

Review Article

Photocatalytic and Photoelectrochemical Water Splitting on TiO_2 via Photosensitization

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The search for an alternative to replace conventional fuel has been going on for years due to the limited storage of fossil fuel and excess CO_2 emission from the fuel. Using H_2 as fuel has gained wide attention recently, as well as consequently splitting of water into hydrogen and oxygen. Seminal semiconductors such as TiO_2 and ZnO have their position of CB and VB in alignment with water reduction and oxidation potential, respectively, but their wide bandgap allows them to absorb only UV light of the solar spectrum. Combining narrow bandgap semiconductors or other visible light active sensitizers with TiO_2/ZnO is a facile route to exploit the visible light region of the solar spectrum. In this review, I make an attempt to summarize the various photosensitizers used in combination with TiO_2 for water splitting with recent reports as examples.

1. Introduction

Rapid growth of urbanization and industrialization resulted in the need of surplus energy and in environmental contamination. In response to the demand of modern generation, finding new sources of energy and its storage have become an essential topic of research. Considering the limited storage of conventional fuel, fossil energy, utilizing the unlimited amount of renewable energy, solar light, to sustain our future needs by converting it to other forms of energy and storable forms is an important field of study. Moreover, the impact of CO_2 emission from fuel consumption on climate change is an increasing global concern. Among various renewable energy resources, solar energy represents the ultimate renewable source. The total solar energy irradiating on the earth is about 120000 TW a year. If it is efficiently harnessed, less than 0.02% of the solar energy is sufficient to entirely replace the total energy consumption originated from conventional fuel [1]. According to Annual Energy Outlook 2015 for high economic growth and high oil price cases, in 2040, solar and wind renewable energy sources account for more than two-thirds of the total renewable generation. The total renewable share of all electricity generation increases from 13% in 2013 to 18% in 2040 (Figure 1) [2]. Achieving this in an economically

and environmentally benign manner is important for the conservation of the global atmosphere.

Instantaneous change from the current carbon-based fuel system to a renewable energy system is not very easy although solutions and technologies exist to support this. Investigations on clean energy technology help the researchers to exploit solar energy efficiently and economically to generate, convert, and store electricity. Generation of hydrogen (H_2)/oxygen (O_2) or both by splitting water and usage of hydrogen as fuel with reduced CO_2 emission conserve the environment. Choosing an appropriate photosensitive material is the primary requisite to absorb solar energy and to convert it to other useful energies. Most of the conventional photoactive materials are selective in their light absorption, thus limiting the usage of the entire solar spectrum, whereas the combination of two or more suitable photoactive materials may fulfill the requirements for photoenergy absorption. Compiling different materials to obtain a new hybrid material with desired properties demands careful designing and engineering in order to reduce any adverse results by the hybridization of different materials.

Splitting of water into H_2 and O_2 using solar light has drawn wide attention due to the abundance of the resources,

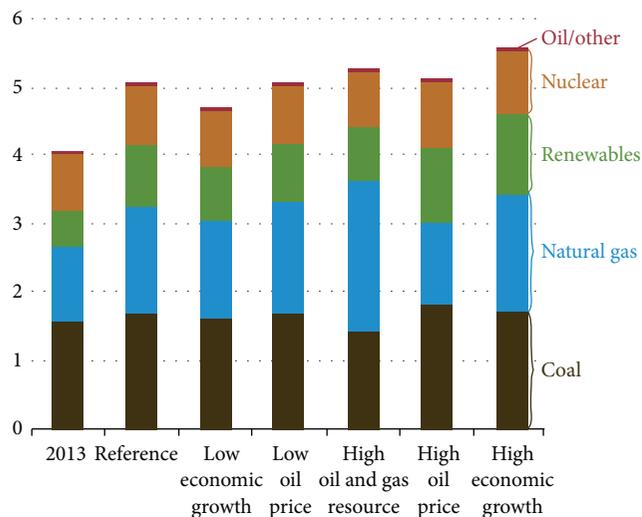


FIGURE 1: Electricity generation by fuel in six cases, 2013 and 2040 (trillion kilowatt-hours). Source: *Annual Energy Outlook 2015 With Projections to 2040, U.S. Energy Information Administration* [2].

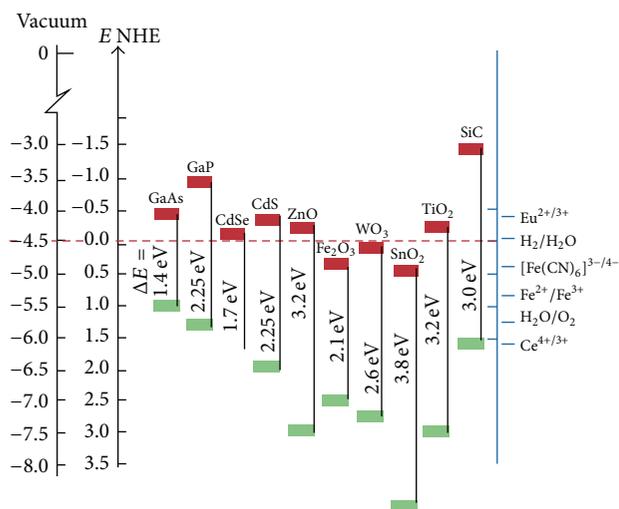


FIGURE 2: The lower edge of the conduction band (red color) and upper edge of the valence band (green color) of various semiconductors are presented along with the bandgap in electron volts. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. Reprinted with permission from [2]. Copyright 2001, Nature Publishing Group.

water, and solar light. Generation and consumption of hydrogen fuel from water are an environmentally friendly method with zero carbon emission. The most important criterion is the electronic bandgap alignment of the photosensitive material with the redox potential of water. Figure 2 shows the comparison between the bandgap of various semiconductors and the redox potential of water. The bandgap and position of conduction band (CB) and valence band (VB) of most of the semiconductors are not fitted within the potential window for splitting the water [12–14].

The position of CB and VB of TiO₂ is in agreement with redox potential of water, which makes TiO₂ one of the apt materials for water splitting. Still, there are other issues which affect the efficiency of water splitting on TiO₂, such as high recombination rate and the wide bandgap which permits the absorption of only UV light. Since UV light comprises only 4% of the solar spectrum, photosensitization using low bandgap materials and altering the position of CB or VB of TiO₂ are a few alternatives to increase efficiency of catalytic activity of TiO₂. In this review, visible light induced splitting of water using titanium dioxide (TiO₂) in combination with photosensitizers is summarized.

