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RAPID COMMUNICATION

Arm length dependency of Pt-decorated CdSe tetrapods on the performance of photocatalytic hydrogen generation

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Abstract−Pt-decorated CdSe tetrapods with different arm lengths were tested for the photocatalytic hydrogen generation reaction. Well-defined CdSe tetrapods with controlled wurtzite arm lengths were synthesized by the continuous precursor injection (CPI) approach. Pt nanocrystals with an extremely small size of ~1 nm were directly decorated on the overall surfaces of CdSe tetrapods. Ligand-exchanged Pt-decorated CdSe tetrapods with different arm lengths were employed as photocatalysts for photocatalytic hydrogen generation reaction in the presence of hole scavengers. Pt-decorated CdSe tetrapods with shorter arm length showed the highest photocatalytic efficiency, which is due to higher probability of charge separation.

Keywords: Colloidal Heterostructured Nanocrystal, CdSe Tetrapod, Photocatalytic Hydrogen Generation

INTRODUCTION

Colloidal heterostructured nanocrystals have recently gained keen attention due to the synergistic effects arising from different compositions within a single nanocrystal. Particularly, metal-semiconductor heterostructured nanocrystals have extensively been studied from synthesis, characterization, and various applications such as photocatalysis, bioimaging, electrical devices, and so forth. Various combinations and morphologies of metals and semiconductors have been reported by many research groups [1,2]. In particular, for the application to photocatalytic water splitting reactions, semiconductor nanocrystals act as the light absorbing region to generate electricity, while metal nanocrystals with proper energy level act as metal cocatalysts for the active sites for photocatalytic water splitting reaction. Therefore, metal-semiconductor heterostructured nanocrystals are regarded as promising nanomaterials for the photocatalytic water splitting reaction to generate future renewable energy resources.

Among the candidates of semiconductor nanocrystals with proper bandgap to split water, cadmium chalcogenide semiconductor nanocrystals with metal cocatalysts have widely been studied due to the well-known synthetic chemistry to control over morphologies and compositions [3-5]. As such, CdSe semiconductor nanocrystals with platinum cocatalysts are suitable model systems to systematically study the influence of each component on the performance of photocatalytic hydrogen generation [6-12]. Despite CdS nanocrystals show better photocatalytic efficiency than CdSe nanocrystals, photocorrosion issues still exist when irradiated with certain wavelength of light. The incorporation of Pt nanocrystals with CdSe or CdS semiconductor nanocrystals are mostly done by the reduction of Pt precursors to spontaneously nucleate and grow from the surfaces of semiconductor nanocrystals with high energy. Photoirradiation method is also used to decorated Pt clusters on semiconductor nanocrystals [13,14], but this method is not ideally suitable to precisely control the size or number density of Pt nanocrystals. Therefore, well-defined CdSe tetrapods, synthesized by the continuous precursor injection (CPI) approach previously reported from our group [15], allowed us to systematically control the size of Pt nanocrystals decorating uniformly at the surfaces of CdSe tetrapods [16].

Herein, we report the effect of arm length of Pt-decorated CdSe tetrapods on the final performance of photocatalytic hydrogen generation reaction. CdSe tetrapods with controlled arm lengths were synthesized by the CPI approach previously reported from our group. These CdSe tetrapods showed high morphological uniformity and shape selectivity with gram-scale final products. The size of Pt nanocrystals, which, in the present study, serve as photocatalytic hydrogen evolution reaction sites, was simply controlled by the amount of Pt precursors during the synthesis. In this work, we chose extremely small size (~1 nm) of Pt nanocrystals that have shown highest photocatalytic hydrogen generation efficiency when compared with larger Pt nanocrystals, as evidenced from the previous work from our group. As a result, Pt-decorated CdSe tetrapods with shorter arm length showed the best photocatalytic hydrogen gen-

