Carbon-shell-decorated *p*-Semiconductor PbMoO₄ Nanocrystals for Efficient and Stable Photocathode of Photoelectrochemical Water Reduction

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ABSTRACT:

Photoelectrochemical (PEC) water splitting using semiconductors is a promising method for the future scalable production of renewable hydrogen fuels. The critical issues in PEC water splitting include the development of the photoelectrode materials with high efficiency and long-term stability, especially for p-type semiconductor photocathodes. Herein, we report the use of citric acid (CA) pyrolysis to prepare carbon-shell-decorated PbMoO_4 (C@PbMoO_4) nanocrystals via a simple solvothermal method. Different carbon shell thicknesses below 10 nm were generated by varying the amount of CA in the precursor solution. In contrast, without using CA, bare PbMoO_4 nanocrystals were obtained. The PEC experiments showed that 2-nm carbon shell could preferably improve the water splitting performance of PbMoO_4 : the photocurrent density of 2-nm C@PbMoO_4 is nearly 2-fold high as that of bare PbMoO_4 at 0 V versus reversible hydrogen electrode (RHE). The surface charge transfer efficiency of 2-nm C@PbMoO_4 in the PEC process was tested to increase from 83% to 90.4%, the charge separation efficiency enhanced 56%, and the PEC stability also greatly increased compared to those of the bare PbMoO_4 nanocrystals. This strategy could be applied to other p-type semiconducting photocathodes for low-cost solar-fuel-generation devices.

Keywords: PbMoO_4 , photoelectrochemical, water splitting, photocathode, carbon shell

1. INTRODUCTION

Hydrogen is a clean and promising sustainable alternative to fossil fuels to meet the global energy demands. With hydrogen fuel as an environmentally and friendly alternative, photoelectrochemical (PEC) water splitting with semiconductor electrode materials has become a suitable option ever since the report of the Honda-Fujishima effect.^[1-6] In contrast to photocatalyst hydrogen generation, PEC water splitting can be achieved through the application of some external bias, even if powdered photocatalysts do not possess energy-band potentials that are suitable for water splitting.^[7] The use of advanced metal oxide and sulfide semiconductors as active photoelectrode materials for PEC cells has been studied widely. However, it remains challenges to develop new semiconductor photoelectrode materials with low cost, high efficiency, and good stability for hydrogen generation via solar energy. In particular, most p-type semiconductor materials are generally unstable when used as photocathodes for proton reduction in an aqueous environment. This phenomenon has been explained using thermodynamics, as the conduction band potential is more negative than the reduction potential of the metal ions in the lattice, leading to the reductive decomposition of the semiconductor surface and the loss of photoactivity.^[8]

Based on these concerns, an investigation targeting core-shell nanostructures for enhancing PEC stability and efficiency might provide an alternative route to engineer semiconductor materials. For example, the p-semiconductor Si is often coated with a corrosion-resistant layer, such as TiO₂, WO₃, SnO₂, Fe₂O₃, etc., to enhance the stability for the PEC evolution of H₂.^[9-12] Additionally, many n-semiconductors were also reported to be coated with various shells, such as ZnO/CdTe core-shell nanocables,^[13] Fe₂O₃/ZnO core-shell

nanowires,^[14] TiO₂/FeOOH nanorods,^[15-16] and WO₃/BiVO₄ core-shell nanowires,^[17] to improve PEC water splitting performances. However, the shell compositions of all the above examples are semiconductor materials with poor conductivity, hindering the transfer of charge carriers at a certain level. As a good conductor, carbon has often been used as shell-coating material on electrodes for the applications in such as Li ions batteries,^[18-20] supercapacitor,^[21] electrocatalysis,^[22] and solar cells.^[23] To the best of our knowledge, there are few reports on carbon-coated semiconductor nanocrystals as photoelectrode materials to improve the stability and efficiency of PEC water splitting.