2. Water Splitting

Generation of H₂ via splitting of water is of great importance in the current renewable energy scenario. To initiate water splitting without the supply of additional energy, the CB level of the semiconductor should be more negative than the water reduction potential and the VB should be more positive than the water oxidation potential. When the semiconductor absorbs energy greater than its bandgap, the electrons in the VB are excited leaving the holes behind. The photogenerated electrons and holes recombine instantaneously, releasing the energy as photons or heat, when they are not effectively separated. Thus, charge separation is a crucial factor in any photocatalytic activities. If the charges are successfully separated, they migrate to the surface of the semiconductor and participate in oxidation and reduction. Further, the thickness of the semiconductor is also important since if the diffusion length of charge carriers is smaller than the thickness of the semiconductor the carriers may recombine before they reach the surface of the semiconductor. Nanosized catalysts can enhance the effective transportation of charges and active surface area for catalysis. To achieve further enhancement in H₂ production, cocatalysts are loaded onto semiconductors, which are believed to provide active sites and decrease the activation energy for water splitting. Noble metals such as platinum and ruthenium are considered typical cocatalysts to promote hydrogen generation although back reaction, that is, formation of water by the combination of hydrogen and oxygen, is an issue.

2.1. Mechanism of Splitting of Water on TiO₂. Reduction and oxidation are the basic chemical reactions that happen during water splitting. As mentioned, to generate H₂ and O₂ feasibly, the position of CB and VB of the semiconductor should fit into the potential window of water reduction and oxidation potential, respectively. When light shines on TiO₂, the electrons in the VB are elevated to the CB leaving holes behind. The excited electrons are involved in the generation of hydrogen and oxygen is generated by holes (Figure 3) [15]. Since hydrogen is used as fuel, improving the generation of hydrogen is very important. Inclusion of photosensitizers is proved to be useful in enhancing hydrogen production to a remarkable extent. The common organic hole scavenger used is ethylenediaminetetraacetic acid (EDTA) since it can be easily oxidized using the holes, thus allowing the

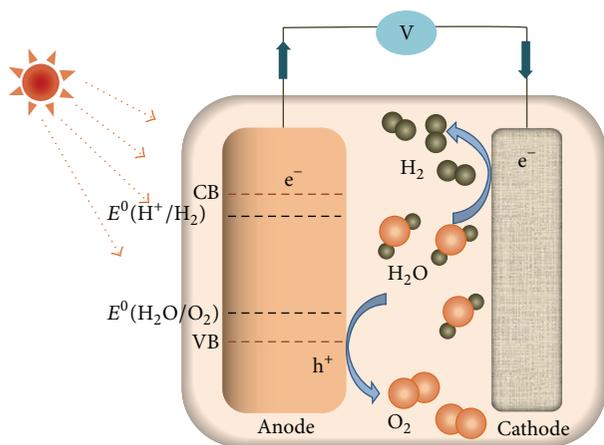


FIGURE 3: Photoelectrochemical water splitting cell based on n-type semiconductor TiO_2 photoanode.

CB electron to produce hydrogen. The ability to produce hydrogen on some common hole scavengers is as follows: EDTA > methanol > ethanol > lactic acid. Decomposition of the agents can add to hydrogen production because hydrogen is one of the products during their decomposition [16].

3. Modification Techniques to Enhance H_2 Production

So far, many techniques are implemented to improve the generation of hydrogen. Incorporation of photosensitizers such as dyes, low bandgap semiconductors, noble metals, and upconversion nanoparticles is a technique used currently. In this review, photosensitizers which absorb visible to near-infrared (IR) light in combination with TiO_2 are discussed.

3.1. Incorporation of Photosensitizers. Photosensitization is used widely to utilize visible to near-IR light of the solar spectrum for energy conversion applications. Dyes are used commonly as sensitizers, but, considering the photostability of dyes, quantum dots, low bandgap semiconductors, and noble metals are considered as better alternatives for dyes. On irradiation with visible light, the photosensitizer is excited and the excited electrons are injected to the CB of TiO_2 , or the emission energy of the photosensitizer is used to excite TiO_2 , and thus the photocatalytic process can be initiated (Figure 4) [3]. Recently, incorporation of upconversion nanoparticles into TiO_2 has drawn attention since upconversion nanoparticles carry out absorption near the IR region of the solar spectrum, which occupies 52% of the solar energy, and emit UV to visible light depending on the dopants present in the matrix. The emitted energy is absorbed by the semiconductor. In this section, various agents used as photosensitizer are discussed.

3.1.1. Dye Sensitization. Dye sensitization is the commonly used technique to explore visible light for energy conversion. When the dye is excited, the electrons are elevated from the HOMO level to LUMO level, and the electrons from

the LUMO level can be transferred to the CB of TiO_2 . There are a few dyes, for example, safranin O/EDTA and T/EDTA, reported as able to generate hydrogen without the presence of semiconductors, but without effective charge separation most of the excited electrons are recombined with the holes, reducing the efficiency of hydrogen generation. In the presence of TiO_2 , the excited electron from the dye molecules can be transferred to the CB of TiO_2 , which then initiates water reduction. Faster electron injection time slows the backward reaction and recombination of excitons, resulting in higher rate of H_2 generation. The oxidized dye molecules can be regenerated by the inclusion of appropriate sacrificial agents (Figure 5) [4].

Mallouk and coworkers have done extensive studies on dye-sensitized semiconductor-based photoelectrochemical water splitting [4, 17]. Hydrated iridium oxide ($\text{IrO}_2 \cdot n\text{H}_2\text{O}$) and Ru(III)tris(bipyridine) were used as water oxidizing catalyst and photosensitizer, respectively. They have obtained a maximum of 1% quantum yield when $[\text{Ru}(\text{bpy})_3]^{2+}$ derivatives as sensitizer were incorporated into layered metal oxide semiconductors [4]. 2.3% quantum yield was achieved by incorporation of electron transfer mediator that is mimetic of the tyrosine-histidine mediator along with ruthenium polypyridyl sensitizer. Later, a series of metal-free organic sensitizers were used to study the oxygen generation, and it was found that the photocurrent generated is less than that of electrodes sensitized with Ru-based dyes, which is due to the lower electron injection yield and slower hole transport of porphyrin sensitizers compared to Ru-based dyes [18]. Gao et al. also worked on Ru-based photoelectrochemical cells and achieved photocurrent density of more than $1.7 \text{ mA} \cdot \text{cm}^{-2}$ under 0.2 V external bias versus NHE [19]. They further developed tandem cell by incorporating Ru based dye on one electrode and Co based dye on the other electrode for water splitting under neutral pH condition without applying any bias [20].

Reisner et al. incorporated Ru-based dye on TiO_2 along with $[\text{NiFeSe}]$ -hydrogenase as H_2 evolution catalyst by adsorption technique and achieved very efficient sunlight conversion without precious metals [21]. Dhanalakshmi et al. prepared sensitized TiO_2 via electrostatic adsorption of ruthenium complex. An optimum concentration of dye molecules on the surface of TiO_2 enhanced H_2 production; further increase in dye concentration decreased the activity of the catalyst due to the saturation in photocatalytic sites on TiO_2 [22]. Physical adsorption of Rhodamine B onto Co doped TiO_2 was reported by Le et al. The dye incorporated catalyst showed 6 times higher H_2 evolution than that with Co/ TiO_2 catalyst without dye [23].

