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Carbon quantum dots coated BiVO₄ inverse opals for enhanced photoelectrochemical hydrogen generation

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Carbon quantum dots (CQDs) coated BiVO₄ inverse opal (io-BiVO₄) structure that shows dramatic improvement of photoelectrochemical hydrogen generation has been fabricated using electrodeposition with a template. The io-BiVO₄ maximizes photon trapping through slow light effect, while maintaining adequate surface area for effective redox reactions. CQDs are then incorporated to the io-BiVO₄ to further improve the photoconversion efficiency. Due to the strong visible light absorption property of CQDs and enhanced separation of the photoexcited electrons, the CQDs coated io-BiVO₄ exhibit a maximum photo-to-hydrogen conversion efficiency of 0.35%, which is 6 times higher than that of the pure BiVO₄ thin films. This work is a good example of designing composite photoelectrode by combining quantum dots and photonic crystal. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4918290>]

Since Fujishima and Honda's first report on TiO₂ photoelectrode in 1972,¹ photoelectrochemical (PEC) or photocatalytic water splitting for hydrogen generation has been studied extensively.^{2–5} BiVO₄ is a well-known photoelectrode material, which absorbs part of the visible light due to its relatively small band gap (~2.4 eV).^{6–8} It also has a favorable conduction band (CB) edge position near the thermodynamic H₂ evolution potential. Although water splitting using BiVO₄ is promising for hydrogen generation, the short carrier diffusion length and poor charge transport property limit the efficiency. To solve these problems, various methods have been employed including doping BiVO₄ with metal ions,^{9,10} heterojunction structure formation,^{11,12} surface modification,¹³ and decorating with noble metal.¹⁴

Alternatively, the morphology of a semiconductor material can also affect the PEC water splitting performance significantly. To date, a variety of BiVO₄ nanostructures with large surface areas have been fabricated, including nanoflake,¹⁵ nanorods,¹⁶ nanotube,¹⁷ and nanowires.¹⁸ Three-dimensional inverse opal structure is of tremendous value because it not only provides high specific surface area and porosity¹⁹ but also improves light harvesting due to multiple scattering.²⁰ Moreover, the periodical structure can provide an additional photonic bandgap effect (slow light effect), which enhances light-matter interactions by controlling the propagation of light.²¹ Zhou *et al.* have shown that Mo doped BiVO₄ inverse opal (io-BiVO₄) can significantly improve the water splitting efficiency, which is attributed to the effective charge collection and utilization properties of periodically ordered porous.²² Zhang *et al.* also report that io-BiVO₄ decorated with Au nanoparticles shows photocurrent more than 4 times

higher than the reference electrodes, and such improvement can be ascribed to the synergistic effects of photonic crystal and metal plasmonic properties.²³

Carbon quantum dots (CQDs) have attracted much attention recently because of their rich photo-physical properties. For example, they show good photocatalytic properties due to the strong size and excitation wavelength dependent photoluminescence behavior and their broadband optical absorption.²⁴ More importantly, their photocatalytic performance can be further enhanced through the construction of semiconductor/CQDs composites.²⁵ Considering their remarkable properties, the combination of inverse opal structure and CQDs may be an ideal strategy to achieve efficient complex photoelectrode.

In this paper, we report a PEC photoelectrode by combining io-BiVO₄ with CQDs for solar-light-driven hydrogen generation. The io-BiVO₄ provides a large surface area for CQDs loading, good carrier transport path and intimate contact with the electrolyte. In addition, the combination of BiVO₄ and CQDs can greatly improve visible-light harvesting and interfacial charge transfer and separation. The excellent properties of the designed io-BiVO₄/CQDs photoelectrode clearly demonstrate the potential of this strategy.