As a p-type semiconductor, lead molybdate (PbMoO₄) has gained increasing interest due to its potential applications in the fields such as photoluminescence, solid-state lasers, scintillating materials, humidity sensors, and photocatalysts.^[24-27] Moreover, PbMoO₄ crystals can be found in the natural form of an abundant mineral called “Wulfenite”. PbMoO₄ crystals in a tetragonal scheelite structure have point group symmetry 4/m and space group *I41/a*, with two formula units per primitive cell.^[28-29] Each Mo atom is surrounded by four equivalent O atoms composed of [MoO₄]²⁻ tetrahedrons, which are linked via Pb²⁺. The semiconductor properties of PbMoO₄ arise due to the interactions between the Mo d states and O 2p orbitals, which have some covalent contribution to the ionic bonds. The value of the band gap as determined experimentally lies between 3.1 and 3.4 eV, whereas calculations give a much wider energy range, i.e., from 2.6 eV to 4.8 eV.^[24, 26, 30-31] In the past decades, although many efforts have been devoted to PbMoO₄ semiconductor preparation, few of them are concerned on the use in PEC water splitting.^[32-35]

In this work, we report the preparation of carbon shell coating on PbMoO₄ nanocrystals

(C@PbMoO₄) via a simple solvothermal method with citric acid (CA) as the C source. The thickness of the carbon shell was controlled facilely to 2 nm, 5 nm, and 8 nm by varying the amount of CA in the precursor solution. The prepared C@PbMoO₄ nanocrystals were investigated as photocathode materials for PEC water splitting. The C@PbMoO₄ with the carbon shell in 2-nm thickness generated the most remarkable PEC photocurrent density than did bare PbMoO₄, as well as the 5-nm C@PbMoO₄ and 8-nm C@PbMoO₄ samples. The surface charge transfer efficiency of 2-nm C@ PbMoO₄ in PEC water splitting were tested to increase by 7.4% (from 83% to 90.4%), the charge separation efficiency enhanced 56%, and the PEC stability increased greatly compared to those of bare PbMoO₄ nanocrystals.

2. EXPERIMENTAL SECTION

2.1 Chemicals

Lead acetate trihydrate (PbAc₂ • 3H₂O, 99%) was purchased from Tianjin Guangfu Co., Ltd. Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄ • 4H₂O, 99% mass fraction) was obtained from Shenyang reagent factory. Citric acid (CA, 99%) was obtained from Beijing chemical factory. Fluorine-doped tin oxide (FTO) coated glass was provided by Tianjin IDA Co., Ltd. Deionized water was used as the solvent in solvothermal synthesis and electrochemical experiments. All chemicals were used as received without further purification.

2.2 Synthesis of 2-nm, 5-nm and 8-nm C@PbMoO₄ nanocrystals and bare PbMoO₄ nanocrystals:

In a typical procedure to prepare 2-nm C@PbMoO₄ nanocrystals, PbAc₂•3H₂O

(0.0759g, 0.2 mmol), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.0353g, 0.028mmol) and citric acid (0.0210 g, 0.5mmol) were added to 12.0 mL deionized water in a Teflon-lined stainless steel autoclave with a capacity of 20.0 mL at room temperature, and stirred for 10 minutes. After the autoclave was sealed and maintained at 200 °C for 1 h in a preheated oven, it was taken out and cooled to room temperature naturally. White products were collected after being repeatedly washed with deionized water and anhydrous ethanol, and then dried in a vacuum oven. Then the obtained sample was re-dispersed in deionized water (~5 ml) and stored for their posterior use.

5-nm and 8-nm C@PbMoO₄ nanocrystals were prepared via a similar method with 2-nm C@PbMoO₄ nanocrystals, but added 0.0420g and 0.210g citric acid into the precursor solution, respectively.

Bare PbMoO₄ nanocrystals were prepared via a similar method with 2-nm C@PbMoO₄ nanocrystals, without adding citric acid into the precursor solution.

2.3 Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max 2200 PC diffractometer with Cu K α radiation ($\lambda = 1.5418\text{\AA}$) and a graphite monochromator from 10° to 80° with a scanning rate of 5.0° per min. Unit cell dimensions and the crystallinity were determined using the JADE 5 program for X-ray diffraction pattern processing, identification, and quantification. The size and morphology of the obtained samples were characterized on a transmission electron microscope (TEM, JEM100-CXII) equipped with a selected area electron diffractometer (SAED). The structure and lattice fringes of nanocrystals were observed by using a high resolution TEM (HRTEM, FEI Tecnai G2 F30) equipped with a