Though dye-sensitized water splitting systems are simpler, the long-term performance is poor due to photodegradation of dye molecules, and the high cost of the Ru-based photosensitizer is another concern.

3.1.2. Noble Metal Sensitization. Considering the stability of the dye and related long-term use, plasmonic metal sensitization is considered as a good alternative to resolve the aforementioned issues. Plasmons are the oscillating

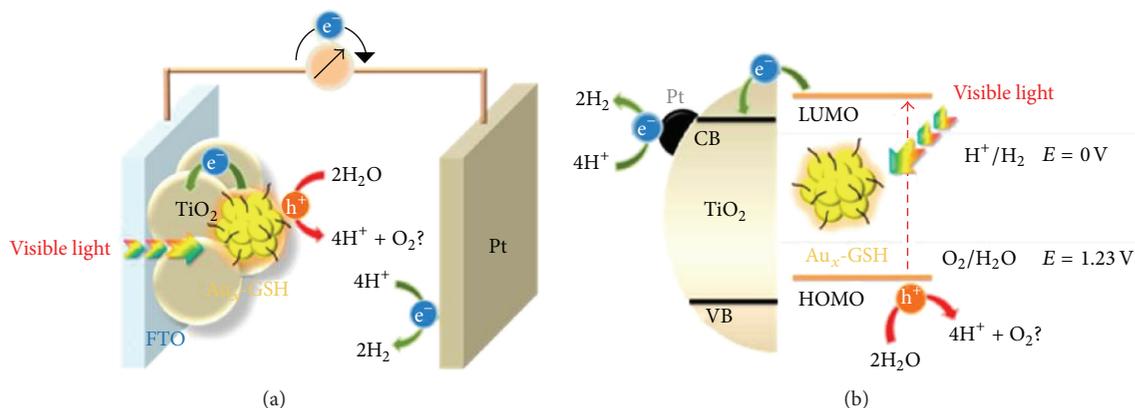


FIGURE 4: Illustration of photosensitization by glutathione capped gold nanoclusters (Au_x-GSH). (a) Au_x-GSH-sensitized TiO₂ film as photoanode of PEC and (b) Au_x-GSH-sensitized Pt/TiO₂ NPs photocatalytic system for water splitting reaction under visible light illumination. Reproduced with permission from [3]. Copyright 2014, American Chemical Society.

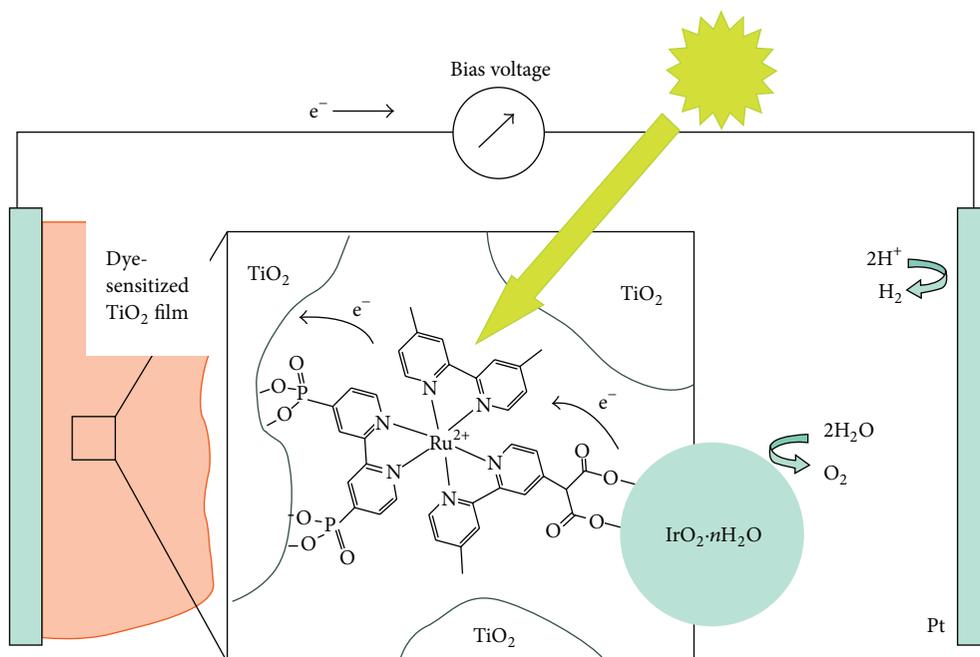


FIGURE 5: Schematic of the water splitting dye-sensitized solar cell. Reproduced with permission from [4]. Copyright 2015, American Chemical Society.

electrons on the surface of metal nanoparticles, and when the frequency of oscillation resonates with the frequency of incident light, the fascinating phenomenon, known as surface plasmon resonance (SPR), is created and leads to the generation of “hot electrons.” Depending on the size, shape, and surrounding medium, the plasmonic nanostructures are able to interact with light in the visible region to the infrared region. The plasmonic nanostructures act as an antenna to concentrate light, which subsequently enhances the electric field around the nanostructure, and the concentrated resultant field between two nanostructures leads to the generation of “hot spots.” Scattering ability of bigger nanostructures increases the optical path length of

photon in the reaction medium (Figure 6) [5]. Owing to the attractive ways of interaction between light and plasmons, metal nanostructures have drawn remarkable attention in various photoenergy applications such as photocatalysis and photovoltaics.

When the size of the semiconductor is larger than the diffusion length of its charge carriers, recombination occurs before electrons/holes reach the surface of the semiconductor. The presence of metal on the surface of the semiconductor localizes the light absorption onto the area of contact between metal and semiconductor and minimizes charge recombination. Using plasmonic metal as photosensitizer in combination with large bandgap semiconductor such as

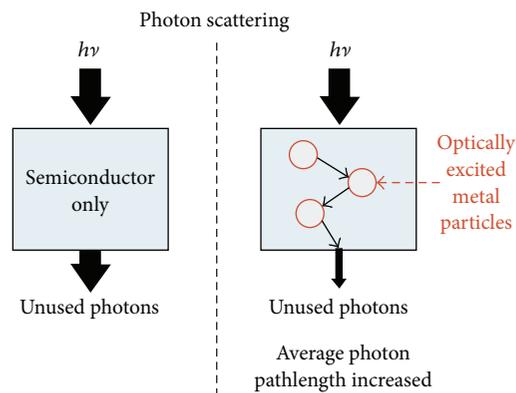


FIGURE 6: Schematic illustrating the scattering mechanism. Reproduced with permission from [5]. Copyright 2011, Nature Publishing Group.