The preparation and characterization of samples are presented in the supplementary material.²⁶ Figure 1(a) shows the SEM image of the colloidal crystal templates produced using 260 nm PS spheres. The top view image clearly demonstrates the perfection in the colloidal order, showing close-packed (111) plane of a face-centered cubic (fcc) arrangement. Figures 1(b) and 1(c) show the corresponding top view of the io-BiVO₄/CQDs and io-BiVO₄. Both samples are uniform and the PS template has been removed completely. Moreover, the io-BiVO₄/CQDs sample has a similar morphology as the io-BiVO₄ sample, indicating that the CQDs

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FIG. 1. The SEM images of top view for (a) the colloidal crystal template self-assembled from PS spheres with diameters of 260 nm; (b) the io-BiVO₄/CQDs sample; (c) the io-BiVO₄ sample; (d) the d-BiVO₄ sample; (e) the BiVO₄ films; (f) the SEM image of cross view for the io-BiVO₄/CQDs sample. The actual photography of the samples is shown in the corresponding insets.

deposition process does not damage the ordered io-BiVO₄. It should be noted that because of their small size, CQDs can not be seen clearly in the SEM image. The insets of Figures 1(b) and 1(c) also show the actual photos of the samples. Uniform color can be seen after precursor infiltration and annealing, which illustrates excellent periodicity over centimeter scale. In addition, the io-BiVO₄/CQDs sample appears darker than the pristine io-BiVO₄ sample, which indicates the improvement in light harvesting ability. For comparison, a disordered porous BiVO₄ (d-BiVO₄) structure (Figure 1(d)) was prepared from a randomly packed template formed with a mixture of 260 and 360 nm PS spheres under the same conditions. Figure 1(f) shows the cross section SEM image of the io-BiVO₄/CQDs sample, which exhibits vertical ordering, and the thickness is around 4.5 μm. The BiVO₄ films (see SEM image in Figure 1(e)) were also fabricated by spin coating using the same precursor. Moreover, the XRD patterns (Figure S2) of all the samples match the Joint Committee on Powder Diffraction Standards File (JCPDS No. 75-2481) for BiVO₄, which confirms that the low anneal temperature is enough for the formation of monoclinic BiVO₄.

In order to study the morphology of the io-BiVO₄/CQDs sample more clearly, TEM measurement was performed. Figure 2(a) shows the TEM image of the fractal of samples obtained after ultrasonication, showing clearly the hexagonal close-packed structure. The pore diameter is about 150 nm, and the wall thickness of the BiVO₄ is about 15 nm. High-

FIG. 2. (a) TEM image of the io-BiVO₄/CQDs sample; (b) high resolution image of the interface region; (c) the FT-IR spectrum of the io-BiVO₄/CQDs sample.

resolution TEM image in Figure 2(b) shows that the lattice spacing is 0.309 nm, which corresponds to the (112) planes of monoclinic BiVO₄. Alongside the BiVO₄, the lattice spacing of 0.321 nm corresponds to the (002) planes of graphitic carbon. Figure 2(c) shows the FTIR spectrum of the io-BiVO₄/CQDs sample, the characteristic peaks of C-H and C=O can be observed at 1250, 1600, and 1720 cm⁻¹. From the above analysis, we can conclude that the desired io-BiVO₄/CQDs composite has been synthesized.

Figure 3 depicts the UV-vis absorption spectra of all samples, and the inset is the UV-vis absorption spectra of CQDs and the BiVO₄ films. It can be seen that the CQDs show stronger spectrum absorption than that of the BiVO₄ films, which implies the CQDs can be served as a photosensitizer. Although our BiVO₄ samples are annealed at a relative low temperature, it is observed that they can still absorb light with wavelengths shorter than 530 nm, which is consisted with previous reports.²⁷ Due to multiple scattering in the porous structure, slightly enhanced optical absorption

FIG. 3. UV-vis absorption spectra of the different samples, the inset are the UV-vis absorption spectra of CQDs and the BiVO₄ films.

can be seen in the d-BiVO₄ sample. The io-BiVO₄ sample has higher absorption intensities than the d-BiVO₄ sample, which may be attributed to the enhanced light-matter interaction due to the slow light effect. More importantly, the absorption range the io-BiVO₄/CQDs sample broadens up to 800 nm after coating with CQDs, which again demonstrates that CQDs can play an important role in solar energy harvesting.