scanning transmission electron microscope (STEM). The chemical composition of the as-prepared PbMoO_4 and C@PbMoO_4 nanocrystals were analyzed by energy dispersive X-ray spectroscopy (EDX, Oxford). To gain a better understanding of the elemental distribution throughout these nanocrystals, the samples were characterized using high angle annular dark field-scanning TEM (HAADF-STEM) imaging in conjunction with EDX mapping. Thermogravimetric analysis (TGA, NETZSCH STA 449F3) was carried out with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from room temperature to $350\text{ }^\circ\text{C}$ under flowing air. Raman spectrum was recorded at ambient temperature with a NEXUS 670 Raman spectrometer. The UV-vis absorption spectra of all the samples were investigated under a UV-vis spectrophotometer (Shimadzu UV-vis 2550).

2.4 Fabrication of Photoelectrochemical (PEC) working electrodes

Fluorine doped tin oxide (FTO) glass substrates ($1\text{ cm} \times 2\text{ cm}$) were cleaned with acetone and deionized water, and dried with pure nitrogen. To prepare a PEC device, an active layer was prepared by spin-coating PbMoO_4 or C@PbMoO_4 nanocrystals dispersed in ethanol (1 mL with a concentration of 0.5 mg mL^{-1}) onto the FTO layer at 3000 rpm . Finally, the obtained product photoelectrodes were annealed in a nitrogen environment at $60\text{ }^\circ\text{C}$ for 1 h before it was used for water splitting experiments.

2.5 PEC water splitting tests

PEC tests were conducted by using a three-electrode configuration connected to a CHI 660D electrochemical workstation (CH Instruments) at about $25\text{ }^\circ\text{C}$, employing an epoxy-sealed nanocrystal samples with an exposed area of 1.0 cm^2 as the working electrode, a Pt mesh as the counter electrode, Ag/AgCl ($1\text{ molL}^{-1}\text{ KCl}$ solution) as the reference

electrode, and 0.5 M H₂SO₄ (pH = 0) solution as the electrolyte. The electrolyte was stirred and bubbled with N₂ gas before the measurements. The scan rate was fixed at 0.1 V s⁻¹ for all PEC analyses. The forward scans swept the bias from positive to negative. A 350 W Xe lamp light source (at a power density of 60 mW cm⁻²) was used to provide light illumination. Transient photocurrent density measurements were performed under constant applied potential (-0.1 V_{RHE}) for 40 s with a 20 s light pulse turned on after 20 s. The illumination power on the sample was adjusted from 60, 40 to 20 mW cm⁻², and measured by using a LP-3A laser power meter. The measured potentials versus Ag/AgCl were all converted to the reversible hydrogen electrode scale according to the Nernst equation:

$$V_{RHE} = V_{Ag/AgCl} + 0.059\text{pH} + V_{Ag/AgCl}^0$$

$$V_{Ag/AgCl}^0 = 0.197\text{V at } 25^\circ\text{C}$$

All the measurements were done under ambient conditions.

3. RESULTS and DISCUSSION

Fig. 1. XRD patterns of as-prepared bare PbMoO₄ and C@PbMoO₄ with different shell thicknesses. The lines at the bottom represent the standard PbMoO₄ pattern.

The phase and crystallization of the obtained PbMoO₄ and carbon-coated PbMoO₄ samples were characterized by Powder X-Ray diffraction (XRD) as shown in Fig. 1. The XRD pattern of bare PbMoO₄ nanocrystals in Fig. 1 demonstrates that all of the diffraction peaks can be indexed to the body-centered tetragonal structure (scheelite-type), in good agreement with the standard PbMoO₄ crystals (JCPDS card no. 44-1486). No characteristic peaks of impurities were observed such as PbO, MoO₃ and PbMoO₃. The unit cell parameters were calculated as $a = b = 5.428 \text{ \AA}$, and $c = 12.133 \text{ \AA}$, in agreement with those in the JCPDS card ($a = b = 5.433 \text{ \AA}$ and $c = 12.110 \text{ \AA}$). Moreover, the relative sharp diffractions of all the peaks indicate that the materials were well-crystallized, suggesting an ordered structure at a long range in the nanocrystals. This structure can be identified by the high crystallinity of ca. 97.25%, according to the Jade software calculation. The XRD patterns of the PbMoO₄ samples that were coated with carbon shell at various thicknesses indicate the same phase and crystallization with the bare PbMoO₄ sample (Fig. 1). No diffraction peak due to graphitic carbon was observed in the XRD patterns, caused by the amorphous nature of carbon in the C@PbMoO₄ samples.

