dynamics occurring on SnP and Ru(dcbpy)₃ sensitized TiO_2 particle. Being less expensive, less toxic, and consisting of more abundant elements unlike the Ru-based sensitizers, SnP could be developed and utilized as a practical sensitizer for solar chemical conversion.

Kathiravan et al. [8] observed that chlorophyll which was extracted from cyanobacteria could act as an efficient photosensitizer. Chlorophyll *a* served as the light-trapping and energy-transferring chromophore in photosynthetic organisms. Chlorophylls were effective photoreceptors because they contained a network of alternating single and double bonds, and the orbitals could delocalize electrons for stabilizing the structure and allowing the absorption of energy from sunlight. The ground state absorption study revealed that there was an interaction of colloidal TiO_2 with chlorophyll through carboxyl group. The process of electron transfer from the excited state chlorophyll to the conduction band of TiO_2 had been confirmed by the decrease in fluorescence lifetime. Thus as a dominant pigment on earth, chlorophyll *a* could be used as a photosensitizer more commonly.

3.1.2. Stability of Sensitizer. Most of the photosensitizers suffered from a stability problem such as dissolution and the photocatalytic degradation of the dyes [31], and the deactivation and separation of fine catalyst powders from the aqueous phase after utilization, and the large-scale applications of this promising method were prevented [2]. The easy separation and reusable ability of PAN/ TiO_2 implied that it was potentially employable in the search for photosensitizer with easy separation and reusable ability which were prerequisites for practical applications under mild condition such as natural light and oxygen from air. Based on above



SCHEME 3: Schematic illustration of the electron transfer dynamics occurring on SnP and Ru(dcbpy)₃ sensitized TiO₂ particle. Reproduced with a perfect scheme copy from [56]. Copyright Royal Society of Chemistry 2011.

analysis, TiO₂ which was sensitized with polyaniline was a promising photocatalyst which should be employed [2].

3.1.3. Modification of Photosensitizers. Up to now, different strategies have been successfully applied in designing sensitizers, coordination metal complexes especially, which absorb over the whole visible spectrum, including lifting the HOMO (highest occupied molecular orbital) level by incorporating strong σ -donor ligands or lowering the LUMO (lowest unoccupied molecular orbital) level of the anchoring ligands. Other crucial factors are high electron injection efficiency from the metal to ligand charge transfer- (MLCT-) based excited state to the conduction band of the semiconductor and a slow back electron transfer or charge recombination process. Both these concerns could be addressed synthetically with appropriate design of an anchoring functionality that could covalently bind the nanoparticulate TiO₂ surfaces very efficiently [39]. The photophysical and photoelectrochemical studies revealed that three kinds of efficiencies, that is, the fluorescence quenching efficiencies of the dyes by colloidal TiO₂, the monochromatic incident photon-to-current conversion efficiencies (IPCEs) for the dye-sensitized TiO₂ electrodes, and the overall photoelectric conversion efficiencies (η) for the dye-sensitized solar cells (DSSCs) based on dye sensitizers, all depended strongly on the anchoring group types [12]. The anchoring group effects are also related with the kind of solvent and the presence of competing adsorbates, such as electron donors and electrolytes.

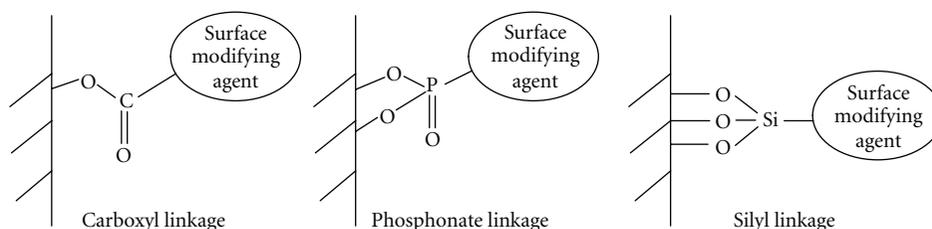
Carboxyl [57], phosphate [37], sulfonate [12], acetyl [7], and silyl [40] functionalities had been demonstrated to be able to form linkage with TiO₂ surface as shown in Scheme 4. Stability of these linkages varies in aqueous medium, and some of these linkages are only stable within certain pH value range and certain solvents. Chen et al. showed that the combination of carboxyl and hydroxyl as anchoring groups led to highly efficient IPCEs over a wide spectrum region with the maximum IPCE of 73.6% [12]. A possible explanation was that the combination of the carboxyl and the

hydroxyl led to a complexation reaction of the corresponding dye molecule with Ti⁴⁺ ion, which induced the observation of the red shift and the isosbestic point. Moreover, the silyl anchoring group seemed to be an ideal surface modification moiety for TiO₂ owing to the high affinity of the silyl functionality for the hydroxyl groups on the surface of the semiconductor and the chemical inertness of the resultant silyl, Si–O bonds [40].

