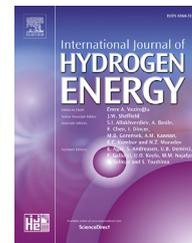




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Enhancement of photoelectrochemical activity of Fe₂O₃ nanowires decorated with carbon quantum dots

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ABSTRACT

Owing to its up-conversion photoluminescence, photo-induced electron transfer property, and excellent conductivity, carbon quantum dots (CQDs) have been established as effective sensitizers in combination with Fe₂O₃ nanowires for enhancing the catalytic activity of photoelectrochemical water oxidation. In comparison to pristine Fe₂O₃ nanowires, Fe₂O₃ nanowires decorated with CQDs demonstrate 27 orders of magnitude increase in photocurrent density at 0.23 V vs. Ag/AgCl. The mechanism of enhanced photoelectrochemical activity of CQDs/Fe₂O₃ composite was also investigated. Thereby, it is confirmed that the enhanced optical absorption, accelerated interfacial charge carrier transfer and effective separation of photogenerated electron-hole pairs induced by CQDs decoration account for the enhancement of CQDs/Fe₂O₃ nanowire arrays in photoelectrochemical application.

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Introduction

Due to their remarkable physical and chemical properties, low-dimensional carbon nanomaterials have inspired considerable interest for decades and made great contributions to materials science. In particular, carbon quantum dots (CQDs), which were accidentally discovered during the synthesis, separation and purification of single-walled carbon nanotubes [1], have become a rising star in the low-dimensional nanocarbon family in terms of their fascinating physical and chemical properties, which include high solubility in water, excellent biocompatibility, chemical inertness,

non-toxicity, photo-induced electron transfer and redox properties, up- and down-converted photoluminescence, electron reservoir and so on [2–10]. Of particular importance are the quantum confinement and edge effect of CQDs as a result of small size that endow CQDs with an HOMO-LUMO gap, which suggests the light harvesting ability of CQDs as well as the possibility of electron injection from CQDs to semiconductors in contact with CQDs. In this regard, CQDs with matched HOMO-LUMO gap are expected to be combined with semiconductive nanostructures as photoanodes for remarkable photoelectrochemical oxidation. Notably, CQDs are composed of large π -conjugated structure, and accordingly are highly electrically conductive, which facilitates

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charge carrier separation to enhance the photocatalytic efficiency. Moreover, the appealing up- and down-converted photoluminescence of CQDs makes them a promising candidate, being capable of promoting the utilization of solar light. So far, many CQDs-based complex systems, such as TiO_2/CQDs [11–14], ZnO/CQDs [15–17], WO_3/CQDs [18], SnO_2/CQDs [19], $\text{MoSe}_2/\text{CQDs}$ [20] and $\text{NiFe-LDH}/\text{CQDs}$ [21], have been fabricated as photoanodes and have shown remarkable photoelectrochemical properties.

On the other hand, hematite ($\alpha\text{-Fe}_2\text{O}_3$), which possesses such advantages as proper bandgap, excellent chemical stability, nontoxicity and abundance in earth, is a promising photoanode material that is widely used in photoelectrochemical cells [22–27]. Notably, compared to their bulk counterparts, $\alpha\text{-Fe}_2\text{O}_3$ nanowire arrays have been demonstrated to be more efficient in photoelectrochemical water splitting in that they can promote the charge transfer and optical absorption, as well as provide a huge contact area with electrolytes [28–31]. Nevertheless, either the bulk or nanostructured photoanodes of pure $\alpha\text{-Fe}_2\text{O}_3$ still suffers the main limitation of severe carrier recombination, which results from the combination of short hole diffusion length and poor electrical conductivity [32–35], thus preventing $\alpha\text{-Fe}_2\text{O}_3$ from achieving a higher solar energy conversion efficiency.

Allowing for the preeminent properties of CQDs and the shortcomings of Fe_2O_3 , surface engineering of Fe_2O_3 electrode with CQDs is expected to optimize photoelectrochemical activity. In this paper, we report an application of CQDs in surface engineering of Fe_2O_3 nanowire arrays for efficient photoelectrochemical water splitting. Compared to pristine Fe_2O_3 , a dramatic enhancement in the photoresponse is observed over the CQDs/ Fe_2O_3 composite. Meanwhile, the key roles of CQDs in the composite are discussed in detail.

