



Size-dependent performance of CdSe quantum dots in the photocatalytic evolution of hydrogen under visible light irradiation



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ABSTRACT

Nanocrystalline materials are widely employed as photocatalysts for water splitting applications. In particular, cadmium selenide quantum dots (QDs) attracted growing interest for their superior photon to H₂ conversion efficiency and their stability under irradiation. A direct insight is here presented on the effects that CdSe QDs size has on their photoactivity in hydrogen evolution from Na₂SO₃—containing aqueous solutions under visible light irradiation. Four highly monodisperse CdSe quantum dots with different nanocrystal diameters were synthesized and, after exchange of the capping ligand, employed as photocatalyst in H₂ production in the absence of any co-catalyst. Their size-dependent photocatalytic activity is discussed in relation to their absorption properties, their conduction band energy and the recombination probability of the photogenerated charges inside the nanocrystals. High quantum efficiency in H₂ generation results from a balance among these three QDs features, their activity scale being not exclusively dominated by the photocatalyst conduction band position.

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1. Introduction

Efficient solar light conversion into fuels such as H₂ or hydrocarbons requires the use of photoactive materials combining good visible light absorption properties, suitable band gap energy position and low electron–hole pair recombination. Semiconductor nanocrystals are emerging as effective photocatalysts because of their size and band gap tunability [1,2], wide range of employed elements [3–6], high energy conduction band [7,8], stability [9–11] and shape control possibility [12–14]. Moreover the combination of different semiconductor materials in nano-heterostructures offers the possibility to host the light absorber, the hole and electron acceptors and the co-catalyst in the same nanoparticle [15–18].

Among all nanostructures, quantum dots (QDs) nanocrystals received much attention in recent years. Because of their high conduction band position, size and band gap tunability, and excellent visible light absorption properties, chalcogenide QDs are amongst the most studied nanostructures for solar energy conversion applications. In particular, cadmium selenide quantum dots, CdSe QDs, have conduction band edges higher in energy than that of TiO₂. Thus, when they are used as photocatalysts, high energy electrons photopromoted in their conduction band are able to

produce thermodynamically up-hill reactions, such as CO₂ reduction or hydrogen production from water and/or electron donors [9,10,19–21]. On the other hand, chalcogenide quantum dots can also be employed in combination with wide band gap semiconductors, such as TiO₂ or ZnO, in quantum dot solar cells [22–24]. Electrons photoexcited in the QD conduction band are injected in this case in the conduction band of the semiconductor oxide and used in photovoltaic and photocatalytic applications [25–27].

Aiming at better understanding the effect of CdSe QDs features on their photoactivity and at determining the optimal nanocrystal size for photocatalytic H₂ production, we synthesized highly monodisperse quantum dots with different size and performed a systematic investigation on their performances in H₂ evolution from aqueous solutions. The experimental results are discussed on the basis of the optical properties of the photocatalyst nanoparticles, their photocatalytic efficiency scale resulting from an optimized balance of their band gap value, conduction band position and rate of photogenerated charges recombination.

2. Experimental

2.1. Materials

All reagents and solvents, *i.e.*, trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), selenium metal powder, cadmium acetate, 3-mercaptopropionic acid (MPA), tetramethylammonium

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Fig. 1. Vials containing a series of CdSe QDs of different sizes obtained by taking aliquots of the reactant solution 5, 15, 30, 45, 60, 120, 240 s (from the left) after the beginning of the crystallization growth.

hydroxide pentahydrate, sodium sulphite, toluene, methanol and acetyl acetate, were highest purity chemicals purchased from Sigma–Aldrich. Milli-Q grade water was used to prepare aqueous solutions in all experiments.

2.2. Synthesis and characterization of CdSe QDs

CdSe QDs were prepared under nitrogen atmosphere using the synthetic route proposed by Qu et al. [28], with slight modifications. In a typical synthesis the selenium metal powder (0.117 g) was dissolved at 160 °C in a TOP and toluene mixture (2.90 g and 0.5 g, respectively). Cadmium acetate (0.0726 g) was dissolved in 2.9 g of TOPO at 180 °C. The resulting selenium-containing solution was then added to the Cd precursor-containing solution at 300 °C. In order to prevent multiple nucleation, a 5:1 Se/Cd stoichiometric excess was employed. The temperature of the so obtained mixture rapidly dropped to ca. 270 °C and was maintained at this temperature as long as the desired CdSe nanocrystal size was reached. Once the desired color (*i.e.*, nanocrystals size) was obtained, the crystal growth was immediately quenched by rapidly pouring the hot solution into a becker containing 30 mL of toluene immersed in an ice bath. The so obtained QDs were then washed three times by precipitating and re-dissolving the nanocrystals in methanol and ethyl acetate, respectively.

