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In situ decoration of CuSCN nanorod arrays with carbon quantum dots for highly efficient photoelectrochemical performance

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ABSTRACT

In this work, the in situ decoration of CuSCN nanorod thin films with carbon quantum dots (CQDs) was achieved through a one-pot electrochemical deposition process. The hybridization of CQDs would not change the nanorod structure and p-type characteristic of CuSCN thin film. Compared with the pristine CuSCN thin film, the CQDs/CuSCN composite thin film exhibited significantly improved photoelectrochemical (PEC) activities. The photocurrent intensity of the composite thin film electrode was approximately 6.5 times that of the CuSCN thin film electrode. The improved PEC activities could be ascribed to the highly efficient generation, separation and migration of excited charge carriers derived from the decoration of CQDs on the surface of CuSCN nanorods, as verified by the electrochemical impedance spectra (EIS), photoluminescence, charge extraction, intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) measurements. The superior PEC properties of the CQDs/CuSCN composite thin film make it a promising hole transporting material or photocathode material for practical PEC applications including solar cells and PEC water splitting.

1. Introduction

In recent years, p-type semiconductor thin films have attracted much attention because of their promising applications in a wide range of fields, such as light emitting diode (LED) [1], photoelectrochemical (PEC) water splitting [2], dye-sensitized solar cells (DSSCs) [3,4], extremely thin absorber (ETA) solar cells [5], and perovskite solar cells (PSCs) [4,6]. Among these p-type thin films, CuSCN thin films are particularly of interest. CuSCN possesses a wide band gap of 3.6 eV [7], high transparency, suitable band gap level position [8], decent hole conductivity ($\geq 5 \times 10^{-4}$ S cm^{-1}) [1], and chemical stability [9] as well as low cost. Thus, p-type CuSCN thin films have many attractive features as a photocathode material for PEC applications, and have recently found wide application as a solid hole-transporting electrolyte in replace of liquid electrolyte in DSSCs [10], ETA solar cells [11] and PSCs [12]. In this regard, many of the current issues occurring in the liquid electrolyte-based solar cells, such as easy leakage, difficult sealing and poor stability, can be solved, though the performances of *p*-CuSCN-based solid state solar cells are not comparable with those of liquid electrolyte solar cells and still needs improvement. Therefore, it is still a great challenge to modify p-type CuSCN thin films for improving their PEC performances.

To date, much effort has been made to regulate the PEC properties of p-type CuSCN thin films, with focuses on the following two strategies. Firstly, the PEC properties of CuSCN thin films can be regulated by controlling the stoichiometric ratio of SCN$^-$ in CuSCN. Different stoichiometric ratios of SCN$^-$/Cu$^+$ in CuSCN thin films would generally result in entirely different PEC activities, which is considered as a consequence of composition defects or self-doping in CuSCN thin films [7,13,14]. For example, Perera et al. [13] have exposed solid CuSCN to halogen gases such as Cl_2 or to a solution of $(SCN)_2$ in CCl_4 and thereby doped the semiconductor with $(SCN)_2$ to improve the conductivity of CuSCN. By using such a doped CuSCN thin film, the conversion efficiency (η) performance of the solar cell was considerably enhanced from 0.75% without SCN doping to 2.39% after SCN doping. Secondly, another effective way to regulate the PEC properties of CuSCN thin films is to control their morphological structure. CuSCN thin films of different morphological structures can be prepared by using a variety of methods, such as dip-coating or spray coating of CuSCN organic solution

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[13,15], chemical bath deposition [16], successive ionic adsorption and reaction [16,17], and electrochemical deposition [18–21]. In contrast to those particulate thin films, CuSCN thin films with one-dimensional morphological structure (such as nanowires, nanorods) have attracted much attention owing to their high surface areas, relatively good charge transport properties, and special light-trapping effect, which can improve the light absorption and facilitate the generation, transfer and separation of photoinduced carriers thus leading to the enhanced PEC properties of CuSCN thin films. For example, Huang et al. [20] has recently reported the influence of annealing temperature on structural, optical, electrical and PEC characteristics of electrodeposited CuSCN thin films. It was found that the crystallographic orientation would change, and the optical energy band gap of thin films slightly increased with increasing annealing temperatures. Moreover, the CuSCN films annealed at 400 °C exhibited much better PEC performance than the as-deposited CuSCN film. Thus, it can be seen that the above two strategies can to some extent boost the PEC characteristics of CuSCN thin films by adjusting their composition and structure, but the boosting effect is not obvious. In consequence, it is of great concern to develop alternative ways to efficiently improve the PEC properties of CuSCN thin films.