Because of such stability of covalent linkage consideration, researchers explored the possibility of the coordination metal complex's derivatives containing the anchoring groups as the photosensitizer for TiO₂; thus the photosensitizer was stable against dissociation even at extreme pH value in aqueous medium or in a wide range of organic solvents. They attempt to utilize dehydration of carboxyl group of xanthene dyes with amino group of silane-coupling reagent fixed on TiO₂ surface leading to a strong chemical fixation of dye on TiO₂ particles and conquering the unstableness of the dye-sensitized photocatalyst in water [22]. There were studies which indicated that the linkage of ground dye and divorce of oxidized dye from TiO₂ could enhance the electron injection and hinder the backward transfer and subsequently improve the photosensitized efficiency [58]. Thus we can prepare more efficient sensitizers that can couple the functions of a sensitizer, which is bound to the surface of TiO₂ and an antenna, which can realize the intramolecular energy transfer from highly absorbing chromophoric groups by tuning the molecular components, and thus the photosensitized efficiency can be enhanced dramatically.

Consequently we know how significantly the anchoring manner of a sensitizer molecule influences its sensitization behavior on a nanocrystalline semiconductor, and the optimization on adsorbing groups may result in more efficient sensitizers for photosensitization applications.

Besides the modification of the anchoring group, another successful strategy for obtaining a broad absorption which extends throughout the visible region is to utilize a combination of sensitizers which complement each other in their spectral features [11]. A series of preformed BODIPY



SCHEME 4: Some of the most common covalent anchoring groups for surface modification of TiO_2 photocatalysts and TiO_2 nanocrystalline electrodes. Reproduced with a perfect scheme copy from [40]. Copyright 2002 Elsevier Science Ltd.

dimers had been investigated by Ventura et al., showing that the molar absorption coefficient of the dimer was about twice with respect to the monomer and making these dimers valuable components of complex molecular structures for light energy conversion [59]. There were also studies which showed that the combination of two different sensitizers was found to exhibit remarkable photosensitized performance, the absorption sites of which on the TiO_2 surface were different, meaning that there was not overlap of the electronic orbitals of two different sensitizers and it was difficult to be electron transfer between two sensitizers stochastically [11, 60]. Cosensitization was found to suppress the aggregation and affect the sensitization performance profoundly. In addition, multilayer films with different numbers of sensitizer/metal-doped- TiO_2 bilayers [61] obtained higher efficiency, which could lower the charge recombination rate in the photosensitized system.

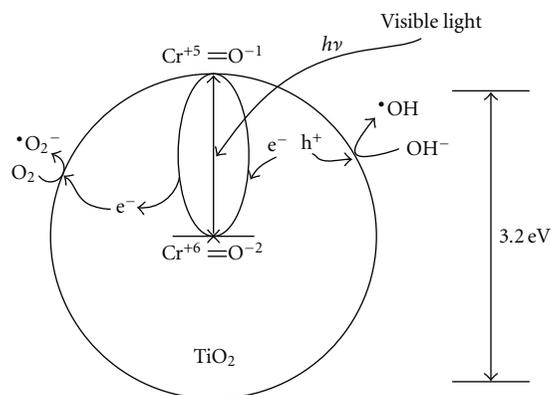
3.1.4. Concentration of Photosensitizers. We think that the effect of photosensitization is significantly influenced by the sensitizer concentration which plays a significant role in the number of electrons transferring from the excited sensitizer to the conduction band of the semiconductor photocatalyst. The photosensitization effect was enhanced with increasing sensitizer concentration within a certain range. However, with further increasing sensitizer concentration, the photosensitization effect was adversely decreased, possibly due to a saturation limit of the sensitizer adsorption sites on the photocatalyst surface [28]. In addition, the excess sensitizers which were dissolved in the reaction solution could be excited but could not inject the electrons to the conduction band of the photocatalyst for inducing the photocatalytic reaction [20]. Thus we must find the optimal sensitizer concentration for facilitating the photocatalytic reaction.