TiO₂ allows the absorption of light below the bandgap of TiO₂ by metal. The excited electrons or the so-called “hot electrons” in metal can be injected to the CB of TiO₂, resulting in effective charge separation, and consequently improved catalytic activity [5, 24].

There are several methods reported on plasmon induced enhancement in water splitting. Ueno and Misawa studied plasmon induced water oxidation on Au nanorods (NRs) arrayed on TiO₂ surface. Stoichiometric evolution of hydrogen and oxygen was obtained with reduced overpotential. No current was observed when bare TiO₂ was illuminated under visible or near-infrared light, whereas anodic photocurrent was clearly observed at a positive potential above -0.3 V (versus saturated calomel electrode) using the Au NRs-loaded TiO₂ photoelectrode (Figure 7). The excited electrons injected into the CB of TiO₂ due to the excitation of plasmons and the holes left behind are involved in the oxidation of water (Figure 8); therefore, photocurrent is increased in the case of Au incorporated TiO₂ nanostructures [6]. The same observation is made by Haro et al. by adding Au NPs to mesoporous TiO₂ on the conducting substrate [25]. Kim et al. found that the photocurrent generated is larger for 50 nm Au NPs overcoated with TiO₂ and a decrement was found in the photocurrent when the size of the Au NPs was increased, which was attributed to the more generated charge carriers in decreased size [26].

The effect of mixture of Au NPs and Au NRs in combination with TiO₂ nanowires on water splitting is studied by Pu et al. [7]. In the case of Au nanoparticles, the electric field intensity was enhanced by two and five times in magnitude under illumination wavelength at 390 and 550 nm, respectively, whereas in the case of Au NRs the enhancement was 15 times at 750 nm irradiation wavelength. The significant enhancement in the visible region and hot electron generation upon SPR excitation are accountable for the observed enhancement in visible light photoactivity (Figure 9) [7]. Liu et al. also reported the near-field optical enhancement increasing the charge generation rate at the surface of the TiO₂, thus increasing photocurrent due to splitting of water [27]. Lee et al. tried reverse morphology by depositing thin

layer of TiO₂ onto Au NRs and obtained 20-fold quantum yields for visible light illumination as compared to UV [28].

There are a few reports on plasmon incorporated photonic crystals for water splitting. Photonic crystals (PCs) are known to trap light within their periodic structures, thereby slowing down the photons [8, 29]. Zhang et al. reported deposition of Au nanocrystals on periodically arranged TiO₂ nanotubes (NTs). The matching of photonic bandgap of TiO₂ with SPR wavelength enhanced the intensity of SPR and thus the performance of the catalyst (Figure 10) [8]. Zhang et al. prepared vertically aligned TiO₂ nanorods on FTO substrate, onto which TiO₂ inverse opal (IO) was fabricated using polystyrene opal template, followed by adsorption of Au NPs. 0.71% solar energy conversion efficiency was reported for Au incorporated TiO₂ PCs, which is ascribed to the improved coupling of the slow-photon effects of the TiO₂ PCs and the plasmonic photosensitization of the Au NPs [29].

Though inclusion metal improves the photocatalytic activity of TiO₂, the mechanisms involved in the charge generation transfer in plasmonic metal still remain unresolved. More studies are required to understand the exact mechanisms behind the results.

3.1.3. Quantum Dots. Semiconductor in combination with low bandgap materials is another technique to use visible light for water splitting. When the large bandgap material is combined with low bandgap material with more negative CB, the excited electrons from the low bandgap material can be transferred to the CB bandgap material. Quantum dots (QDs) such as CdSe, CdTe, and CdS are the widely used narrow bandgap materials since the position of the CB of them meets the requirement for the electrons transfer. Moreover, the bandgap of CdS and CdSe is 2.4 and 1.7 eV, respectively, which allows the absorption of visible light and facile transfer of excited electrons to the CB of TiO₂ (Figure 11) [9]. QDs can be attached to TiO₂ by postsynthesis or by presynthesis strategy. In the presynthesis strategy, some organic linker molecules are to be used to ensure the TiO₂. Direct growth of QDs on semiconductor offers intimate contact between the semiconductor and QDs and consequent facile charge transfer. Using either CdS or CdSe as photosensitizer in combination with TiO₂ is explored by many groups because of the simple synthesis techniques and suitable band alignment. Liu et al. prepared TiO₂-CdSe nanohybrid by emulsion-based bottom-up self-assembly (EBS) method [30]. The organic capping agents were removed by calcination, so that direct contact between TiO₂ and CdSe can be provided. The photocurrent produced was found to be larger in CdSe-TiO₂ compared to the current obtained in bare TiO₂. Further, the photocurrent response was found to be lower when organic linker molecule between TiO₂ and CdSe was present. Enhanced photocurrent generation on CdSe decorated on nanoporous TiO₂ nanotubes was reported by Xiao et al. [31]. CdSe QDs deposited on the inner and outer surface of TiO₂ nanotubes decreases the charge transfer resistance and consequently improves the photocurrent generation. Gao et al. deposited CdS nanoparticles on TiO₂ nanotubes by close space sublimation (CSS) technique and carried out a comparison with chemical bath deposition (CBD)