As well-known, a promising strategy to enhance the PEC performance of a photocatalyst is to fabricate semiconductor heterojunctions, which can simultaneously optimize light absorption and promote charge separation at the interface between the two semiconductors [22]. Recently, carbon quantum dots (CQDs), which are predominantly composed of graphitic carbon (sp^2 carbon) with a size below 10 nm [23], have been widely used to couple with semiconductor nanostructures, such as Cu_2O microspheres [24], TiO_2 nanostructures [25,26], $BiVO_4$ nanostructures [27], g-C_3N_4 [28] and Cu_2S nanowire arrays [29], by which the photocatalytic and PEC properties can be remarkably enhanced due to the quantum size effect, broad band optical absorption and high electrical conductivity of CQDs [30]. Enlightened by this, we attempt to markedly improve the PEC performance of CuSCN thin films by the coupling of CQDs. To the best of our knowledge, there is no research on the CQDs-decorated CuSCN thin films in association with their PEC performances.

Herein, CQDs were decorated in situ on the surface of CuSCN nanorod array thin films through a facile one-pot electrochemical deposition process. Various techniques were used to characterize the morphological and structural features of the CQDs/CuSCN composite thin films, and their PEC activities were then evaluated by using different electrochemical or PEC measurements. After the decoration of CQDs, the PEC activities of the CuSCN thin film were greatly improved compared with pristine CuSCN nanorod array thin film. The superior PEC properties of the CQDs/CuSCN composite thin film make it a promising hole transporting material or photocathode material for practical PEC applications, such as DSSCs, PSCs, ETA solar cells and PEC water splitting.

2. Experimental

2.1. Preparation of CQDs/CuSCN thin films

All chemicals were of analytical grade without further purification. The colloidal solution of CQDs was firstly synthesized by a similar hydrothermal synthesis process as reported elsewhere [31]. Typically, 1.54 g of citric acid was dissolved in 80 mL of deionized water under vigorous stirring to form a transparent solution. The solution was then transferred to a Teflon-lined stainless steel autoclave and heated at 220 °C for 24 h. When the reactor was cooled down to room temperature naturally, the resulting colloidal solution containing CQDs was then obtained after centrifugation and dialysis.

The CQDs/CuSCN composite thin films were prepared via a facile one-pot electrochemical deposition process. The electrochemical deposition was carried out on a CHI-660 E electrochemical working station in a conventional three-electrode electrochemical cell using an FTO conductive glass as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The aqueous electrolyte solution containing 0.012 M $CuSO_4 \cdot 5H_2O$, 0.012 M ethylenediamine tetraacetic acid (EDTA) and 0.003 M KSCN was enriched with a dispersion of 5 mg mL^{-1} CQDs. Prior to the electrochemical deposition, the solution was deaerated by thoroughly stirring. The CQDs-decorated CuSCN nanorod layers were grown potentiostatically on the FTO surface at a cathodic potential of −0.4 V with total passed charge of 40 mC/cm^2. The deposited thin films were rinsed with purified water and dried in air at room temperature. For comparison, the CuSCN nanorod array thin film was also prepared by using the same procedure as mentioned above without the addition of CQDs in the electrolyte solution.

2.2. Characterizations

The crystalline structure of the obtained thin films was characterized by X-ray powder diffraction (XRD) using a Bruker D2 X-ray diffractometer equipped with Cu K_α radiation ($\lambda = 0.15406$ nm). The morphological features of the films were analyzed by field emission scanning electron microscopy (SEM, Hitachi SU 8010) attached with energy dispersive X-ray Spectroscope (EDS). The microstructures were also observed by a field-emission transmission electron microscope (TEM, JEOL JEM 2100) at an accelerating voltage of 200 kV. The absorbance measurement was employed to characterize the optical properties of the films by using an UV–Vis-NIR spectrophotometer (Shimadzu UV-3600) and using an identical FTO-coated glass substrate as the reference. The photoluminescence (PL) spectra were recorded on a Hitachi High-Tech F-7000 fluorescence spectrophotometer with a 450 W xenon lamp as an excitation source (excitation wavelength $\lambda = 394$ nm).

2.3. Photoelectrochemical measurements

The PEC tests were conducted on a Zennium potentiostat/galvanostat (CIMPS-2, ZAHNER-elektrik GmbH & Co. KG, Germany) in a three-electrode configuration with a quartz window, where the obtained CQDs/CuSCN or CuSCN thin film as the working photoelectrode, a SCE electrode as the reference electrode, and Pt plate as the counter electrode in 0.5 M Na_2SO_4 aqueous solution. The photoelectrode sample with an identical reactive area of 1.0 cm^2 was placed in the electrochemical cell at a distance of 5.0 cm from the quartz window. All measurements were performed in a screened dark box, and care was taken to eliminate stray light. The cells were illuminated from the substrate side with a high intensity white light emitting diode (LED WLC02, ZAHNER-elektrik GmbH & Co. KG, Germany), and the intensity was calibrated to 100 mW/cm^2. The photocurrent measurements of all the samples were recorded under chopped light irradiation by controlling the LED light source using a LED driver (PP211, ZAHNER-elektrik GmbH & Co. KG, Germany) that synchronically allowed the switching of the cell between light-on and light-off state. For the intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) measurements, modulated illumination was provided by a high intensity white LED controlled by a LED driver (PP211) that allowed the superimposition of sinusoidal modulation (~10%) on a dc illumination level. Electrochemical impedance spectra (EIS) were recorded in the same three-electrode