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Size- and composition-dependent photocatalytic hydrogen production over colloidal Cd_{1-x}Zn_xSe nanocrystals

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ABSTRACT

Colloidal nanocrystals (NCs) have emerged as a new kind of photocatalysts for solar hydrogen production due to the tunable optical and photoelectrical properties. Herein, size- and composition-tunable alloyed Cd_{1-x}Zn_xSe NCs were successfully prepared via a one-step hot injection method for photocatalytic hydrogen production under visible light irradiation. By prolonging the reaction time, CdSe NCs with the varied particle sizes were firstly fabricated. It is found that the driving force derived from the difference between conduction band position of CdSe NCs and water reduction potential played a key role in determining the photocatalytic performance. The larger driving force from smaller particle size would give rise to a faster electron transfer and better photocatalytic activity. Furthermore, a series of alloyed Cd_{1-x}Zn_xSe NCs with different compositions were prepared. With the increased zinc amount, the photocatalytic activity of Cd_{1-x}Zn_xSe NCs was initially increased and then decreased. Cd_{1-x}Zn_xSe with the moderate Zn content exhibited the best photocatalytic hydrogen production. It is inferred that the photocatalytic performance of Cd_{1-x}Zn_xSe NCs has a close relationship with the driving force and crystal structure. The present study can provide a guidance to develop efficient nanocrystal photocatalysts by simply controlling the particle size and composition.

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Introduction

Photocatalytic hydrogen production from water over semiconductors offers a promising approach to solve the increasing energy and environmental problems [1–5]. Since the first report of solar water splitting in 1972 [6], a large number of semiconductors, including metal oxides and metal sulfides, have been explored [7–10]. For example, TiO₂

photocatalyst is widely studied due to suitable valance and conduction band positions to drive water splitting reactions. However, it can only utilize the limiting UV radiation in the solar spectrum [11–15]. CdS photocatalyst, owing to suitable band edges and visible light absorption, shows remarkable photocatalytic hydrogen production in the presence of sacrificial reagents [16–23]. Although steady efforts and some breakthroughs are achieved, solar water splitting technology still face a great challenge for the industrial application. The

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key issue is to develop efficient and low cost photocatalysts that can harvest more solar energy especially in the visible light and near-infrared regions, own high efficiency of charge separation and transfer, and have superior surface catalytic property.

Colloidal quantum dots (QDs) are single crystalline semiconductors with their sizes in the quantum confinement regime. Compared with bulk materials, QDs have advantages of tunable light absorption and band-gap positions, short charge migration distance, and large surface to volume ratio [24]. QDs are usually known as emissive materials because of their color-tunable and narrow emission under photo excitation [25–29]. They are also generally used as photo-absorbers in solar cells for broad band absorption [30–33]. Recently, chalcogenide QDs have emerged as a new kind of photocatalysts for solar-to-hydrogen application due to their good photoelectrical properties [34–40]. As is known, photo-excited electrons in bulk CdSe have insufficient energy to drive the water reduction reaction. Band-gap widening induced by the quantum confinement effect in CdSe nanocrystals (NCs) could lead to the conduction band raising, which would make it possible to reduce water to hydrogen. Osterloh et al. firstly demonstrated CdSe as a photocatalyst for hydrogen evolution from strong quantum confinement [41]. The nanocomposite photoelectrodes, consisting of CdS QDs modified TiO₂ photoanode and CdSe QDs modified NiO photocathode, even displayed overall water splitting [42]. Amirav et al. reported Pt-tipped CdSe@CdS rods had a 100% photon-to-hydrogen production efficiency under visible light irradiation [43]. Although high photocatalytic performances have been achieved by modification of QDs with other semiconductors or noble-metal cocatalysts, understanding the fundamental relation between the physicochemical properties and photocatalytic hydrogen production was essential to enhance the photocatalytic performance of pristine semiconductor QDs. In particular, decreasing the nanocrystal size can give rise to higher conduction band position, which can provide stronger driving force for water reduction. However, it can simultaneously enlarge the band gap, resulting in the lower photo absorption. Forming alloyed NCs is another effective way to tune the band positions and band gap [9]. Nevertheless, seldom research has been focused on alloyed NCs for photocatalytic hydrogen production. Accordingly, it seems a feasible route to examine the influence of energy band characteristics on photocatalytic hydrogen production of NCs by simply adjusting the particles size and composition.

