INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–15

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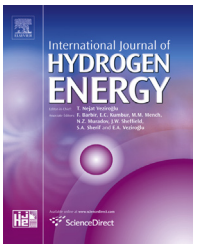

Review Article

Quantum dots as enhancer in photocatalytic hydrogen evolution: A review

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ARTICLE INFO

Article history:
Received 11 November 2016
Received in revised form
13 February 2017
Accepted 23 February 2017
Available online xxx

Keywords:
Quantum dots
Enhancer
Hydrogen
Visible light

ABSTRACT

Advanced energy conversion processes like photochemical and photoelectrochemical water splitting now a day plays a very important role in challenging the present energy crisis of our world. The successful utilization of this process depends on development of highly efficient, more stable, low cost and outstanding environmental benign semiconductor materials. From recent advancements, it is revealed that quantum dots (QDs) are very outstanding and promising material for the mentioned processes due to their favorable physical and chemical characteristics like high absorption co-efficient, quantum confinement effect, thermal, chemical, mechanical and optical stability, high conductivity and recyclability. In this review article, we have clearly explained the importance of QDs in water splitting along with the general mechanism involved in the process. Following that the enhancement of different materials like metal oxides, layered double hydroxides (LDH), carbonaceous materials (g-C_3N_4, benzene and benzene like materials) by QDs have discussed in the field of water splitting.

Contents

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http://dx.doi.org/10.1016/j.ijhydene.2017.02.166
0360-3199/

Introduction

Nanoscience has become one of the most intensely studied areas of research over the last few decades. In the last three decades quantum dots as a very effective nanomaterial have drawn much attention in the field of various research and development like electrocatalysis, LEDs, solid state lighting, displays, Infrared photodetectors, photovoltaics, transistors, quantum computing, medical imaging, biosensors and many others [1–6]. QDs have also been established as a very efficient material (enhancer) in the field of photocatalytic water splitting.

QDs are zero dimensional semiconductor nano crystals or nano crystallites usually composed of group II–VI, III–V or IV–VI elements and are defined as particles with physical dimension smaller than the exciton Bohr radius or de-Broglie's wavelength. But now-a-days QDs of elements like carbon [7], silicon [8], bismuth [9] and noble metal [10] are established. Small QDs such as colloidal semiconductor nano crystals can be as small as 1–10 nm which contains 10–50 atoms in diameter and 100–100,000 atoms within the quantum dot volume [11]. Quantum dot is considered to be zero dimensional and named as dot because the motion of electrons, holes and excitons is restricted in all 3 dimensions. As a result of which a quasi-zero dimensional system is formed. The word 'quantum' is included in its name because one property of it is analogous to quantum mechanical particle in a box in which the energy is inversely related to the size of the box. In the same manner, the band gap energy of semiconductor nanocrystal (QD) increases as the particle size decreases. In other words the electron and hole energy states within the nanocrystals are discrete and band gap is a function of QD diameter. QDs are also known as "artificial atoms" because it shows the real atom behavior i.e. the electrons are confined to quantized states with discrete energies. Because of quantization there is enhancement of band gap as compared to bulk semiconductors. The difference between atom and QD is that QDs consists of hundreds or thousands of atoms having different shape, size and energy.

Various reviews have been reported on synthesis methods, characterization, surface chemistry, nature of capping agents and optoelectronic properties of QDs [12–15]. Therefore; we limit our domain to depth discussion on modification of certain semiconductor materials by QDs and cover one very crucial photocatalytic application i.e. water splitting. This review has evidently clarified the importance of QDs in photocatalytic water splitting on the basis of Gerischer theory [16]. In the next section, the role of QDs for the improvement in catalytic activity of different semiconductors and carbonaceous materials has been discussed. The semiconductor materials included here are metal oxides, layered double hydroxides, and the carbonaceous materials are g-C_3N_4, benzene and benzene like materials. We have focused on the recent developments in the utilization of QDs as sensitizer and the mechanism of water splitting associated with above mentioned materials. For the first time, our review represents a different angle of QDs which is brand spanking new and it is expected that this review will try to make up the deficiency of current energy status. Desirably, new perspectives towards research and developments of QDs will be accessible in a productive manner with the help of this review article.

Many semiconductor photocatalysts have been developed for photocatalytic as well as photoelectrochemial water splitting but among them the role of quantum dot is very idiosyncratic. Hence the benevolent use and importance of quantum dots in water splitting is described in the following section of our review.

Importance of QDs for photocatalytic water splitting

There are many efforts devoted in the last decades for utilizing quantum dots in photocatalysis. Ultra small sized quantum dots are widely delved as sensitizer because of their high extinction coefficients, quantum confinement effect and large intrinsic dipole moments. The beneficial effects of QDs in water splitting are shown pictorially in Fig. 1(a). In the field of photocatalytic water splitting the former two properties plays very vital role. In comparison to other semiconductors, QDs have high value of extinction coefficients in visible region of solar spectrum i.e. maximum probability of minimizing the recombination of charge carriers and reinforcement of charge injection processes. It can be explained as bulk semiconductor materials show weak interaction with photons while very small amount of QDs have more capacity to interact with photons resulting maximum flux of photons. This is because QDs can emit up to 3 electrons per photon of solar radiation whereas it is only one electron in case of semiconductor bulk materials. This multiple exciton generation property is only possible due to quantum confinement effect of QDs and is noticed only when the particle size is very small enough with widening of band gap and the energy level spacing is more than kT where the symbols carry their usual meaning, k is Boltzmann's constant and T is temperature. According to Gerischer theory [16], band gap of the QDs decreases with increasing size which opens up the path to cover the entire solar spectrum. Additionally, in case of large band semiconductor materials the transfer of electrons from CB of QDs to that of semiconductor can be made thermodynamically favorable and is shown in Fig. 1(b). This is because the CB edge position can be moved towards more negative potential and VB edge position towards more positive potential with decreasing the particle size or increasing the band gap (Fig. 2).

As a consequence the free energy change required for migration of electron from QD to semiconductor decreases and the thermodynamic driving force increases which increases the interfacial charge transfer. Homles et al. [17] has proved this charge transfer with CdSe QDs by plotting a graph between normalized photocatalytic proton reduction rates with respect to band gap on logarithm scale results a logarithm dependence relationship between these two parameters. This relation is also supported by Gerischer theory but at illuminated semiconductor–electrolyte surface. As per this theory

$$k_{Red} \propto exp\left[\frac{(\Delta G - \lambda)^2}{4kT\lambda}\right]$$

Please cite this article in press as: Kandi D, et al., Quantum dots as enhancer in photocatalytic hydrogen evolution: A review, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.02.166