Fig. 2. TEM images of as-synthesized bare PbMoO₄ and C@ PbMoO₄ with different shell thicknesses: (a) bare PbMoO₄, (b) 2-nm C@PbMoO₄, (c) 5-nm C@PbMoO₄, and (d) 8-nm C@PbMoO₄. Raman spectra (e) of the bare PbMoO₄ and C@ PbMoO₄. Plots of the carbon shell thickness with the amount of CA (f).

The series of PbMoO₄ nanocrystals were further observed by transmission electron microscopy (TEM). As seen in Fig. 2a, the PbMoO₄ nanocrystals that were synthesized without CA in the precursor solution were in the size of 40-100 nm. No obvious shell could be observed in this sample, as shown in the inset of Fig. 2a. Fig. 2b-2d show the TEM images of the produced nanocrystals with adding CA to the precursor solutions, showing that the shells presented around the PbMoO₄ nanocrystals. By increasing the amount of CA in the precursor solutions from 0.5 mmol to 1.0 mmol and 5.0 mmol, the outer shells grew to 2 nm, 5 nm and 8 nm, coating on the nanocrystals. These results illustrated well that the coated carbon shell

was derived from the decomposition of CA because of its low decomposing point at 175 °C, as confirmed by thermogravimetric (TG) analyses (see supplementary materials, Fig. S4). The relationship between the carbon shell thickness and the amount of CA is shown in Fig. 2f. To evaluate the carbon nature of the shell, Raman spectroscopy was used to further characterize PbMoO₄ and C@PbMoO₄ nanocrystals, as shown in Fig. 2e. The Raman spectrum of bare PbMoO₄ nanocrystals (black line) demonstrated that no coating carbon layer existed. However, two obvious peaks of around 1363 and 1595 cm⁻¹ were observed in the Raman spectra of C@PbMoO₄ (pink, red and blue lines in Fig. 2e), corresponding to the disordered carbon (D-band) and the ordered graphitic carbon (G-band), respectively. The former band (D-band) is associated with disorder, allowing zone edge modes of the graphite structure to become active due to the lack of a long-range order in the amorphous and quasi-crystalline forms of carbon materials. The latter band (G-band) corresponds to the E_{2g} mode (stretching vibrations) in the basal plane of the crystalline graphite.^[36-38] The *I_D/I_G* intensity ratio of 2-nm C@PbMoO₄, 5-nm C@PbMoO₄, and 8-nm C@PbMoO₄ was respectively calculated as 0.89, 0.87 and 0.82. These values were larger than those of the reported amorphous carbon materials, indicating that the shells around the PbMoO₄ nanocrystals were amorphous carbon rather than graphite.^[39-40]

Fig. 3. TEM image (a), enlarged single image (b), HRTEM image (c) and FFT pattern (d) of the typical prepared 2-nm C@PbMoO₄ nanocrystals.

To elucidate the microscopic structure of the PbMoO₄ nanocrystals coated with carbon shell, we conducted a detailed investigation using high-resolution TEM (HRTEM). Fig. 3a and 3b show the HRTEM images of the 2-nm C@PbMoO₄ sample that was synthesized with 0.5 mmol of CA in the precursor solution. The HRTEM images also further confirm that the prepared C@PbMoO₄ has a core-shell nanostructure and confirm the crystalline nature of the core and the amorphous nature of the shell. Fig. 3c shows the HRTEM image of the core component; it shows that the two sets of interplanar distances of 0.27 nm with a crossing angle of ~90° are dominant, corresponding to (200) in the tetragonal wulfenite PbMoO₄ crystals. The corresponding fast Fourier transformation (FFT) pattern (Fig. 3d) can also be assigned to the tetragonal structure. These results suggested that the PbMoO₄ nanocrystal in the core-shell nanostructure was of a single-crystalline nature.

Fig. 4. HAADF-STEM image (a) and EDX spectrum (b) of the typically prepared 2-nm C@PbMoO₄ nanocrystals; Elemental mappings of Pb (c), Mo (d) and O (e) as acquired from the 2-nm C@PbMoO₄ nanocrystal structure.