3.2. Loaded Metals. As we know, the linkage between the sensitizer molecules by metal ions is able to establish energy levels inside the band gap which lead to significant visible light absorption for photocatalyst and overcome the quenching and the insulating effect for the photocatalyst to achieve very high light harvesting efficiency and photocatalytic activity simultaneously. The existing research suggested that the combination between dye sensitizers and metal was much stronger than the combination between dye sensitizers and semiconductor photocatalysts [21]. This can be achieved by using coupled semiconductor layers which own appropriate electron energy levels where the edge of the conduction

band of the first semiconductor is lower than that of the second one. There were many researches about the function of loaded metals, such as Fe^{3+} [18], Cr^{3+} [61, 62], and Pt [18, 19] in especial, indicating that highly enhanced visible light-induced photocatalytic reaction could be obtained when the sensitized photocatalysts were additionally modified by surface metal deposits.

Pt showed the best activity among the metals which should be ascribed to the fact that electron trapping in Pt was fast enough to compete with the back electron transfer [38, 55]. The existing research showed that the combination of different size of metal particles could promote the photosensitized reactions markedly. Chen et al. found that the TiO_2 /large size-CdS/small size-CdS electrode showed enhancement and broadening of the absorption spectrum in visible light region, in comparison with the electrodes which were sensitized with single size CdS nanoparticles [36]. Chromium(VI)-doped glasses as well as mesoporous silicas are known for their tetrahedral coordination of chromium. Such coordination allows for a special transition under visible light irradiation: $\text{Cr}^{6+}=\text{O}^{2-} \rightarrow \text{Cr}^{5+}-\text{O}^{1-}$. In particular, the Cr^{5+} can possibly donate an electron into the surrounding TiO_2 , and O^{1-} can scavenge an electron from the surrounding TiO_2 . In this case, the charge separation will occur, which will result in a hole and an electron in TiO_2 . If this process happens at or near the catalyst surface, the charges can interact with the surface hydroxyl groups or adsorbed oxygen to produce active oxygen radicals. Scheme 5 describes this process. Davydov et al. [62] investigated the proposed mechanism of photooxidation on TiO_2 /Cr-(Ti)-MCM-41 and obtained prominent photosensitized effect.

3.3. Electron Donor. The regeneration of the sensitizers in the presence of suitable electron donors is a prerequisite for the development of the practical photosensitization application. In order to regenerate the electron-deficient sensitizer in photocatalytic system, some electron donors, or sacrificial agents, have to be used by adding them to a reaction solution to sustain the photoreaction cycle. The existing experiments have shown that the dechlorination rate of visible light-induced degradation of carbon tetrachloride on dye-sensitized TiO_2 decreased due to the depletion of the RuII-species sensitizers when the reaction proceeded without addition of the electron donor. On the other hand, when the electron donor 2-propanol was present, the dechlorination rate remained constant for 6 h of irradiation without showing any signs of deceleration [45]. Notoriously, various



SCHEME 5: Proposed mechanism of photooxidation on $\text{TiO}_2/\text{Cr}(\text{Ti})\text{-MCM-41}$. Active Cr^{6+} species are incorporated in SiO_2 matrix. Reproduced with a perfect scheme copy from [62]. Copyright 2001 Academic Press.

alcohols and acids can be used as sacrificial electron donors to regenerate the sensitizer. There were some commonly employed electron donors, such as acetonitrile [25, 33], methanol [12, 24], isopropanol [13, 45], cyclohexanone [15], diethanolamine [20], and ethylenediaminetetraacetic acid (EDTA) [32, 63]. We also found that IO_3^-/I^- (or I^{3-}/I^-) shuttle redox mediator could act as electron donors similarly [33]. Scheme 6 describes potential energy diagram of H_2 production from water over dye-sensitized Pt/TiO_2 photocatalysts with I^- as an electron donor, in which system the dye is merocyanine. Moreover, the polarity of the solvent has a significant influence on the photosensitized efficiency. Thus it is necessary to take into account the influence of the solvent on the energy potentials of them in constructing an efficient sensitized photocatalysis system in aqueous solutions.