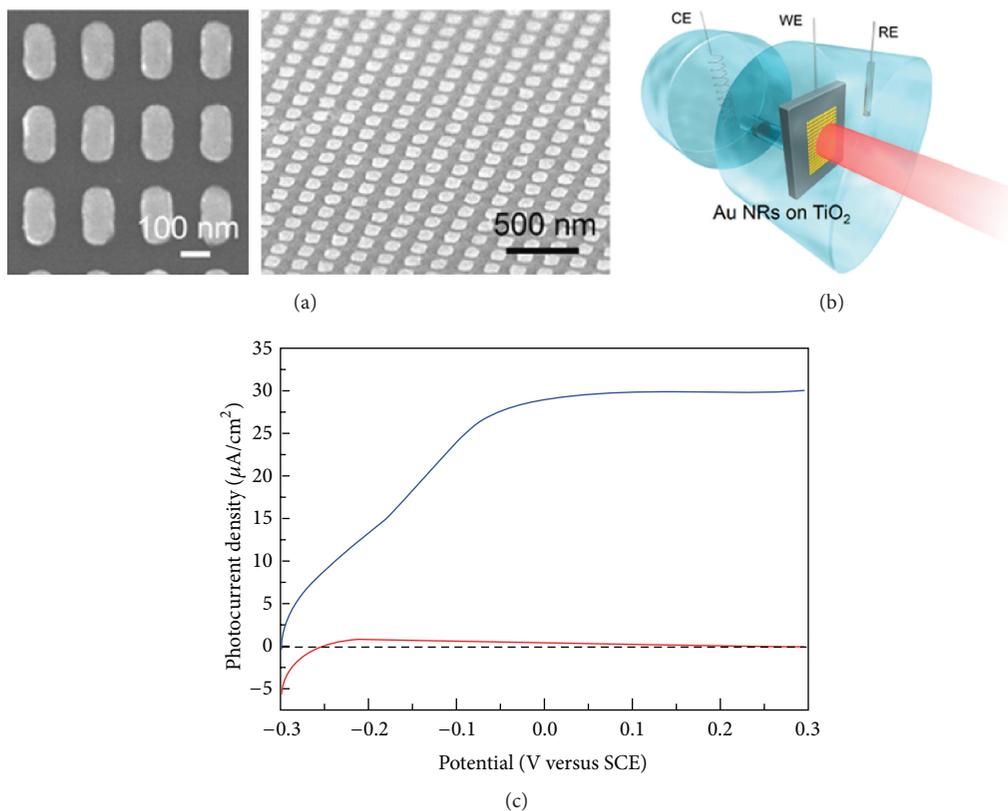


FIGURE 7: (a) Scanning electron microscope images of Au NRs on TiO_2 (left). Scanning electron microscope image of the same substrate tilted by 75° (right). (b) Schematic illustration of the photoelectrochemical cell. (c) Linear sweep voltammograms under irradiation with light in the wavelength range from 500 to 1300 nm with (blue) and without (red) Au NRs. The sweep rate was 5 mV s^{-1} . Reproduced with permission from [6]. Copyright 2013, Nature Publishing Group.

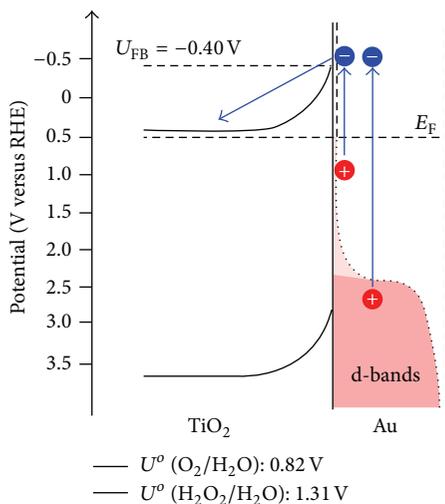


FIGURE 8: Energy diagram of the Au NR-loaded TiO_2 photoelectrode system. U_{FB} and U° exhibit the flat band potential of TiO_2 and the redox potentials versus reversible hydrogen electrode, respectively. The symbols [-] and [+] indicate the electron and the hole, respectively. Reproduced with permission from [6]. Copyright 2013, Nature Publishing Group.

and presynthesized techniques. The TiO_2 -CdS nanohybrid prepared by CSS and CBD techniques had shown better performance over the presynthesized method and bare TiO_2 (Figure 12) [10]. Cosensitization using CdSe and CdS together on TiO_2 was reported by a few groups [9, 32–34]. Lee et al. used CBD method to codeposit CdS and CdSe on TiO_2 . This cascade structure of $\text{TiO}_2/\text{CdS}/\text{CdSe}$ reaches band edge equilibrium through Fermi level alignment (Figure 13), which facilitates facile electron injection through the interfaces between QDs and TiO_2 and between QDs resulting in the generation of high photocurrent [9]. CBD technique was further used by Chi et al., and further they studied the effect of sequential annealing and coannealing of CdS and CdSe on performance. This two-step annealing was employed to reduce the chances of counter diffusion of the two types of QDs by single step annealing, and the codiffusion is expected to decrease the performance. The cosensitized electrodes showed better performance than the electrodes sensitized by single material and the coannealed electrodes [32]. Cheng et al. also reported cosensitization using three types of QDs, CdSe, CdS, and ZnS , together on TiO_2 nanotubes with nanowires (NTWs) by successive ionic layer adsorption and reaction (SILAR) method. The stepwise band edge structure