The prepared 2-nm C@PbMoO₄ nanocrystals were further characterized using high-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) imaging in conjunction with energy-dispersive spectroscopy (EDS) mapping, as shown in Fig. 4. The molar ratio of Pb and Mo to O were calculated as approximately 1:1:4 from the peak areas (Fig. 4b). These findings were consistent with their element signals, and the stoichiometry was within the expected error margins. Along the nanocrystal, the Pb, Mo and O elements were uniformly distributed intermittently across PbMoO₄, as shown in Fig. 4c-e.

Fig. 5. Scheme of the electron–hole pair separation and transfer process as well as electrode reactions in the PEC test of p-type semiconductors (a). *J*–*V* curves of the C@PbMoO₄ and PbMoO₄ photocathodes under 350-W Xe lamp irradiation (b). *J*–*t* curves of the 2-nm C@PbMoO₄ and PbMoO₄ nanocrystal photocathodes as performed at 0 V_{RHE} (c).

The as-prepared series nanocrystals were evaluated to generate H₂ as a photocathode material by measuring the photocurrent density–voltage (*J*–*V*) curve under 350-W Xe lamp irradiation. All of the samples exhibited an almost negligible dark current in the potential between 0.4 and -0.2 V versus reversible hydrogen electrode (RHE). Fig. 5b shows that the *J*–*V* curves of all the prepared photocathodes as scanned at a power density of 60 mWcm⁻². The photocurrent density of carbon-shell-free PbMoO₄ nanocrystals had an onset potential of ca.

0.2 V_{RHE} and reached 0.44 mAcm^{-2} at 0 V_{RHE} and 0.82 mAcm^{-2} at -0.2 V_{RHE} . On the other hand, the photocurrent densities of the other samples of carbon-shell-coated PbMoO_4 varied as clearly shown in Fig. 5b. The J - V curves of 2-nm C@PbMoO_4 , 5-nm C@PbMoO_4 and 8-nm C@PbMoO_4 show the photocurrent densities reached 0.75 mAcm^{-2} , 0.62 mAcm^{-2} , and 0.30 mAcm^{-2} at 0 V_{RHE} , respectively. Meanwhile, the photocurrent densities of 2-nm C@PbMoO_4 , 5-nm C@PbMoO_4 and 8-nm C@PbMoO_4 at -0.2 V_{RHE} reached 2.7 mAcm^{-2} , 1.9 mAcm^{-2} , and 0.50 mAcm^{-2} , respectively. All the obtained photocurrent density data at different bias (0 V_{RHE} and -0.2 V_{RHE}) were collected and shown in Table 1. The results demonstrated that the PEC activity increased when the PbMoO_4 nanocrystals were coated with 2-nm and 5-nm C shells but decreased when the C shell was greater than 8 nm in thickness. We speculated that this increase with 2-nm or 5-nm C shells could be a consequence of altered surface or interface defect concentration caused by the carbon coating. As proof of concept, the thickness of the 2-nm carbon-shell-coated PbMoO_4 described here generated the greatest PEC activity for water splitting.

Table 1. PEC water splitting performances of the obtained bare PbMoO_4 and C@PbMoO_4 -based nanocrystals

Materials	C thickness (nm)	Electrolyte	PCE (%) (at 0.05 V_{RHE})	J (mA/cm^2)	
				at 0 V_{RHE}	at -0.2 V_{RHE}
PbMoO_4	0	H_2SO_4 (0.5 M)	0.33	0.44	0.82
C@PbMoO_4	2		0.40	0.75	2.70
C@PbMoO_4	5		0.35	0.62	1.90
C@PbMoO_4	8		0.19	0.30	0.50

The PEC details of the sample with the highest activity, 2-nm C@PbMoO₄ nanocrystals, were further investigated here. As mentioned above, the chemical stability against the cathodic reduction reaction is important for photocathode materials. Fig. 5c displays the photocurrent density to time (J-t) curves of the 2-nm C@PbMoO₄ nanocrystals at a constant potential of 0 V_{RHE} under illumination for 80 min compared to the bare PbMoO₄ nanocrystals. The photocurrent density of PbMoO₄ decreased rapidly by $\sim 66.7\%$ over 80 min under the same conditions, indicating the instability of the bare PbMoO₄ as photocathode due to the preferential reduction of the lattice metal cations.^[8, 41-42] In contrast, the prepared 2-nm C@PbMoO₄ electrode showed high PEC stability when H₂ was present as the electron acceptor (Fig. 5c). We speculated the excellent stability of the 2-nm C@PbMoO₄ sample was attributed to the protection by the outer carbon shells, which coated the *p*-semiconductor PbMoO₄ nanocrystals and blocked the contact between the nanocrystals and the electrolyte.