3.4. Dissolved Oxygen. There is actually an argument about the effect of dissolved oxygen. Shang et al. [45] observed that the initial dechlorination rates of CCl_4 decreased in the order of $\text{N}_2 > \text{air} > \text{O}_2$ -saturated system by dye-sensitized TiO_2 under visible light irradiation. The presence of O_2 in the suspension lowered photosensitization efficiency by two ways: direct quenching of the excited sensitizer and scavenging CB electrons. However, Song et al. [51] confirmed that oxygen played an important role during the degradation chain reaction because it was responsible for the generation of $\bullet\text{O}_2^-/\text{HO}\bullet$ radicals. We think that whether dissolved oxygen is needed in the system of photosensitization depends on the pollutants which will be degraded and different degradation mechanisms.

3.5. pH Value of Solutions. The adsorbing power of the sensitizers is strongly influenced by the surface charge. The positively charged TiO_2 surface at acidic conditions strongly attracts negatively charged sensitizer molecules, while the negatively charged TiO_2 surface at basic conditions attracts

positively charged sensitizer molecules [44, 46]. However, what we want is that the adsorbing power of the sensitizers is unaffected by the pH value of the solution, and it is the direction of the researches.

4. Apparent Quantum Efficiency of Photosensitization

Although it is very difficult to compare the results of the present reported studies because the photocatalytic apparent quantum yields appear to vary according to the reaction conditions and the measurement methods. With a view to knowing the current state of sensitization study in the field of photocatalysis, here we tried to list several research results of apparent quantum yields for hydrogen evolution (Table 1) and degradation rates of organic pollutants (Table 2) according to the results which were reported in our references.

5. Prospect

Up to now, the most efficient sensitizers of the solar cell are ruthenium polypyridyl complexes. Although the present study demonstrated the potential use of the sensitized semiconductor photocatalysts for visible light-induced degradation of pollutants and energy conversion, the problems such as high cost, long-term unavailability, and undesirable environmental impact of these noble metal complexes make this method unsuitable for large-scale industry production. There remains the need for alternative photosensitizers which have larger extinction coefficient and extend the absorption range into the red visible region [11, 14].

Besides the methods for enhancing the effect of photosensitization which was mentioned above, some researchers explored certain new ways by which noteworthy results were achieved. For instance, the photodegradation of plastic (PS) could be realized by preparation of $\text{PS}-(\text{TiO}_2/\text{CuPc})$ composite thin films under the sunlight irradiation with little formation of toxic byproducts [45]. An integrated chemical system was designed for hydrogen evolution which utilized photosensitized oxide semiconductors [66]. The system was spatially organized by a linear channel zeolite into a vectorial array of electron donor/sensitizer/semiconductor/electron acceptor/catalyst. The ion-exchange properties and size-exclusion effects of the zeolite cause the donor, the sensitizer, and the acceptor to occupy their appropriate places in the electron transport chain. Li et al. prepared an efficient visible-light active photocatalyst of multilayer-Eosin Y-sensitized TiO_2 through linkage of Fe^{3+} between not only TiO_2 and Eosin Y but also different Eosin Y molecules to form three-dimensional polymeric dye structure [18]. The multilayer-dye-sensitized photocatalyst was found to own high light-harvesting efficiency and photocatalytic activity for hydrogen evolution under visible light irradiation. Scheme 7 illustrates the multilayer adsorption of Eosin Y via linkage of Fe^{3+} on TiO_2 for photocatalytic hydrogen evolution.

Considering the possible practical applications of photosensitization systems, we have to make sure that the photosensitizer or the mediator which was utilized to destroy

TABLE 1: The photocatalytic hydrogen evolution by sensitized photocatalysts under visible light irradiation.