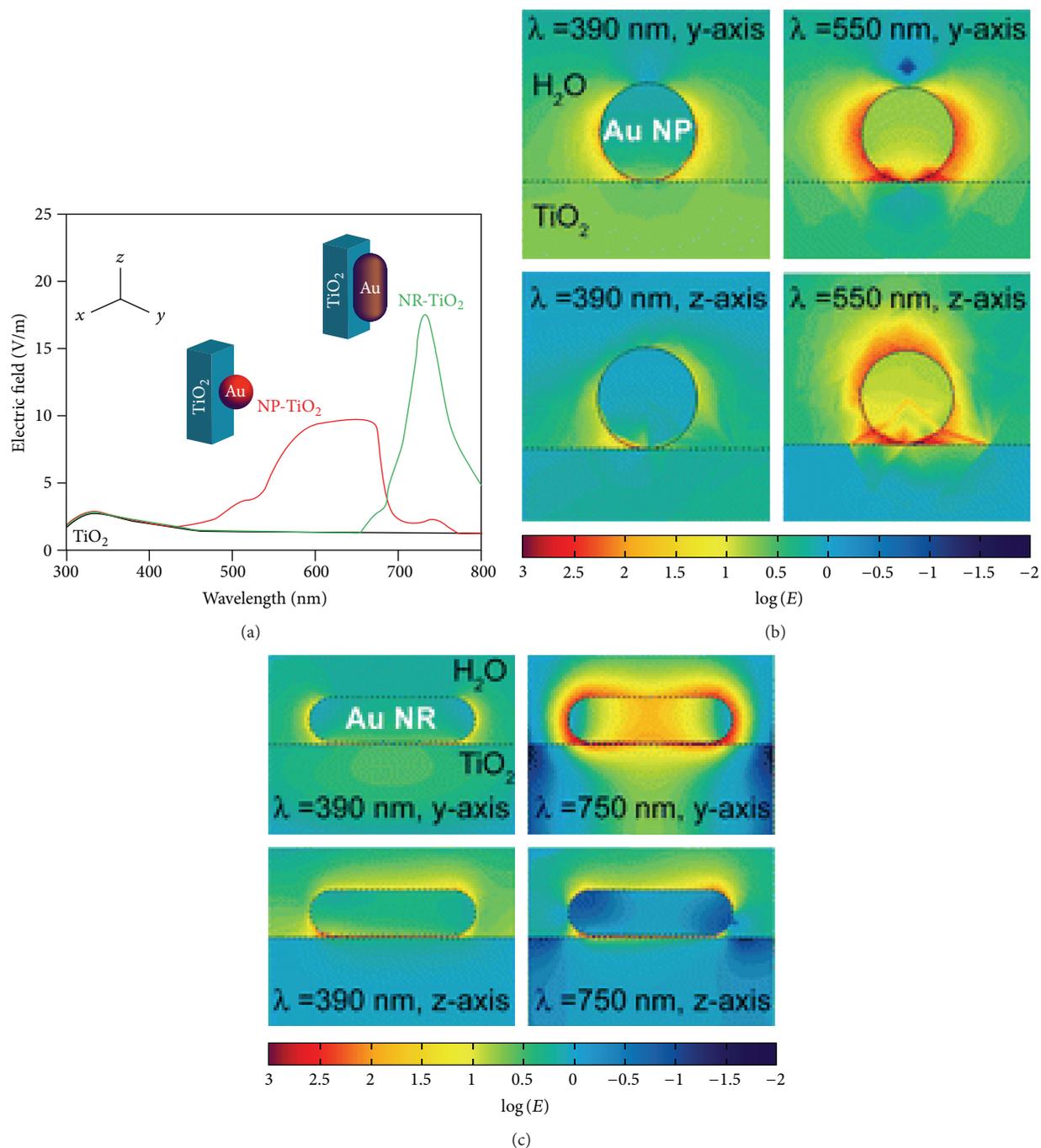


FIGURE 9: (a) Simulated electric field intensity plot for bare TiO_2 , NP- TiO_2 , and NR- TiO_2 nanowires as a function of incident light wavelength. Inset shows schematic model of NP- TiO_2 and NR- TiO_2 nanowires for FDTD simulation. (b, c) Spatial distribution of electric field on the y - z plane for NP- TiO_2 and NR- TiO_2 nanowires. The incident light is along a specific direction (y - or z -axis). Reproduced with permission from [7]. Copyright 2013, American Chemical Society.

in the $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$ heterojunction electrode would create efficient charge transfer channel. The TiO_2 NTWs with multiple QDs showed higher photocurrent compared to that comprised of single QD and TiO_2 [34]. Luo et al. compared the effects of three different QDs, CdS, CdSe, and CdSeS, and found that the photocurrent generated by TiO_2 -CdSeS hybrid

was larger than the current produced by TiO_2 -CdS and TiO_2 -CdSe, owing to the better band alignment between TiO_2 and CdSeS [33].

Though the performance of TiO_2 electrode in combination with single or multiple QD is higher than that of bare TiO_2 , most of the QDs are sensitive to photocorrosion,

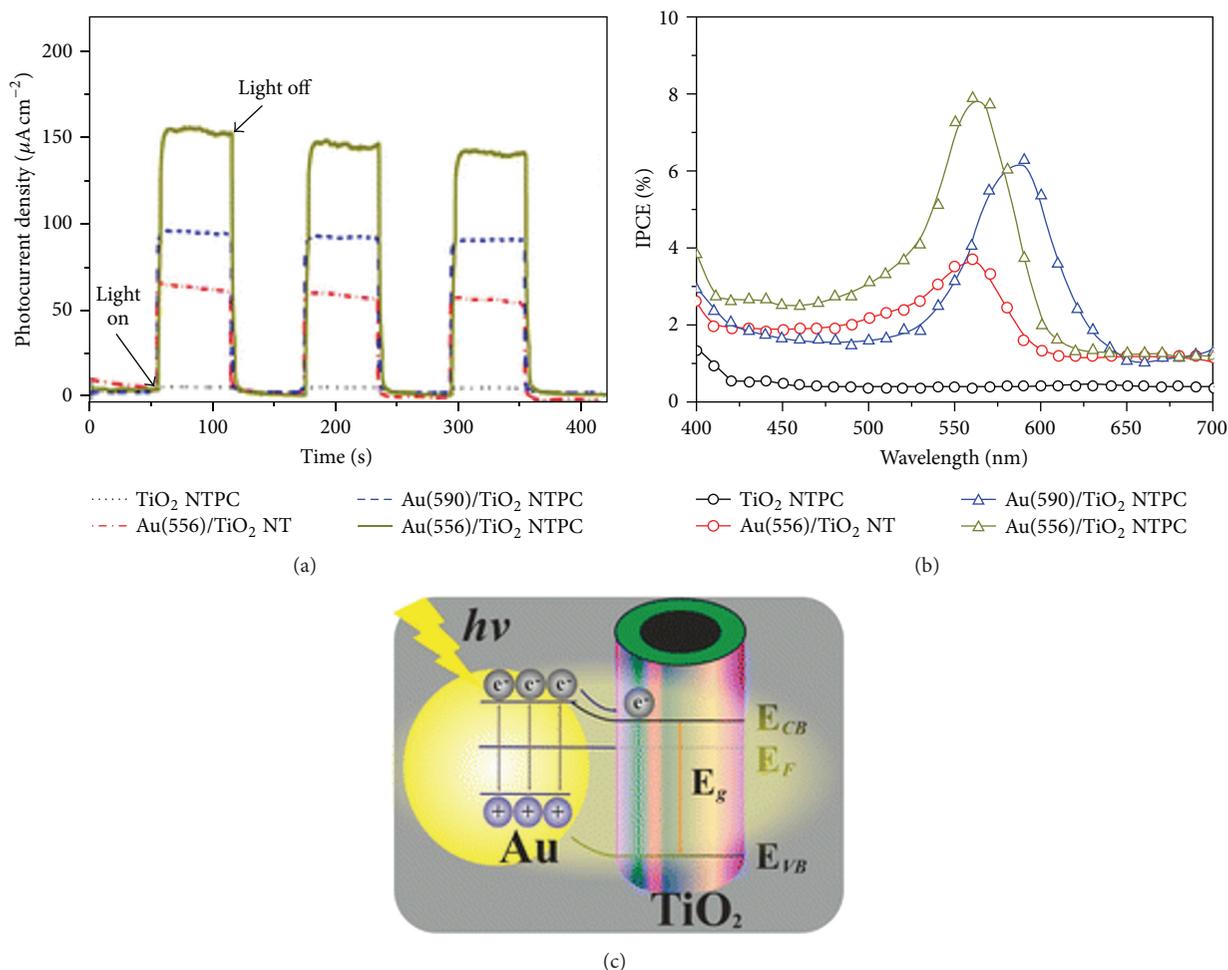


FIGURE 10: Photoelectrochemical properties of TiO_2 NTPC and Au/TiO_2 NTPC and schematic diagram of SPR charge carrier transfer mechanisms. (a) Amperometric $I-t$ curves at an applied potential of 1.23 V versus RHE under illumination of visible light with wavelength ≥ 420 nm with 60 s light on/off cycles. (b) IPCE plots in the range of 400–700 nm at 1.23 V versus RHE. (c) SPR charge carrier transfer under visible light irradiation at Au/TiO_2 interface. Reproduced with permission from [8]. Copyright 2013, American Chemical Society.

which restricts the long-term use and recyclability of these photoelectrodes.

3.1.4. Upconversion Nanoparticles. Upconversion phosphors, which can transform low energy photons to high energy photons, have been considered as one of the best candidates to utilize NIR region of solar light. By varying the amount and nature of dopants present in the upconversion (UCN) NPs, the emitted light can be tuned from UV to visible. When UV light emitting UCNs are incorporated into TiO_2 , the emitted light can be utilized to excite TiO_2 (Figure 14) [11].