Fig. 6. (a) On-off switching of the 2-nm C@PbMoO₄ photocathode with an interval of 20 sec and a bias of -0.1 V_{RHE}. (b) Photoconversion efficiency (PCE) as a function on the applied potential, E_{app} , for 2-nm C@PbMoO₄ under the irradiation of 60 mWcm⁻². (c) J - V curves of the 2-nm C@PbMoO₄ sample depended on different illumination power. (d) Photocurrent density as measured versus different incident optical densities. The corresponding functions are $I = 78.85 P^{0.81}$.

Fig. 6a shows the J - t cycle of 2-nm C@PbMoO₄ tested with light irradiation (60 mWcm⁻²) on and off; the current density of the devices displayed two distinct states: (1) a “low”-current state under dark conditions and (2) a “high”-current state under light conditions. The switching in these two states was reversible and fast, as a high-quality photosensitive switch. As shown in

Fig. 6a, the obtained 2-nm C@PbMoO₄ nanocrystals can easily shift from on (“high”-current state) to off (“low”-current state). Meanwhile, Fig. 6a also shows that the time responses of the 2-nm C@PbMoO₄ nanocrystal-based devices were highly stable and reproducible. No degradation was found in two minutes of on-off switching cycles, confirming the preferable stability and rapid response of our device.

The photoconversion efficiency (PCE) of water splitting for the prepared 2-nm C@PbMoO₄ photocathode in the presence of external applied potential is calculated with the following equation:^[7]

$$\text{PCE} = \frac{J_p(E_{\text{app}} - E_{\text{rev}}^0)}{I_0}$$

where J_p is the observed photocurrent density; E_{rev}^0 is the standard reversible potential, which is 0 V vs RHE for water splitting; E_{app} is the applied potential (vs RHE); and I_0 is the power density of the incident light. The total photoconversion efficiency is calculated by setting E_{app} to zero in the above equation. The PCE performance of the 2-nm C@ PbMoO₄ is listed in Fig. 6b, which demonstrates that the ideal PCE performance of the 2-nm C@ PbMoO₄ is 0.42%. The important features of the Fig. 6b are that the maximum PCE increases very dramatically with an applied potential below 0.075 V and reduces enormously from 0.075 V to 0.4 V; also in addition, the PCE increase and decrease are highly nonlinear with the applied potential. This nonlinear behavior of the PCE characteristics is consistent with that previously reported.^[43] In addition, the PCE performances of all the four samples at 0.05 V_{RHE} were listed in Table 1, which shows the highest PCE for the 2-nm C@ PbMoO₄ nanocrystals.

Fig. 6c shows the power-dependent photocurrent responses for the 2-nm C@PbMoO₄ as used in PEC water splitting. By increasing the Xe lamp light power from 0 to 60 mWcm⁻², the

photocurrent densities gradually increased, and the photocurrent density of the 2 nm-C@PbMoO₄ nanocrystals increased with the amplification of light power because more photons were absorbed (Fig. 6c). In general, the photocurrent can be expressed as a power function of the light intensity: $I \sim P^{C_2}$, where C_2 corresponds to the photocapture coefficient and determines the response of the photocurrent to the light intensity.^[44-46] The relationship between the photocurrent and incident optical power densities (Fig. 6d) demonstrates a power dependence of ~ 0.81 ($I \approx P^{0.81}$), which is close to 1, indicating an excellent efficiency of photocapture in the obtained 2-nm C@PbMoO₄ nanocrystals. These findings showed the potential of 2-nm C@PbMoO₄ nanocrystals for use in solar water splitting and photoswitching, as well as in photoelectronic devices.

