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Quantum dots sensitization for photoelectrochemical generation of hydrogen: A review

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ABSTRACT

In the ongoing pursuits for efficient photoelectrochemical (PEC) cell for solar generation of hydrogen via splitting of water, quantum dots (QDs) sensitization on photoelectrodes have emerged as promising technique. Present review discusses the operation and principle of QDs sensitized PEC cell (QD-SPEC) along with the status of the worldwide research in this domain. Method of sensitization, nature of QDs, quantity and size-dimensions of QDs, the nature and morphology of basic photoelectrodes are the important factors that govern the hydrogen generation rate in QD-SPEC systems. All these factors along with their effect on the efficiency of the QD-SPEC system have been critically examined and presented.

1. Introduction

Quantum dots (QDs) sensitization of semiconductors has recently emerged with great potential for their efficient use in solar driven systems for energy applications [1,2]. There are few review reports in the area focussing mainly on cadmium chalcogenide QDs sensitized solar cells and comparing QDs/ dye sensitization specifically for photocatalytic applications [1,2]. This review aims to present world-wide research on quantum dots (QDs) sensitized semiconductors specifically in the field of solar generation of hydrogen via splitting of water in a photoelectrochemical (PEC) cell. Readers will find a comprehensive view of almost all the research in the area, critically examined along with challenges at one place. PEC cells are the most promising systems for production of hydrogen fuel via splitting of water [3,4]. In PEC cell, hydrogen is generated electrochemically in a cell where at least one of the two electrodes is made up of semiconductor (n or p-type) and is able to absorb the falling light. Water decomposition process in a PEC cell occurs in four steps: (i) Production of electron–hole pairs at semiconductor/electrolyte junction by the absorption of solar energy, (ii) Separation of electron–hole pairs followed by transport of holes from the photo-anode to the cathode through the electrolyte and transport of electrons from photo-anode to the cathode through the external circuit, (iii) Reduction of hydrogen ions (H^+) at the cathode by electrons to produce hydrogen and iv) Oxidation of hydroxide (OH^-) at the photo-anode by holes to produce oxygen.

In order to drive the process of water splitting successfully and efficiently, the employed semiconductor photoelectrode must possess following specific properties; (i) it should have band gap between 1.8 and 3.2 eV in order to provide required amount of energy to the photogenerated carriers for splitting of water, (ii) band edges of semiconductor should straddle with the redox level of water for easy and rapid transfer of photo generated carriers from semiconductor to electrolyte [4] (iii) life time and mobility of photogenerated carriers should be large enough to counter recombination [5,6]. (iv) overall electrical resistance of the semiconductor should be low for efficient flow of carriers in the bulk of the material [7]. Additionally, to achieve a durable PEC hydrogen production system, semiconductor should be stable and must not corrode in electrolyte upon illumination [8]. None of the semiconductors investigated so far fulfill all the above requirements. Therefore, in order to develop a semiconductor photoelectrode, which can produce hydrogen efficiently using solar energy in PEC cells, research groups are working on different strategies, mainly aiming to modify the properties of semiconductor photoelectrode for improved performance in a PEC cell. Few of the strategies are, use of nanostructures [9,10], elemental doping [11,12], use of heterostructures [13], organic dye sensitization [14].

A relatively recent development in this context is the use of quantum dots (QDs) for sensitizing semiconductor photoelectrode [15,16]. QDs are semiconducting nanocrystals that show attractive tunable properties due to quantum confinement in all the three dimensions. The use of QDs sensitized photoelectrodes in PEC splitting of water has shown significant efficiency enhancement in few cases [17,19]. There are reports on the sensitization of semiconductors like

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TiO_2 and ZnO by QDs with improved PEC performances [17,20]. Electrodes of different morphologies, such as mesoporous films [21], nanotubes (NTs) [18,22], nanorods (NRs) [23], and nanowires (NWs) [24], sensitized with QDs of CdSe [25,26], CdS [27,28], CdTe [29], PbS [30,31] and InP [32], have been studied. Most of the research has been carried out on the QDs sensitization of wide band gap semiconducting photoelectrode e.g. TiO_2 and ZnO by Cd Chalcogenide (CdX, X = Se, S, Te) QDs. This may be because of the easy synthesis procedure, favourable band gap for efficient visible light absorption for CdS, CdSe and CdTe (band gaps ~ 2.25 eV, 1.73 eV and 1.49 eV respectively) [33], and tunable optical and electronic properties of Cd chalcogenide. There have been few recent reports on other metal oxides also e.g. NiO, α-Fe_2O_3, $BaSnO_3$ and WO_3 sensitized by low band gap QDs [34,39].

This short review presenst an overview of researches carried out pertaining to the use of QDs sensitization of semiconducting photoelectrodes for PEC applications. The report.covers the basic principle of QDs sensitized PEC (QD-SPEC) cell, factors controlling the efficiency of such cells, and significant results on various QD-SPEC systems studied for their PEC response. **The** issue of stability of QD-SPEC cells has also been briefly undertaken.

2. Mechanism of action of QD-SPECs

QDs are special cases of semiconducting nanocrystals, having diameter less than or of the order of exciton Bohr radius (EBR) of the corresponding bulk semiconductor. The size restrictions affect their optical and electronic properties. The properties of QDs that contribute favourably are (i) tunable energy band gaps with size, which can provide matching of absorption spectra of the material with the spectrum of sunlight for efficient solar energy absorption [40]. Besides, it may also provide the band edge straddling for transportation of carriers; (ii) large extinction coefficients due to the quantum confinement effect for greater absorption [41,42]; (iii) large intrinsic dipole moments, which may lead to rapid separation of photogenerated charge carriers [43,44]. (iv) increased number of carriers due to multiple exciton generation effect [45,46]. Thus, QDs sensitization on semiconductor helps all the way in generation, separation and transportation of charge carrier, thereby in improving the PEC response.