Li et al. prepared TiO_2/UCN composite by ultrasonic dispersion and liquid boiling method, followed by calcination at different temperatures. The catalysts calcined at 550°C showed the best performance in H_2 generation. As an upconversion luminescence agent, $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ absorbs visible light in solar light and then emits ultraviolet light, which can effectively excite the TiO_2 crystal. In the ultraviolet light irradiation produced by $\text{Er}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ with upconversion

luminescence effect, the excited electrons in the CB are transferred to Pt NPs on the surface of TiO_2 and are involved in H_2 generation [35].

Considering various strategies to induce visible light activity in TiO_2 , appropriate incorporation and hybridization between the sensitizer and TiO_2 are very important since if the contact between the components is not intimate effective charge transfer from the sensitizer to TiO_2 cannot be achieved. Choosing suitable sensitizers and incorporating them into TiO_2 are very important to achieve the desired results. Physical and chemical stability of the sensitizers is another factor to be considered before selecting the sensitizer. Concerning the chemical and photostability of QDs and dyes, noble metals and upconversion nanoparticles are better candidates to hybridize with TiO_2 .

4. Conclusions

A trial to overview a few representative photosensitizers to harvest visible light from the solar spectrum and their

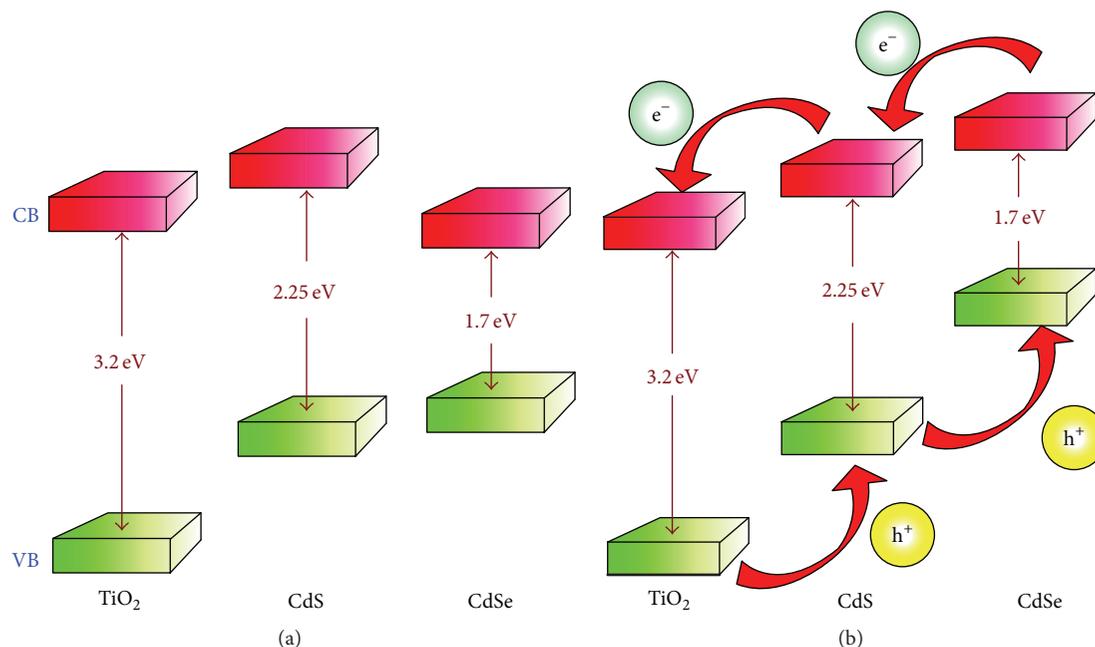


FIGURE 11: (a) Relative energy levels of TiO_2 , CdS, and CdSe in bulk phase (a) and (b) ideal stepwise band edge structure for efficient transport of the excited electrons and holes in a CdS/CdSe cosensitized electrode. Reprinted with permission from [9]. Copyright 2010, American Chemical Society.

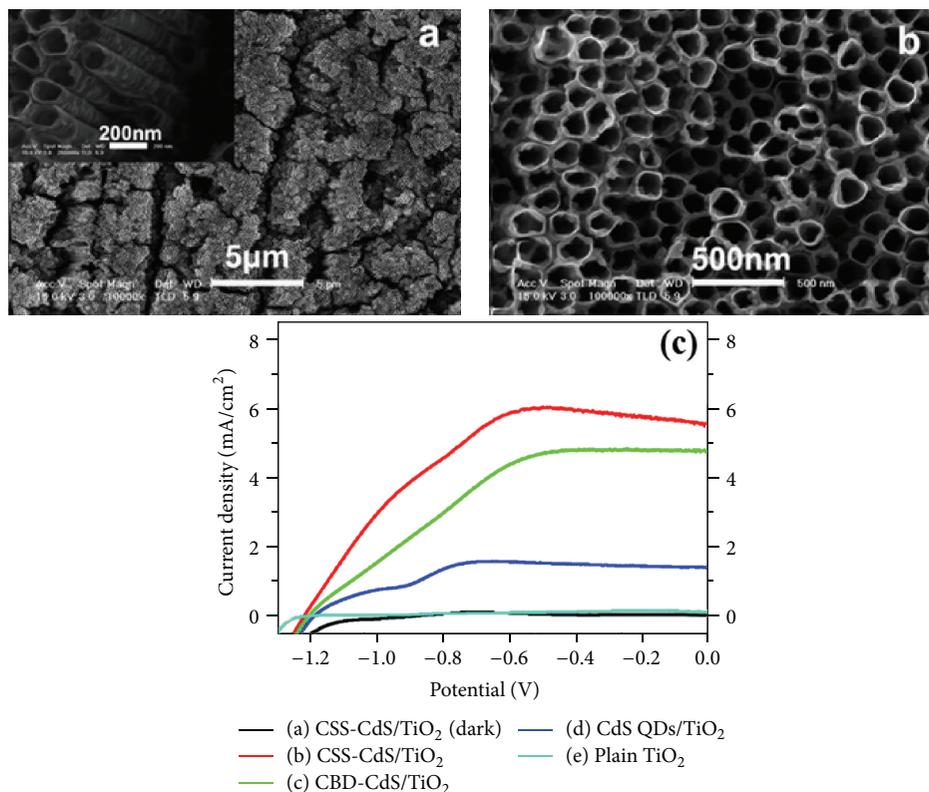


FIGURE 12: SEM images of TiO_2 nanotube arrays after CdS deposition with low (a) and high (b) magnification. The inset is a cross-sectional SEM image of the modified film. (c) Current density-voltage characteristics measured from the CdS/ TiO_2 photoelectrode made by the CSS technique under dark condition (a) and under AM 1.5 G illumination (b). For comparison, photocurrents obtained from a plain TiO_2 nanotube film (e) and a CdS/ TiO_2 photoelectrode made by the CBD method (c) and presynthesized QD deposition (d) are also given. Reprinted with permission from [10]. Copyright 2009, American Chemical Society.