The intrinsic reason for the amorphous carbon shell enhancing the PEC activity of the PbMoO₄ nanocrystals was further investigated. The theoretical maximum water-splitting photocurrent density ($J_{\max}$) for photoelectrode materials was higher than the practical photocurrent density (J_{H_2O}) in PEC water splitting due to the limited light absorption, charge separation, and surface charge transfer efficiencies (η_{abs} , η_{sep} and η_{trans} , respectively) of the semiconductor photoelectrodes. Therefore, the photocurrent density arising from the practical PEC water reduction for the PbMoO₄ photocathodes can be expressed according to previous reports as follow:^[17, 47]

$$\begin{aligned} J_{H_2O} &= J_{\max} \times \eta_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{trans}} \\ &= J_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{trans}}, \end{aligned}$$

where J_{abs} is the photocurrent density resulting from an absorbed photon conversion efficiency of 100%. Therefore, the effect of the carbon shell outside of the PbMoO_4 on PEC water reduction can be determined from J_{abs} , η_{sep} and η_{trans} .

Fig. 7. (a) Room-temperature UV-Vis absorption spectra and (b) bandgap curves of the bare PbMoO_4 and the 2-nm C@PbMoO_4 . (c) J - V curves under chopped 350-W Xe lamp irradiation with AgNO_3 in electrolyte as the hole scavenger, demonstrating the photocurrent was generated when the surface charge transfer efficiency was nearly 100%.

To compare the J_{abs} between bare PbMoO_4 and 2-nm C@PbMoO_4 nanocrystals, the UV-visible absorption spectra of the two samples are characterized in Fig. 7a. The black line represents the absorption spectrum of the bare PbMoO_4 . An absorption peak at 332 nm is obviously observed from the Fig. 7a, and the absorption spectrum of 2-nm C@PbMoO_4 was

analogous to the obtained PbMoO₄ nanocrystals. From Fig. 7b, we can see the photo energy of the bare and 2-nm C@PbMoO₄ nanocrystals is 3.07 eV and 3.05 eV, respectively, which were both in agreement with a previous study in little errors.^[48] These results demonstrated that light absorption changed very slightly when the PbMoO₄ nanocrystals were coated with the 2-nm carbon shell due to its ultrathin thickness. Moreover, Zheng's group reported an example of the WO₃/W:BiVO₄ nanowires relationship between light absorption and practical photocurrent, indicating that light absorption is not the main reason for the difference in performance of these core-shell photoelectrodes.^[17] Thus, the J_{abs} for the bare PbMoO₄ sample and the 2-nm C@PbMoO₄ sample can be considered as the same with approximate values.

For n-type semiconductor electrode materials, a fast hole scavenger, H₂O₂, is often added to the electrolyte to explore the charge separation and surface transfer efficiencies towards PEC water splitting.^[49-50] Because the rate of charge (hole) transfer to the electrolyte by the oxidation of H₂O₂ at the n-semiconductor/electrolyte interface is very fast, it can be assumed that the surface recombination of charges is eliminated and that $\eta_{\text{trans}}(\text{H}_2\text{O}_2) \approx 100\%$.^[17, 47, 51] Inspired by this, to illustrate the effect of the carbon shell on the η_{sep} and η_{trans} of our p-type semiconductor PbMoO₄, the fast electron scavenger AgNO₃ was added to the electrolyte. The rate of photo-produced electron transfer to the electrolyte by the reduction of AgNO₃ at the p-semiconductor/electrolyte interface is very fast due to its high oxidation. It can be assumed that the surface recombination of charges is eliminated and that the η_{trans} of the photocathode in AgNO₃ aqueous solution is overall (100%). While the H₂O reduction photocurrent is given by $J_{\text{H}_2\text{O}} = J_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{trans}}$, the AgNO₃ reduction photocurrent is given by $J_{\text{AgNO}_3} \approx J_{\text{abs}} \times \eta_{\text{sep}}$. Because the addition of AgNO₃ did not change the light absorption, pH or flat band potentials

of the photocathodes, the saturated photocurrents for H₂O and AgNO₃ reduction were the same for each electrode, indicating that J_{abs} and η_{sep} were the same for J_{AgNO3} and J_{H2O}. The surface charge transfer efficiencies of the photocathode for water reduction can be individually calculated as η_{trans} ≈ J_{H2O}/J_{AgNO3}.