Experimental details

Materials

$\text{FeCl}_3 \cdot \text{H}_2\text{O}$ was purchased from Aladdin Chemical Reagent Co. Ltd. NaNO_3 was bought from Tianjin Kemiou Chemical Reagent Co. Ltd. Glucose was obtained from Shanghai Bio Science & Technology Co. Ltd. NaOH was acquired from Chengdu Union Chemical Industry Reagent Institute. Deionized (DI) water employed in this work was produced using a GWA-UN pure water system (Beijing, China). Fluorine-doped tin oxide (FTO)-coated glass was bought from Nippon Sheet Glass Company (Japan).

Preparation of the samples

Fe_2O_3 nanowires were synthesized by a hydrothermal procedure [36]. First, an aqueous solution containing 0.15 M $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ and 1 M NaNO_3 was prepared. Then, 10 ml of the precursor solution were transferred into a 20 mL Teflon-lined autoclave, where four pieces of FTO glass were put at the bottom with the conductive side facing the wall of the Teflon, and then hydrothermally heated at 95 °C for 4 h. Subsequently, the yellow $\beta\text{-FeOOH}$ nanowires were fabricated on the FTO glass. The obtained $\beta\text{-FeOOH}$ film was rinsed with DI

water, dried naturally, and subsequently sintered at 550 °C for 2 h in air to obtain the Fe_2O_3 nanowires.

CQDs were prepared by an alkali-assisted ultrasonic process [18]. In detail, 9.0 g of glucose were dissolved in 50 ml DI water, while 50 ml NaOH aqueous solution (1 M) was added slowly. Subsequently, the mixing solution was subjected to ultrasonic treatment for 4 h at room temperature, followed by adjusting to $\text{pH} = 7$ with HCl . Finally, the dark brown product was dialyzed using a semipermeable membrane (MWCO1000) to obtain CQDs aqueous solution.

The CQDs were anchored to the Fe_2O_3 nanowires surfaces by soaking Fe_2O_3 nanowires in CQDs solution at room temperature for 1 h, followed by rinsing with DI water, dried naturally, and subsequently sintered at 200 °C for 30 min under N_2 to improve the structural stability. The amount of the CQDs on Fe_2O_3 nanowires surfaces was controlled by varying the concentration of CQDs solution. For the films reported herein, four different concentrations of CQDs solution were used, i.e., 2, 4, 6, and 8 ml raw CQDs solution diluted with 15 ml DI water, respectively. Subsequently, the obtained films were named as 2CQDs/ Fe_2O_3 , 4CQDs/ Fe_2O_3 , 6CQDs/ Fe_2O_3 and 8CQDs/ Fe_2O_3 , respectively. For the control experiments, bare Fe_2O_3 was also sintered at 200 °C for 30 min under N_2 .

Materials characterization

X-ray diffraction (XRD) of the as-prepared films was performed using an X'Pert MPD Pro X-ray diffractometer. Scanning electron microscopy (SEM, Merlin, Zeiss) was used to observe the morphologies of the Fe_2O_3 and CQDs/ Fe_2O_3 nanostructures. Fourier-transform infrared (FT-IR) spectra were obtained by an IR Affinity-1 FTIR spectrometer. UV–vis spectroscopy was recorded on a Hitachi U3010 spectrophotometer using BaSO_4 as a reference and the fluorescence emission (PL) spectra were acquired with an F-4500 fluorescence spectrophotometer.

Photoelectrochemical and impedance measurements

Photoelectrochemical measurements were carried out on a CHI 660C working station with a three-electrode cell, using platinum plate as the counter electrode, Ag/AgCl electrode as the reference, and 1.0 M NaOH aqueous solution as the electrolyte. A 500 W Xe lamp equipped with an ultraviolet cutoff filter ($\lambda > 420$ nm) was chosen as the light source. Linear sweep voltammograms were recorded at 20 mV/s and the chronoamperometry curves of the films were obtained at an applied potential of 0.23 V vs. Ag/AgCl . The electrochemical impedance spectroscopy (EIS) was conducted in an aqueous electrolyte containing $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, and KCl , applying a 10 mV amplitude perturbation at frequencies between 0.01 Hz and 10^5 Hz. The Mott-Schottky plots were obtained at an AC frequency of 1 kHz.

Results and discussion

In our work, CQDs were synthesized via an alkali-assisted ultrasonic treatment. Fig. 1A presents the representative transmission electron microscopy (TEM) image of CQDs. As

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