No.	Catalyst	Reaction conditions	Irradiation type	Hydrogen evolution ($\mu\text{mol/h}$)	Apparent quantum efficiency	References
(1)	Eosin Y sensitized 1.0 wt% CuO/TiO ₂	Catalyst: 20 mg; 70 mL 15% diethanol amine (DEA) H ₂ O; DEA as sacrifice electron donors	A 200 W halogen lamp with a cut-off filter ($\lambda > 420$ nm)	10.56	5.1%	[16]
(2)	Eosin Y sensitized 0.5 wt% Pt/N-TiO ₂ -300°C	Catalyst: 0.100 g; 80 mL 0.79 mol/L triethanolamine (TEA) solution as sacrifice electron donors; pH 7.0; initially N ₂ -saturated	A 400 W high pressure Hg lamp with a cut-off filter ($\lambda > 420$ nm)	Average about 80	Unclear	[17]
(3)	Eosin Y-Fe ³⁺ (1 : 1)-1.0 wt% Pt/TiO ₂	Catalyst: 0.100 g; 80 mL 0.79 mol/L TEA solution as sacrifice electron donors; pH 7.0; initially N ₂ -saturated	A metal halide lamp (400 W) with a cut-off filter ($\lambda > 420$ nm)	275	19.1%	[18]
(4)	Eosin Y sensitized 1.0 wt% Pt/Ti-MCM-41 zeolite	Catalyst: 40 mg; 80 mL 15% TEA H ₂ O; TEA as sacrifice electron donors; pH 7.0; initially Ar atmosphere	A 300 W tungsten halogen lamp with a cut-off filter ($\lambda > 420$ nm)	~10	12.01%	[19]
(5)	Eosin Y sensitized 0.5 wt% Pt/SrTiO ₃	Catalyst: 0.2 g; 150 mL 15% DEA H ₂ O; DEA as sacrifice electron donors; pH 11.6; initially Ar atmosphere	A 300 W Xe arc lamp with a cut-off filter ($\lambda > 400$ nm)	~3	Unclear	[20]
(6)	Eosin Y sensitized 1.0 wt% Rh/TiO ₂	Catalyst: 20 mg; 70 mL, 15% DEA H ₂ O; DEA as sacrifice electron donors; initially Ar atmosphere	A 200 W halogen lamp with a cut-off filter ($\lambda > 420$ nm)	14.63	7.10%	[21]
(7)	Eosin Y sensitized 0.1 wt% Pt/TiO ₂	Catalyst: 0.3 g; 250 mL, 15% DEA H ₂ O; DEA as sacrifice electron donors; initially Ar atmosphere	A 300 W Xe lamp with a cut-off filter ($\lambda > 460$ nm)	Average about 65	10%	[22]
(8)	Eosin Y sensitized 1.0 wt% Pt/multiwalled carbon nanotube (MWCNT)	Catalyst: 20 mg; 80 mL, 15% TEA H ₂ O; TEA as sacrifice electron donors; initially Ar atmosphere	A 300 W tungsten halogen lamp with a cut-off filter ($\lambda > 420$ nm)	54.20	12.14%	[23]
(9)	Merocyanine sensitized 1.0 wt% Pt/TiO ₂	Catalyst: 50 mg; 100 mL 95% AN-H ₂ O; acetonitrile and I anions as sacrifice electron donors	A 300 W Xe lamp with a cut-off filter ($\lambda > 440$ nm)	Average about 17	~2%	[33]
(10)	Merocyanine and coumarin dyes sensitized 1.0 wt% Pt/TiO ₂	Catalyst: 50 mg; 100 mL 95% AN-H ₂ O; acetonitrile and I anions as sacrifice electron donors	A 300 W Xe lamp with a cut-off filter ($\lambda > 440$ nm)	Unclear	1.8% for M-Pt/TiO ₂ and 2.5% for C-Pt/TiO ₂	[31, 32]
(11)	Ru complex sensitized 0.1 wt% Pt/NS-K ₄ Nb ₆ O ₁₇	Catalyst: 5.0 mg; aqueous solution (2.0 mL) containing 10 mM EDTA as an electron donor; initially Ar atmosphere	A xenon lamp (300 W) with a cut-off filter ($\lambda > 420$ nm)	3.6	10.5%	[63]
(12)	3.1 wt% WS ₂ sensitized 1 wt% Pt/TiO ₂	Catalyst: 0.2 g, 200 mL aqueous solution; Na ₂ S as the hole scavenger	A 350 W Xe lamp with a cut-off filter ($\lambda > 430$ nm)	2.13	Unclear	[9]
(13)	Carboxylate versus phosphonate in Ru-complex-sensitized 3.0 wt% Pt/TiO ₂	Catalyst: 15 mg; EDTA as sacrifice electron donors	A 450 W Xe lamp with a cut-off filter ($\lambda > 420$ nm)	Maxima about 132	22.4%	[57]
(14)	Sensitization of TiO ₂ film with zinc-substituted cytochrome	EDTA as a sacrificial electron donor	100 W tungsten halogen lamp with filters ($\lambda > 475$ nm)	About 1020 for the first 20 min of illumination	10 \pm 5%	[64]
(15)	Ru-, Rh-, and Ir-doped SrTiO ₃ loaded with Pt cocatalysts (0.1 wt%)	Catalyst: 300 mg; 380 mL of 10 vol% aqueous MeOH	A 300 W Xe lamp with cut-off filters ($\lambda > 440$ nm)	Maxima about 117	5.2% at 420 nm	[65]

TABLE 2: The photodegradation effects of target contaminants by sensitized photocatalysts under visible light irradiation.