As shown in Fig. 7b, when AgNO₃ was added to the electrolyte, the bare PbMoO₄ and the 2-nm C@PbMoO₄ nanocrystals generated a photocurrent density of approximately 0.53 mAcm⁻² and 0.83 mAcm⁻² at 0 V_{RHE}, respectively. However, Fig. 5b shows that the bare PbMoO₄ and the 2-nm C@PbMoO₄ generated a photocurrent density of approximately 0.44 mAcm⁻² and 0.75 mAcm⁻² at 0 V_{RHE}, respectively. Thus, the surface charge transfer efficiencies of the bare PbMoO₄ and the 2-nm C@PbMoO₄ in PEC water reduction can be determined as follows:

$$\begin{aligned}\eta_{trans}^{PbMoO_4} &\approx J_{H_2O}^{PbMoO_4} / J_{AgNO_3}^{PbMoO_4} \\ &= 0.44 \text{ (mAcm}^{-2}\text{)} / 0.53 \text{ (mAcm}^{-2}\text{)} \times 100\% = 83.0\% \\ \eta_{trans}^{2-nmC@PbMoO_4} &\approx J_{H_2O}^{2-nmC@PbMoO_4} / J_{AgNO_3}^{2-nmC@PbMoO_4} \\ &= 0.75 \text{ (mAcm}^{-2}\text{)} / 0.83 \text{ (mAcm}^{-2}\text{)} \times 100\% = 90.4\%\end{aligned}$$

In other words, the transfer efficiency of 2-nm C@PbMoO₄ increased by 7.4% (from 83.0% to 90.4%) compared to that of PbMoO₄ at 0 V_{RHE}, indicating that the amorphous carbon layer that coated on the PbMoO₄ nanocrystals could accelerate the transfer of electric charge.

Moreover, the charge separation efficiencies of the PbMoO₄ and 2-nm C@PbMoO₄ nanocrystals for PEC water reduction can be roughly calculated as η_{sep} ≈ J_{AgNO3}/J_{abs}. As mentioned above, the J_{abs} for the bare PbMoO₄ and the 2-nm C@PbMoO₄ are approximately same; consequently, the ratio of the charge separation efficiency for the 2 nm-C@PbMoO₄

and PbMoO₄ was 0.83 mAcm⁻² to 0.53 mAcm⁻². Therefore, the charge separation efficiency of 2-nm C@PbMoO₄ enhanced 56% ($\frac{\eta_{sep}^{2\text{ nmC@PbMoO}_4}}{\eta_{sep}^{PbMoO_4}} = 1.56$) compared to that of the bare PbMoO₄ in PEC water reduction at 0 V_{RHE}. As the result, the 2-nm C-shell on the nanocrystals played more charge separation function than light absorption and surface transfer functions in improving the PEC performance of water splitting.

4. CONCLUSION

In summary, we demonstrated the controlled synthesis of the C@PbMoO₄ nanocrystals via a simple solvothermal synthesis method. Carbon shell thicknesses of 2 nm, 5 nm and 8 nm of as-synthesized C@PbMoO₄ nanocrystals were adjusted by varying the amount of CA in the precursor solutions. The PEC water-splitting measurements demonstrated, under an optimized preparation procedure, that 2-nm C@PbMoO₄ produced a nearly 2-fold-increasing photocurrent density compared to that of bare PbMoO₄ nanocrystals at 0 V_{RHE}. The PEC experiments with AgNO₃ as a surrogate substrate revealed that the 2-nm carbon layer almost completely eliminated losses due to surface electron-hole recombination ($\eta_{trans} = 90.4\%$) and enhanced 56% of the charge separation efficiency compared to uncoated carbon-layer PbMoO₄ nanocrystals. Meanwhile, the PEC stability of 2 nm-C@PbMoO₄ also greatly increased compared to bare PbMoO₄ nanocrystals. The enhanced stability of H⁺ reduction with C@PbMoO₄ is ascribed to electron transfer to the coated carbon layer, which blocked the contact between the p-semiconductor PbMoO₄ nanocrystals and the electrolyte. Our experiments improve our understanding of the synergistic effect on PEC stability and activity and provide a blueprint for the design of materials for solar hydrogen application.

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