To investigate the characteristics of the different BiVO₄ samples as photoelectrodes, PEC measurements were performed. The chronoamperometric *I*-*t* curves (Figure 4(a)) recorded under chopped light illumination at 0.9 V external potential versus RHE reveal an instantaneous photoelectric response of all the photoelectrodes. Clearly, the d-BiVO₄ sample exhibits higher photocurrent intensities than that of the BiVO₄ films. The improvement may be attributed to two reasons: first, the porous structure can improve light harvesting due to multiple scattering effects. Second, the electrolyte can easily infiltrate the pores and result in more effective redox reactions at the BiVO₄/electrolyte interface. The io-BiVO₄ sample has even higher photocurrent intensity than that of the d-BiVO₄ sample, which is related to the photonic crystal effect and will be discussed later. Most importantly, the io-BiVO₄/CQDs sample exhibits the largest photocurrent density in all the samples, which demonstrate the positive role of CQDs in enhancing the PEC property of BiVO₄ photoelectrodes. Moreover, it should be pointed out that there is an optimized CQDs amount and less or more the optimized CQDs electrodeposition time (5 min) will lead to decreasing photocurrent density (Figure S3).

Figure 4(b) shows a set of linear sweep voltammetry of the different samples in dark and under 300 W Xe-lamp illumination. The result in dark for the BiVO₄ films only shows a small background current density at $\mu\text{A cm}^{-2}$ scale. The

photocurrent densities of all samples increase after the external potential exceeds the onset potential of around 0.4 V vs. RHE. Again, the io-BiVO₄/CQDs sample shows the highest photocurrent density in the whole potential window. The photoconversion efficiency (η) of a water-splitting photoelectrode with an external potential can be calculated via the following equation:

$$\eta = I(1.23 - V_{\text{app}})/P_{\text{light}}, \quad (1)$$

where V_{app} is the applied external potential versus RHE, I is the current density, and P_{light} is the power density of the illumination. Figure 4(c) shows the calculated photoconversion efficiencies as a function of external potential versus RHE. The maximum photoconversion efficiencies for the BiVO₄ films, d-BiVO₄, io-BiVO₄, and io-BiVO₄/CQDs photoelectrodes are 0.06% (at 1.05 V vs. RHE), 0.16% (at 0.98 V vs. RHE), 0.20% (at 0.92 V vs. RHE), and 0.35% (at 0.87 V vs. RHE), respectively.

To further quantify the performance of these electrodes, we show the amount of H₂ and O₂ generation in the PEC water-splitting experiment under 300 W Xe-lamp illumination for 4 h in Figure 4(d). For all the photoelectrodes, H₂ and O₂ evolve simultaneously from the surface of the Pt counter electrode and photoelectrode with a stoichiometric ratio of approximately 2:1, which suggests complete water splitting. In addition, the linear increase of the amount of H₂ and O₂ production with time reveals the excellent stability of these photoelectrodes under operation condition. The hydrogen evolution rates (and Faradic efficiencies) of the BiVO₄ films, d-BiVO₄, io-BiVO₄, and io-BiVO₄/CQDs photoelectrodes are 5.9 $\mu\text{mol h}^{-1}$ (90.2%), 10.6 $\mu\text{mol h}^{-1}$ (91.5%), 11.78 $\mu\text{mol h}^{-1}$ (92.1%), and 18.8 $\mu\text{mol h}^{-1}$ (92.6%), respectively. The amounts of H₂ and O₂ are slightly less than the theoretical values, possibly due to gas leakage or dissolution in the

FIG. 4. (a) Chronoamperometry measurements of the different samples at an external potential of 0.9 V vs. RHE with repeated on/off circles under UV-visible light irradiation; (b) linear sweep voltammetry measurements with a scan rate of 50 mV s⁻¹ under light irradiation, the dashed line represents the current density of the BiVO₄ films in dark; (c) photoconversion efficiency as a function of applied potential vs RHE; (d) the evolution of H₂ and O₂ gases of the different samples under light illumination.

FIG. 5. (a) Chronoamperometry measurements of the different samples under visible light irradiation ($\lambda > 530$ nm) at an external potential of 0.9V vs. RHE; (b) luminescence emission spectra (485 nm excitation) of the CQDs in water without and with the quenchers N,N-diethylaniline (0.03 M). Inset: Luminescence decays (485 nm excitation) of the CQDs with N,N-diethylaniline.

electrolyte. Figure S4 also shows the corresponding photocurrents of all samples during 4 h hydrogen generation measurements, which imply all the samples are stable.