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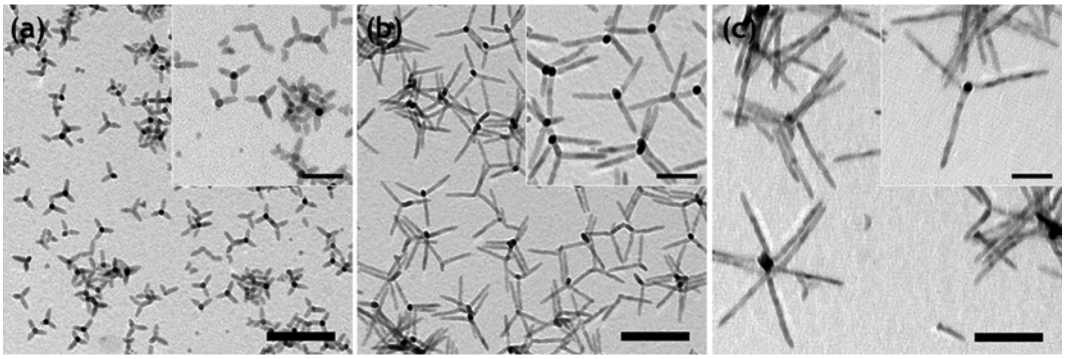

Fig. 1. TEM images of Pt-decorated CdSe tetrapods with different arm lengths: (a) L=17.42±1.8 nm, D=6.15±0.5 nm (b) L=46.8±2.4 nm, D=6.14±0.5 nm (c) L=83.78±7.4 nm, D=6.2±0.5 nm (scale bar: 100 nm & 50 nm (inset)).

eration efficiency, which we assume is due to higher chance for electrons and holes to separate excitons. This systematic study on the morphological effect will provide insights to design high-performance metal-semiconductor heterostructured photocatalysts.

RESULTS AND DISCUSSION

Fig. 1 shows transmission electron microscopy images of Pt-decorated CdSe tetrapods with controlled lengths of wurtzite CdSe tetrapod arms. First, CdSe tetrapods were synthesized by the CPI approach with zincblende CdSe quantum dots as seeds to grow wurtzite CdSe tetrapod arms. During the synthesis of CdSe tetrapods, certain amount of alkyl halide ligands with 1-oleic acid, which, in the present case, are cetyltrimethylammonium bromide (CTAB), is necessary to maintain the crystal structures of zincblende CdSe seeds as well as wurtzite CdSe tetrapod arms. During the CPI to grow the wurtzite CdSe tetrapod arms, injection solutions containing cadmium oleate and SeTOP were injected with syringe pumps by monitoring first excitonic peaks from the absorption spectra of reaction mixtures in real-time. Since the growth of wurtzite CdSe tetrapod arms with the CPI method is mostly governed by monomer concentrations of Cd and Se within the kinetic growth regime, the control over injection rate and temperature is important to obtain desired arm length and diameter. The growth of wurtzite CdSe tetrapod arms occurs primarily along the length direction, followed by the growth of the diameter, therefore when the diameter of CdSe tetrapods reached at a desired point, reactions were immediately quenched. With this synthetic strategy, the length of wurtzite CdSe tetrapod arms was varied from ~15 to ~90 nm, while the diameter remained the same as the target value of ~6 nm.

The direct decoration of Pt nanocrystals on overall surfaces of CdSe tetrapods was performed by the procedure from literature. From the previous study, with CdSe tetrapods prepared by the CPI approach, we observed that controlling the amount of Pt precursor resulted in the decoration of Pt nanocrystals with different size. The effect of the size of Pt nanocrystals on the photocatalytic hydrogen generation reaction has been studied by our group, in which smaller size of Pt nanocrystals has shown the highest efficiency [16]. As a result, in the present study, CdSe tetrapods with different arm lengths were decorated with Pt nanocrystals with a size of around 1 nm. To confirm the uniform decoration of Pt nanocrystals at the surface of CdSe tetrapod arms, high-angle annual dark field scanning transmission electron microscopy (HAADF-STEM) with energy-dispersive spectrometry (EDS) was conducted. From Fig. 2, by the elemental mapping of Pt-decorated CdSe tet-