No.	Catalyst	Reaction conditions	The light source	Target contaminants	Degradation rate	References
(1)	Ru-complex-sensitized TiO ₂	Catalyst: [TiO ₂] = 0.5 g/L, Ru-complex = 3 μM; pH = 3; 2-propanol as sacrifice electron donors; [CCl ₄] = 1 mM, N ₂ -saturated	A 450 W Xe-arc lamp with an UV cut-off filter ($\lambda > 420$ nm)	CCl ₄	Dechlorination quantum yield, $\Phi_{Cl^-} = 10^{-3}$	[46]
(2)	Ru-complex-sensitized 0.2 wt% Pt/TiO ₂	Catalyst: [TiO ₂] = 0.5 g/L, Ru-complex = 10 μM; pH = 3; 0.1 M isopropyl alcohol as sacrifice electron donors; [CCl ₄] = 1 mM, initially N ₂ -saturated	A 450 W Xe-arc lamp with an UV cut-off filter ($\lambda > 420$ nm)	CCl ₄	Initial dechlorination rates is 4.7 μM/min	[38]
(3)	Ru-complex-sensitized TiO ₂	Catalyst: 0.3 g; 150 mL of CCl ₄ saturated aqueous solution (pH 7), containing 5.0 mM of KI as sacrifice electron donors	A 100 W tungsten lamp ($\lambda > 450$ nm)	CCl ₄	Rate constant is 0.446 μM min ⁻¹ g-catalyst ⁻¹	[37]
(4)	Ru-complex-sensitized TiO ₂	Catalyst: 0.3 g; 150 mL of CCl ₄ saturated aqueous solution (pH 6.5–7.0), containing 5.0 mM of KI as sacrifice electron donors, initially N ₂ -saturated	A 100 W tungsten lamp ($\lambda > 450$ nm)	CCl ₄	Rate constant is 0.585 μM min ⁻¹ g-catalyst ⁻¹	[40]
(5)	Polyaniline-sensitized TiO ₂	Catalyst: 100 mg; 50 mL H ₂ O without sacrifice electron donors, [MB] = 10 mg/L	Natural light irradiation for 90 min between 11.00 a.m. and 1.00 p.m.	Methylene blue (MB)	Decolorization efficiency is 80%	[2]
(6)	CuPc sensitized-TiO ₂	Catalyst: 0.7 wt% CuPc/TiO ₂ ; the ratio of TiO ₂ /CuPc to PS is 2.0 wt % in the composite film	Three 8 W fluorescent lamps (310 nm < λ < 750 nm)	Plastic (PS)	6.9% weight loss for composite film after 250 h	[45]
(7)	Ru-complex-sensitized TiO ₂	Catalyst: [TiO ₂] = 1 g/L, c (sensitizer) = 1 × 10 ⁻⁵ mol/L; [terbutryne] = 2 × 10 ⁻⁵ mol/L; pH = 3	A 500 W high-pressure xenon lamp with a cut-off filter ($\lambda > 420$ nm)	Herbicide terbutryne	100% after 4 h	[44]
(8)	1 wt% poly(flourene-co-thiophene) (PFT)-sensitized TiO ₂	Catalyst: 50 mg; 50 mL aqueous phenol solution with an initial concentration of 10 mg/L	A 250 W GaI ₃ lamp with a cut-off filter (400 nm < λ < 700 nm)	Phenol	74.3% after 10 h	[51]