On the basis of the above experiment results, the enhanced PEC water splitting efficiency of the io-BiVO₄/CQDs photoelectrode can be explained as follow. In the case of io-BiVO₄, the position of the red edge of the photonic stop-band is at 450 nm, which is in accordance with the absorption maximum of BiVO₄. In other words, io-BiVO₄ can absorb photons with ~ 450 nm wavelength by reducing their group velocity. Moreover, CQDs can absorb visible light, which also improves light absorption. Thus, more electrons and holes can be generated in the io-BiVO₄/CQDs photoelectrode.

In addition, it has been demonstrated that CQDs play an important role in the photoexcited electron transfer.²⁸ Two different mechanisms have been reported. In some systems, CQDs act as electron sink that receives electrons from the semiconductor and thus suppress the recombination of photo-generated carriers.²⁹ The opposite occurs in other systems, where the electrons in CQDs are injected into the semiconductor.³⁰ In the present system, we suggest that the enhanced PEC properties is likely due to the first mechanism. This can be confirmed by performing the photocurrent measurement under light of different wavelength. As shown in Figure 5(a), both io-BiVO₄ and io-BiVO₄/CQDs samples show high photocurrent densities of the order of mA cm⁻² under UV-vis light illumination. However, under visible light ($\lambda > 530$ nm), both samples show small current densities at μ A cm⁻² scale. Since CQDs can still absorb enough visible light, and if the electrons in CQDs can be photoexcited, one should able to observe a high value photocurrent density in the io-BiVO₄/CQDs sample.

In order to verify electron-accepting capability of CQDs, photoluminescence measurement was performed.³¹

Figure 5(b) shows the luminescence spectrum of the CQDs in water, and the inset is the corresponding luminescence decays spectrum. It is observed that CQDs exhibit a broad luminescence peak around 550 nm with the excitation at 485 nm. However, the emission is quenched by adding the well-known electron donor, N,N-diethylaniline. As for the observed efficient quenching of luminescence emissions in the CQDs, we can conclude that CQDs are excellent as electron acceptors.

The EIS measurement was also performed to further elucidate the role of the CQDs in the photogenerated charge separation and transport properties (Figure 6). The arc radius of the EIS Nyquist plots without or with light irradiation shows similar trend as the PEC properties, i.e., the BiVO₄ films > d-BiVO₄ > io-BiVO₄ > io-BiVO₄/CQDs. Moreover, the arc radii for all the samples are significantly reduced with light irradiation. Since a smaller radius of the arc in the EIS spectra indicates a smaller electron transfer resistance at the surface of photoelectrodes,³² a more effective separation of photogenerated electron-hole pairs and faster interfacial charge transfer are expected in the io-BiVO₄/CQDs sample.

Up to now, the most efficient decorating materials for BiVO₄ photonic crystal for PEC system are Au and other noble metals. However, more economical materials based on non-precious metals and metal-free materials are necessary for large-scale applications. Here, CQDs are demonstrated to be excellent materials for efficient light absorption and charger transferring. Given its earth-abundance, low cost, environmentally friendliness, and ease of fabrication, CQDs are very promising for energy conversion. Most recently, it is demonstrated that CQDs embedded in C₃N₄ matrix lead

FIG. 6. EIS Nyquist plots of the different samples (a) without light irradiation; (b) under light irradiation.

to an overall solar energy conversion efficiency of 2.0% for water splitting.³³ Therefore, this finding is not limited to the CQDs/BiVO₄ platform but provide a general method for PEC hydrogen production.

In conclusion, we have demonstrated a photoelectrode design for PEC water splitting by combining io-BiVO₄ with CQDs. The highly ordered three-dimensional structure leads to efficient light harvesting and more effective redox reactions. In addition, coating the io-BiVO₄ with CQDs can further improve the photocurrent and hydrogen production, which is ascribed to the strong visible light absorption property of CQDs and enhanced separation of the photoexcited electrons. The photo-to-hydrogen conversion efficiency of the io-BiVO₄/CQDs sample is about 6 times higher than the reference BiVO₄ thin films. This unique composite photoelectrode can have great potential in the construction of high performance PEC cells.

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