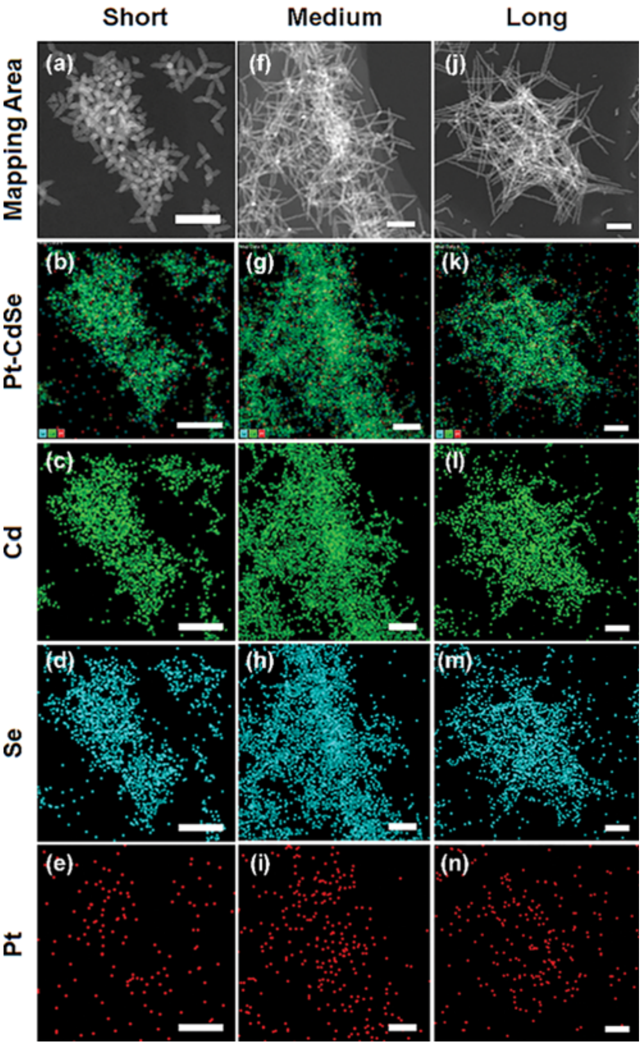

Fig. 2. EDS mapping of Pt-decorated CdSe tetrapods with different arm lengths: (a)-(e) 17 nm, (f)-(i) 47 nm, and (j)-(n) 84 nm.

rapods with different arm lengths, the existence of Pt nanocrystals was confirmed. All the mapping images showed the atomic ratio of Cd, Se and Pt as 56 : 43 : 1, which almost matches with the amount of Pt precursors used for the decoration of Pt nanocrystals with respect to the amount of CdSe tetrapods (see Supporting Information). As mentioned above, the size of Pt nanocrystals was mainly controlled by the amount of Pt precursors. Therefore, we can assume that different numbers of CdSe tetrapods with different arm lengths with respect to the same amount of Pt precursors could be introduced during the decoration of Pt nanocrystals. Inductively-coupled plasma atomic emission spectroscopy (ICP-AES) was conducted to analyse the amount of Cd, Se, and Pt for the same weight percent (see Supporting Information). As a consequence, regardless of the arm length of Pt-decorated CdSe tetrapods, the amount of Pt nanocrystals remained almost the same. This result explains that when the same amount of Pt-decorated CdSe tetrapods with different arm lengths is present, the total amount of Pt nanocrystals with respect to CdSe tetrapods are the same, implying that the number densities of Pt nanocrystals are similar for Pt-decorated CdSe tetrapods with different arm lengths.