The TOPO capping the CdSe QDs was exchanged for mercaptopropionic acid (MPA), in order to make the CdSe QDs soluble in protic solvents such as methanol and water. According to a widely employed procedure [29], MPA was dissolved in methanol and the pH was adjusted to 11 by addition of tetramethylammonium hydroxide. The TOPO-capped QD solutions were thus added to the basic solution. Exchange of the capping ligand takes place immediately. The MPA-capped CdSe QDs were precipitated by adding ethyl acetate and the collected precipitate was washed several times with ethyl acetate to remove residual MPA and TOPO. The so prepared QDs were soluble in protic solvents and were stored in methanol solutions in the dark, before being employed in photocatalytic hydrogen production tests.

The colloidal CdSe QDs suspensions were characterized through UV–vis absorption measurements employing a Jasco V650 spectrophotometer. The estimation of the QDs size was obtained from the maximum of the first excitonic peak of the QDs using an empirical equation reported by Jasieniak et al. [30] (see Appendix A for details).

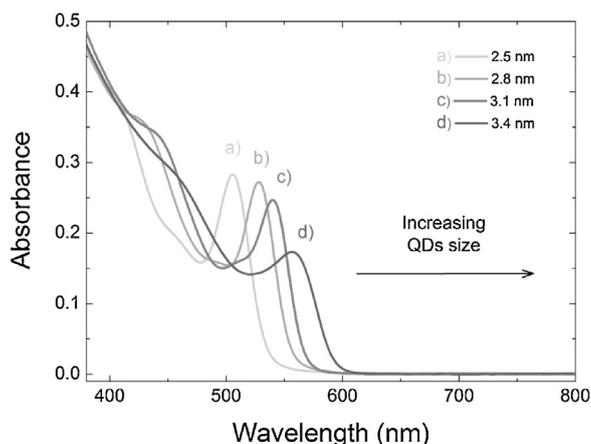


Fig. 2. UV–vis absorption spectra of four QDs samples with different nanocrystal size: (a) 2.5 nm, (b) 2.8 nm, (c) 3.1 nm and (d) 3.4 nm.

2.3. Photocatalytic H₂ production from irradiated QDs in aqueous solution

Photocatalytic activity tests were performed using a bench-scale apparatus connected to a liquid phase recirculating closed system [31–33]. As methanol can notoriously act as an electron donor, it was removed from the stored QDs methanol solutions by drying the nanocrystals employing a vacuum rotary evaporator system (Heidolph) in the dark. Once methanol was completely removed, the QDs were dissolved in a 0.1 M Na₂SO₃ aqueous solution.

The so obtained photoactive colloidal suspension (0.003 g of CdSe in 30 mL of 0.1 M Na₂SO₃ aqueous solution) was placed in a 45 mL cylindrical quartz vessel, which was magnetically stirred during the runs. The photoreactor was connected to a closed stainless steel recirculation system, in which an inert gas (N₂) was continuously fluxed by means of a bellows pump (Metal Bellows). The gaseous species evolving from the aqueous suspension under irradiation accumulated in the gas phase, which was analyzed on line by sampling at regular time intervals and injection into an Agilent 6890N gas chromatograph (GC), equipped with two capillary columns (MolSieve 5A and HP-Plot Q), a flame ionization detector (FID) and a thermoconductivity detector (TCD). N₂ was used as carrier gas. The GC response was first calibrated by injecting known volumes of H₂ into the recirculation system through a six ways sampling valve.

A Lot Oriel, 300 W xenon lamp was used as light source. The photon flux was used both as generated by the lamp and after removal of the high energy photons in the UV region by means of a 420 nm longpass filter, hereafter recalled as full lamp and visible light irradiation conditions. The emission spectra of the xenon lamp with and without the filter were collected with a Thorlab CCS200 M spectrometer (see Appendix A). The power intensity of light, measured by means of a Thorlab PM200 power meter equipped with a S130VC power head with Si detector, was 170 W cm⁻² under full lamp emission conditions and 160 W cm⁻² under filtered visible light emission conditions.

Each QDs solution was tested during three days-long kinetic runs, which were repeated twice, to check reproducibility. The nanocrystals were activated under full lamp irradiation during the first day and then the stability in hydrogen evolution under visible light was tested during the following two days. Prior to the beginning of irradiation, the undesired gaseous species (air on the first day and mainly H₂ on the second and third day) were completely removed by purging the photocatalyst suspension with N₂ for 40 min.

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