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Surface states engineering carbon dots as multi-band light active sensitizers for ZnO nanowire array photoanode to boost solar water splitting

Xiaoyong Xu [a, ***, 1], Zhijia Bao [a, 1], Wenshuai Tang [a], Haiyan Wu [a], Jing Pan [a], Jingguo Hu [a, *], Haibo Zeng [b, **]

[a] College of Physics Science and Technology, Yangzhou University, Yangzhou 225002, China
[b] Institute of Optoelectronics & Nanomaterials, Nanjing University of Science and Technology, Nanjing 210094, China

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ABSTRACT

Efficient capture of solar photons is crucial in photo-electrochemical (PEC) water splitting devices for converting solar energy to hydrogen as an energy-dense carrier. Herein, we first reported the unique multi-band light absorption character on carbon dots (CDs) with controllable surface states and built an efficient photoanode by bonding such CDs as favorable solar photosensitizers on one-dimensional (1D) ZnO nanorod arrays (NRAs) for the PEC solar-to-hydrogen (STH) conversion. The multi-transition models related to surface C═O, and C−OH states with different energy levels were identified to dominate the CDs' multi-model optical absorption covering the full-range visible region in the solar spectrum, which renders an excellent advantage of CDs in serving as the solar photosensitizer for photoelectric systems. Moreover, the fabricated ZnO@CDs heterostructure photoanode with the functionalized CDs used to harvest solar photons along with subsequent charge separation at heterointerface and transport along 1D directional channels was demonstrated to boost the photocurrent output and the photoconversion efficiency for solar water splitting.

1. Introduction

Artificial photosynthesis, which can drive the conversion of solar energy to chemical fuels, is considered as one of the most promising strategies for solar energy conversion and storage [1–4]. Solar-to-hydrogen (STH) conversion through photo-electrochemical (PEC) water splitting on semiconductor photoelectrodes has attracted widespread attention since Honda and Fujishima first explored the PEC water splitting on the TiO_2 photoanode [5–12]. In addition to TiO_2, ZnO materials with various nanostructures have emerged as promising photoanodes due to their low cost, easy preparation, nontoxicity and high electron mobility [13–16]. Especially, one dimensional (1D) ZnO nanorod arrays (NRAs) have been developed as an optimal architecture for PEC photoanodes based on their large surface area, long light-scattering pathway, 1D directional carrier transport, and low charge recombination loss [17,18]. However, ZnO with wide band gap of about 3.2 eV suffers from the limited response to ultraviolet (UV) light which composes less than 5% of the solar spectrum [19], imposing a fundamental restriction of the poor solar harvesting on the resultant STH efficiency. Therefore, extending the response spectrum of ZnO-based photoanodes to cover more of the visible and near-infrared (NIR) regions has been of great significance.

Many efforts have been taken to overcome the lack in sunlight response of ZnO photoelectrodes through several strategies, such as doping with hetero-ions [20], coupling with noble metal plasmon [21], and sensitizing with dye or narrow-band-gap quantum dots (QDs) [22–25]. Recently, earth-abundant and low-cost carbon dots (CDs) have emerged as a promising photosensitizer in combination with semiconductor catalysts for solar hydrogen evolution because of their light-harvesting and electron transfer properties [26–30]. Noting that the inherent light absorption from the π-π* transition of little sp^2 clusters in CDs was usually observed at UV or near

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: xxy@yzu.edu.cn (X. Xu), jghu@yzu.edu.cn (J. Hu), zeng.haibo@njust.edu.cn (H. Zeng).
[1] These authors contributed equally to this work.

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visible regions [31,32], thus from this point, CDs are not enough suitable as visible-light active sensitizers. Interestingly, Kang and Liu et al. demonstrated the optical up-conversion properties of CDs and opened a seminal avenue for the design of visible- or even NIR-light responsive TiO_2-based photoanodes by combining CDs as an up-converted-spectrum converter [33,34]. In view of the usually poor efficiency in up-conversion processes, it is strongly expected to cultivate more effective transition models in CDs for favoring solar photon harvesting in CDs-based solar conversion systems.

In studies on photoluminescence (PL) characters of CDs, the involvement of surface states in the photo-induced charge transition models has been widely accepted despite of the controversy on PL mechanism [35–37]. The surface states with a series of specific energy levels located below lowest unoccupied molecular orbital (LUMO) have been thought to associated with the excitation-dependent PL behavior, implying the existence of photo-induced charge multi-transition models involved with surface states [38]. Such the multi-transition models behind the PL process are unfavorable for the emission quality and yield whereas can make the CDs' photoelectric response unlimited to the certain single- or two-photon absorption localized by the π-π^* transition of sp^2 carbons. On the basis of this knowledge, we speculate that the multi-transition models involved with surface states can be engineered to effectively broaden the working spectrum of CDs as photosensitizers in combination with wide band-gap ZnO PEC electrodes for solar water splitting.

Herein, we first described the photo-induced charge multi-transition models in CDs with the controllable surface states and its consequence of multi-model optical absorption. Then we built the unique CDs-sensitized ZnO NRAs (ZnO@CDs) photoanode for solar water splitting, which exhibited the significantly enhanced PEC activity relative to bare ZnO NRAs one. The laden CDs were demonstrated to function as an excellent solar photosensitizer to facilitate photon harvesting with subsequent charge production and separation, being responsible for the enhanced solar PEC activity.