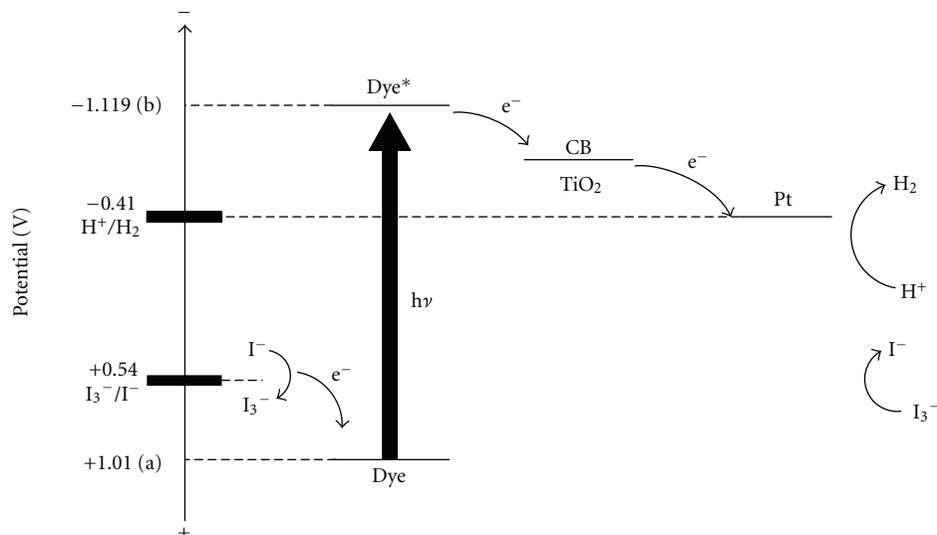
the pollutant does not pollute the environment by itself. Thus there is a growing interest for developing environmentally benign materials and/or biodegradable materials as the photosensitizers. Thus, the utilization of natural polymers seems to be especially attractive. Novel photoactive water-soluble modified polymers which were based on starch [67] and polysaccharides [13] were prepared. These polymeric systems were quite promising photosensitizers for demonstrating the reaction of organic compounds in an aqueous solution, while the photosensitizers will not result in environmental pollution.

6. Conclusions

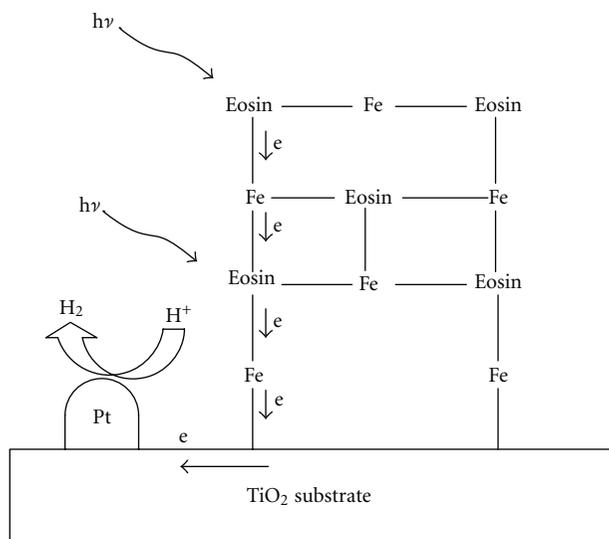
In this paper, we have enumerated various photosensitized ways which have been reportedly utilized successfully for the degradation of organic pollutants and energy conversion by

using the visible range of the solar spectrum. Though extensive works on this field have been carried out, only significant developments and researches which were completed have been referred to in this paper.

According to the studies which were reported in the literatures, inorganic sensitizers, organic dyes, and coordination metal complexes were very effective sensitizers that were studied mostly. The method of photosensitization has been applied to many fields in recent years, including the visible-light-promoted photodegradation of the contaminants, the dye-sensitized solar cell and semiconductor-sensitized solar cells, visible-induced hydrogen evolution from water. The proposed mechanism of the primary electron pathways over dye-sensitized semiconductor photocatalyst is illustrated in our paper. There are many methods to enhance the photosensitized effects, and we must develop novel sensitizers with high absorption coefficients in the visible part of the



SCHEME 6: Potential energy diagram of H_2 production from water over dye-sensitized Pt/TiO₂ photocatalysts with I^- as an electron donor. HOMO (a) and LUMO (b) energy levels of merocyanine dye derived from CV measurement in DMF solvent containing 0.1 M tetrabutylammonium perchlorate. Reproduced with a perfect scheme copy from [33]. Copyright 2002 Elsevier Science B.V.



SCHEME 7: Schematic model for multilayer adsorption of Eosin Y via linkage of Fe^{3+} on TiO₂ for photocatalytic hydrogen evolution. Reproduced with a perfect scheme copy from [18]. Copyright 2009 International Association for Hydrogen Energy Published by Elsevier Ltd.

spectrum, high mobility of charge carriers, and good stability for the industrialized application in the future.

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