In QD-SPEC cells, semiconducting working electrodes are normally sensitized with low band gap QDs. In such systems, layers of QDs are coated on the electrode [47,48]. Depending on the morphology of the electrode, which may be meso/nanoporous, NTs or NWs, QDs may decorate the pores, tubes and wires respectively. To understand basic principle, a typical PEC cell with CdSe QDs sensitized TiO_2 photoelectrode has been shown in Fig. 1. Visible light photons falling on the surface are absorbed by the CdSe QDs and electron-hole pairs are produced. With suitable energetic, i.e. conduction band of QDs being at higher energy level than the conduction band of TiO_2; electrons are spontaneously transferred to the conduction band of TiO_2. This rapid transport is attributed to the discrete and increased band gap of CdSe QDs. Band energetic is, thus, important for a successful QD-SPEC system, and the performance of a QDs sensitized photoelectrode based PEC cell mainly depends on the alignment of energy band edges of semiconductor and QDs with respect to the redox level of water..

3. Why QDs sensitization

Better performance of QD-SPEC cell can be mainly attributed to improved absorption of visible light and better charge transport of photogenerated carriers. This section deals with the specific properties of QDs, which makes them useful in PEC water splitting.

3.1. Improved visible light absorption

QDs are well known to absorb a wide range of visible light photons due to their extraordinary properties stimulated from quantum confinement effect [40]. The discrete energy level and size dependent tunable band gap, which are mainly responsible for the increased absorption in the visible region of electromagnetic radiations, has been depicted by a schematic in Fig. 2(a). Increased visible absorption and the resulting enhanced PEC response after QDs sensitization has been reported by many workers [32,47,50]. Sensitization of InP, CdSe, PbS QDs on TiO_2 mesoporous films have shown increased absorption as compared to the pristine TiO_2 mesoporous films [32,47,48,51]. Similar trend of increase in absorption by CdSe QDs has been reported for visible light absorbing low band gap α-Fe_2O_3 semiconductor also [35]. Further, sequential co-sensitization of metal oxides with two types of QDs, has also been found attractive in enhancing the absorption. In a report by Seol et al.., higher absorbance of ZnO NW sequentially co-sensitized with CdSe and CdS QDs has been shown as compared to single sensitized sample or pristine sample. Co-sensitized photoelectrode CdSe/CdS/ZnO NWs have also shown higher absorbance than CdS/CdSe/ZnO NWs [50]. Even in the wavelength range 550–700 nm, where only CdSe QDs absorb, CdSe/CdS/ZnO NWs showed higher absorbance by a factor of 2 as compared to CdSe/ZnO NWs, reason being the support given by CdS QDs to the well defined uniform deposition of CdSe QDs. Similar results with ZnO NW, double sided co-sensitized by CdS and CdSe QDs has been reported by Wang et al.. Doubly sensitized CdS-ZnO-ZnO-CdSe NW (on a double sided ITO coated glass) showed better absorption, as the light was absorbed by both layers and incident light was transmitted through the CdS-ZnO layer to the CdSe-ZnO layer at the back of the substrate [24]. In fact, one of the main purposes to sensitize large band gap TiO_2 or ZnO photoelectrodes with QDs has been to make photoelectrode visible light absorbing. Sensitization of Carbon QDs on TiO_2 has shown shift in the absorption spectra to visible region from 410 nm to 600 nm [49]. UV absorption of Al doped ZnO (AZO) NR array thin film has also been found to be shifted to visible region after sensitization by CdS QDs [23]. Amount of this shift in absorption band edge is highly dependent on the procedure for QDs sensitization, viz in this particular report, it was found that the number of cycles of chemical bath deposition (CBD) controlled the shift [23]..

3.2. Better charge transport and separation

Quantum confinement effect increases the band gap of QDs and creates discrete energy bands, which is expected to lead **a** more favourable band energetic for the transport of photogenerated charge carriers [40,44]. Thus, QDs sensitization on semiconducting photo-

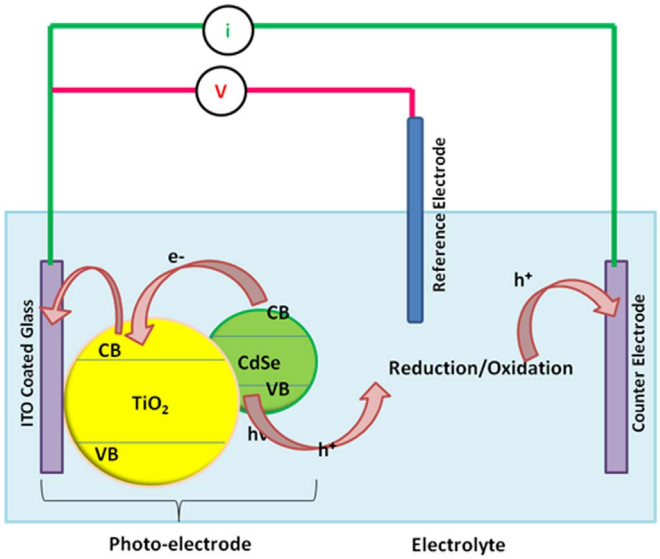

Fig. 1. Schematic of a typical QD-SPEC cell.