2. Experimental section

2.1. Synthesis of CDs

Well-crystallized CDs with surface oxygenous groups were synthesized by the polymerization reaction between citric acid and urea under solvothermal condition similar to a previously reported method [37]. Typically, 1 g of citric acid and 2 g of urea were dissolved in 10 mL dimethylformamide (DMF) solvent. The mixture was transferred to a Teflon autoclave and heated at 160 °C for 6 h. After the reactor cooled naturally to room temperature, the solution was centrifuged at 16,000 rpm for 10 min to remove larger particles. The precipitate was collected, washed thrice with ethanol by centrifugation at 16,000 rpm for 10 min to remove residual salts and alkali. Finally, the dissolution in deionized water produced a concentrated purple solution of CDs with the long-time stability in air at room temperature. For exploring the surface origins of optical properties, the surface-reduced and surface-passivated CDs were also prepared via a reduction treatment of introducing sodium borohydride ($NaBH_4$, 0.05 g) as reducing agent into the 20 mL of 1 mg mL^{-1} CDs solution with magnetic stirring overnight at room temperature and a hydrothermal reaction from the citric acid (1 g) and urea (0.5 g) at 160 °C for 6 h. We found that the different solvents could induce difference in their reactions to form CDs from the polymerization reaction between citric acid and urea. The DMF solvent tends to form the nitrogen-rich CDs with abundant carboxyl and hydroxyl groups on surface; the aqueous solvent tends to form the nitrogen-rich CDs conjugated with amino-groups on surface.

2.2. Fabrication of ZnO@CDs NRAs electrodes

The CDs-sensitized ZnO NRAs photoelectrode was fabricated according to the preparation process shown in Scheme S1. Fluorine-doped tin oxide (FTO) coated glasses (1 cm × 2 cm) were washed successively with acetone, ethanol and deionized water by ultrasonication, and then dried with N_2 stream at room temperature. The clear FTO substrate was firstly immersed twice into the 0.005 M ethanol solution of $Zn(CH_3COO)_2$ for about 10 s and dried at 60 °C, then annealed at 350 °C for 30 min to form ZnO dense seed layer on the conducting side. The FTO substrate with seed layer was placed vertically into the Teflon-lined stainless-steel autoclaves filled with 20 mL of equimolar $Zn(NO_3)_2 \cdot 6H_2O$ and $C_6H_{12}N_4$ (0.05 M) aqueous solution and kept at 95 °C for 3 h. After naturally cooled to room temperature, the deposited substrate was taken out of solution, and carefully rinsed with deionized water and ethanol. Well-aligned ZnO NRAs grown on FIO substrate were used as the scaffold to anchor the CDs by spin-coating method. The 20 mL of aqueous solution containing 20 mg of as-synthesized CDs was prepared as the spin-coating sol. Spin coating in five times ensures the CDs uniformly deposited on the entire surface of the ZnO nanorods. Finally, the ZnO@CDs composite NRAs were annealed at 150 °C in N_2 stream for 30 min to improve the ZnO crystallization and conjunction with CDs.

2.3. Microstructural and optical characterizations

The morphology and microstructure of the samples were investigated by using field emission scanning electron microscopy (FESEM, Hitachi, S-4800II), transmission electron microscopy (TEM, Tecnai F30, FE), and high-resolution TEM (HRTEM) equipped with X-ray energy dispersive spectrum (EDS). Fourier transform infrared (FT-IR) spectra were measured with a Varian Cary 670 spectrometer. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi spectrometer with a monochromatic Al Kα X-ray source operating at 150 W, and the binding energy was calibrated according to the C 1s peak at 284.6 eV. UV–Vis absorption spectra were drawn by UV–Vis spectrophotometer (Varian Cary 5000) in the range from 200 to 800 nm. The PL spectra were recorded at room temperature with a luminescence spectrophotometer (Hitachi FL4600) using Xe lamp emission with regulatory wavelength as excitation source.

2.4. PEC performance measurements and calculations

Photo-electrochemical measurements were carried out using an electrochemical workstation (CHI660E) with standard three electrode configuration, including Pt wire as counter electrode, Ag/AgCl (saturated KCl) as reference electrode, and ZnO NRAs decorated with and without CDs as two contrastive working electrodes. Aqueous solution of Na_2SO_4 (0.1 M) with pH adjusted to 7.0 was prepared as the electrolyte for all PEC experiments. The working electrodes were irradiated from the front side under the simulated sunlight from a Xe lamp equipped with an AM 1.5G filter, and the light power intensity was uniformly calibrated to 100 mW cm^{-2} at working electrode position. The linear sweep voltammetry (LSV; $J-V$) curves with a scan rate of 5 mV s^{-1} at the bias potential range from −0.5 to +1.5 V vs. Ag/AgCl and the amperometric $J-t$ curves with the chopped illumination at the bias potential of 0 V vs. Ag/AgCl were measured for two working photoanodes to compare their photocurrent outputs. The amount of evolved hydrogen was