Pt-decorated CdSe tetrapods with different arm lengths were ligand-exchanged with 11-mercaptoundecanoic acid under pH11 condition according to the literature [4]. These heterostructured photocatalysts were dispersed in water for further photocatalytic hydrogen generation. Photocatalyst solutions containing 0.35 Na_2SO_3/ 0.25 M Na_2S as hole scavengers were transferred to a homemade quartz tube sealed with a vacuum rubber septum. Samples were irradiated with a solar simulator (Sun 2000, ABET Technologies) under 1 SUN condition for 2 hrs. Certain amount of gas was collected directly from the head space with a gas-tight microsyringe for every 30 min, followed by the injection to a gas chromatograph equipped with a pulsed discharge ionization detector (YL6500, YL Instruments). Fig. 3 shows the photocatalytic hydrogen generation of Pt-decorated CdSe tetrapods with different arm lengths after 2 hrs of irradiation. We note that Pt-decorated CdSe tetrapods with shorter arm length showed the highest photocatalytic hydrogen generation efficiency. Bare CdSe tetrapods without Pt nanocrystals showed the lowest photocatalytic efficiency when compared with Pt-decorated CdSe tetrapods regardless of the different arm length. As the length of the wurtzite CdSe arms is increased, the photocatalytic efficiency gradually decreases. We believe that this result could be explained based on the previous study from the literature that excitons generated by the CdSe tetrapods mostly remains at the zincblende CdSe quantum dot cores due to the quasi type-II band alignment [17]. Photocatalytic hydrogen generation results, obtained in the present study, are based on the total weight of photocatalysts, which is the weight of Pt-decorated CdSe tetrapods with different arm length. The same amount of photocatalysts was employed for all the photocatalytic hydrogen generation experiments despite the fact that the weight of a single photocatalyst is different. As a result, we could argue that different numbers of Pt-decorated CdSe tetrapods were introduced, which, in turn, leads to different numbers of zincblende CdSe tetrapod cores (i.e., more zincblende CdSe cores with shorter arms for the same total weight of Pt-decorated CdSe tetrapods). This argument supports our results that shorter CdSe tetrapods have higher probability for excitons to separate charges, given the fact that the amount of Pt with respect to CdSe is the same for different arm lengths of Pt-decorated CdSe tetrapods. Further detailed experiments on the transient behavior of Pt-decorated CdSe tetrapods to confirm our arguments are now under way.

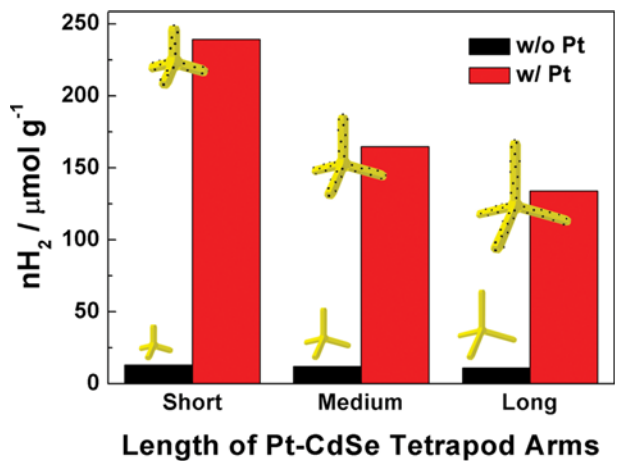

Fig. 3. Photocatalytic hydrogen generation results of bare and Pt-decorated CdSe tetrapods with different arm lengths.

CONCLUSION

Pt-decorated CdSe tetrapods with different arm lengths were successfully prepared. Pt-decorated CdSe tetrapods with shorter arm length showed the highest hydrogen generation efficiency, while the densities of Pt nanocrystals per surface area of CdSe tetrapods remained almost the same. This indicates that the photocatalytic hydrogen generation behavior of Pt-decorated CdSe tetrapods with different arm lengths mainly depends on the length of wurtzite CdSe tetrapod arms due to higher probability for as-generated excitons to separate charges.

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SUPPORTING INFORMATION

Experimental details with characterizations are introduced in supporting information. The materials are available via the Internet at http://www.springer.com/chemistry/journal/11814.

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