Herein, size- and composition-tunable colloidal Cd_{1-x}Zn_xSe NCs were prepared via a one-step hot injection method and examined as photocatalysts for hydrogen production under visible light irradiation. By increasing the reaction time, the particle size of CdSe NCs was increased, giving rise to the reduced band gaps. CdSe NCs synthesized with the smallest particle size displayed the highest hydrogen evolution rate using ascorbic acid as the sacrificial reagent. Introducing Zn into CdSe could further improve the photocatalytic performance. Cd_{1-x}Zn_xSe with the moderate amount of Zn displayed the best photocatalytic performance. The reasons accounting for the size- and composition-dependent photocatalytic properties over colloidal Cd_{1-x}Zn_xSe NCs were discussed.

Experimental

Chemicals

All chemicals including cadmium oxide (CdO, 99.5%), zinc oxide (ZnO, 99.95%), selenium powder (Se, 99.5%), octadecene (ODE, 90%), oleic acid (OA, 90%), tri-*n*-butylphosphine (TBP, 95%), mercaptopropionic acid (MPA, 99%), potassium hydroxide (KOH, 95%), ascorbic acid (AA, 99.7%), hexane (97%), chloroform (99%), methanol (99.5%), isopropanol (99.7%), and ethanol (75%) were used as purchased without further treatment.

Synthesis of Cd_{1-x}Zn_xSe NCs

Cd_{1-x}Zn_xSe NCs with different compositions were prepared via a one-step hot injection method. In a typical synthesis of CdSe, 0.5 mmol of CdO, 20 mL of ODE, and 0.56 mL of OA were added into a three-necked flask with stirring. The reaction mixture was heated at 120 °C for 2 h under vacuum to remove water and other low-boiling impurities. The solution was then placed under Ar, heated to 300 °C and refluxed for 0.5 h to coordinate Cd²⁺ ions with the ligands. Upon completion, the temperature was lowered to 250 °C and the selenium solution (0.5 mmol of Se powder dissolved in 2 mL of ODE and TBP) was rapidly injected. The subsequent growth of NCs was carried out at 250 °C. To get size-tunable NCs, the solution was taken out at different reaction time (5 s, 30 s, 3 min, 5 min, and 9 min), and rapidly transferred into hexane. As the solution cooled down to the room temperature, NCs were washed with isopropanol, and finally dispersed in hexane for storage. To change the composition of Cd_{1-x}Zn_xSe NCs, CdO and ZnO were used as the precursors. The molar ratio of Cd/Zn was varied and the total amount of CdO and ZnO was kept to be 0.5 mmol.

To conduct photocatalytic hydrogen production from water, a ligand exchange process is necessary to replace hydrophobic ligands of Cd_{1-x}Zn_xSe NCs with hydrophilic MPA. In a typical process, NCs were firstly precipitated with isopropanol and dispersed in 4 mL of chloroform. 0.02 mL of MPA and 4 mL of KOH solution (0.1 g of KOH dissolved in 20 mL of deionized water) were then added. The mixture was vigorously shaken and centrifuged at 5000 rpm for 2 min, resulting in the phase separation. The top aqueous phase became colored, which indicated that Cd_{1-x}Zn_xSe NCs were successful transferred into water. The NCs after ligand exchange were washed with methanol and re-dispersed in 4 mL of deionized water.

Characterization

UV-visible (UV-vis) absorption spectra were measured on a HITACHI U-4100 spectrophotometer. Steady-state photoluminescence (PL) properties were characterized at room temperature using a PTIQM-4 fluorescence spectrophotometer with an excitation wavelength of 350 nm. X-ray powder diffraction (XRD) pattern was determined using a PANalytical X'pert MPD Pro X-ray diffractometer (Cu K α radiation). The morphology examination and size measurement were performed on a FEI Tecnai G2 F30 S-Twin transmission electron microscope (TEM) attached with an OXFORD MAX-80 energy

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