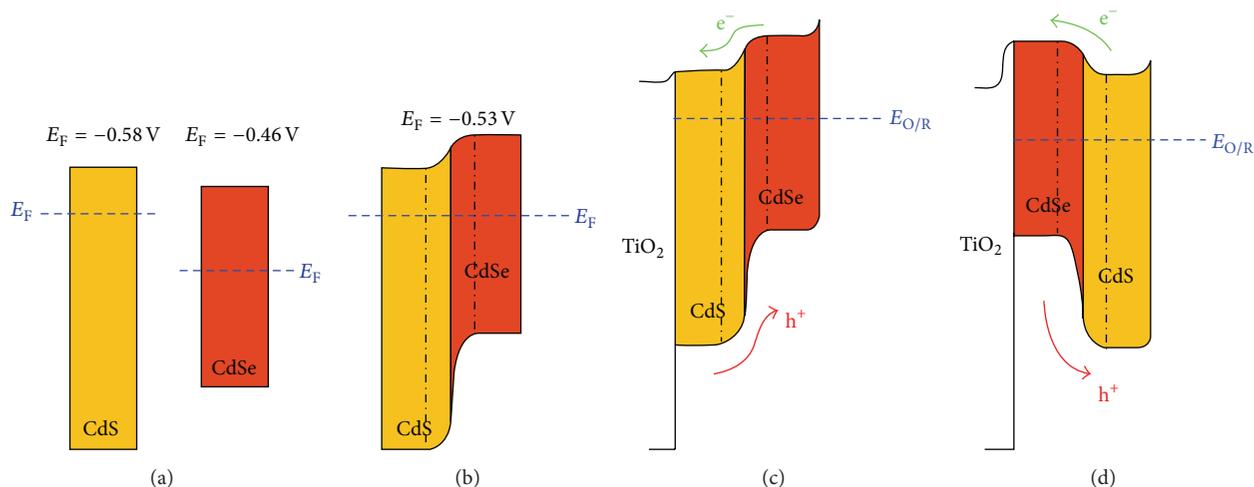


FIGURE 13: Relative Fermi level and band edge positions of CdS and CdSe before (a) and after (b) Fermi level alignment due to their contact. The proposed band edges structures for the $\text{TiO}_2/\text{CdS}/\text{CdSe}$ (c) and $\text{TiO}_2/\text{CdSe}/\text{CdS}$ (d) electrodes in equilibrium with the redox couples in the electrolyte. The Fermi levels (E_F) indicated in (a) and (b) are OCPs (versus Ag/AgCl) measured in dark conditions. Reprinted with permission from [11]. Copyright 2009, American Chemical Society.

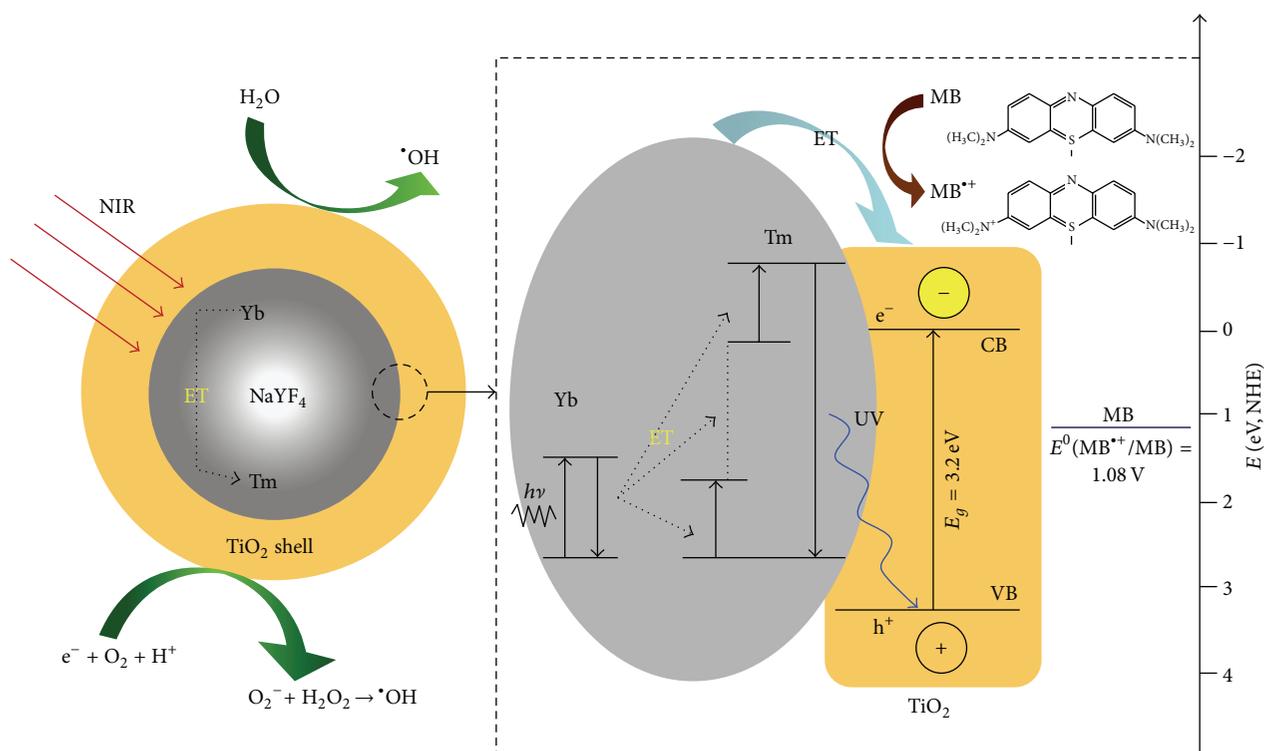


FIGURE 14: Illustrative diagrams of energy transfer among Yb^{3+} , Tm^{3+} , and TiO_2 ; the generation of OH radicals via the reaction of electron and hole with the surface species of TiO_2 ; and the energy scales. Reprinted with permission from [11]. Copyright 2013, American Chemical Society.

incorporation into TiO_2 so that the whole system can act as visible light active photocatalyst is done in this review. Dyes and QDs are excellent in absorbing visible light and the absorption properties of QDs can be varied by tuning the size, but the chemical stability and photostability of these candidates are a serious concern. Owing to the chemical

and thermal stability of plasmonic metals, using them as light harvesters got wide attention, but the cost of making metal NPs restricts their large-scale applicability. In this respect, upconversion NPs are more appropriate if they are combined with semiconductors aptly. Therefore, instead of randomly choosing a sensitizer, a detailed research is required

to exploit the maximum benefits of each and every sensitizer in combination with TiO_2 in splitting of water.

Competing Interests

The author declares that there are no competing interests regarding the publication of this paper.

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