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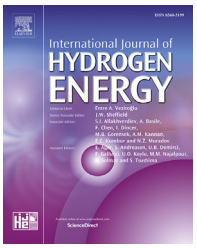

Co-sensitization of TiO_2 electrode with Eosin Y dye and carbon dots for photoelectrochemical water splitting: The enhanced dye adsorption and the charge transfer route

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ABSTRACT

According to a stepwise adsorption approach, TiO_2 NT photoanode was co-sensitized with Eosin Y and carbon dots for photoelectrochemical water splitting. The adsorption amount of Eosin Y in co-sensitized samples increases due to the presence of carbon dots regardless of co-sensitization sequence. The absorbance of Eosin Y/carbon dots/TiO_2 NT in visible light region is stronger than that of carbon dots/Eosin Y/TiO_2 NT, while carbon dots/Eosin Y/TiO_2 NT exhibits higher photocurrent density and hydrogen production rate. Based on the shortest electron transport time, the electron diffusion coefficient in carbon dots/Eosin Y/TiO_2 NT electrode is up to $14.94 \times 10^{-19} cm^2 s^{-1}$. A favorable energy levels alignment dominates in carbon dots/Eosin Y/TiO_2 NT, which can further account for enhancement in charge transfer.

Introduction

Photoelectrochemical water splitting is a promising route for solar energy storage and hydrogen production. TiO_2 has been widely studied as photoanode because of its photochemical stability, nontoxicity and low cost [1–3]. However, the energy conversion efficiency of TiO_2 is low due to the large band gap (3.2 eV) and the rapid electron-hole recombination. To extend the optical absorption to visible-light region and promote the separation of the photogenerated electron-hole pairs, the sensitizers such as the organic dyes [4–7] or the narrow band gap semiconductors [8,9] are often used. Recently, co-sensitization is a new approach to expand largely the optical absorption range through the combination of two or more sensitizers. Ruthenium-based dye C106 and organic D131 sensitizers with the complementary absorption properties and different molecular sizes have been judicially chosen for co-sensitization, which yields a higher light-harvesting efficiency as well as better dye coverage to passivate the surface

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of TiO_2 [10]. Eosin Y (EY) belongs to the xanthene dye, which has been used as dye sensitizer of TiO_2 for the photocatalytic hydrogen evolution [11–13]. To enhance the light harvesting capacity of dye-sensitized TiO_2, the loading amount of dye is needed to be increased. Another issue is the stability of dye in applications of sensitization system. Li et al. [14] found that an average apparent quantum efficiency over EY sensitized CuO/TiO_2 can be up to 5.1% in a water splitting system of diethylamine (DEA) solution under visible light irradiation ($\lambda > 420$ nm). The addition of CuO can strongly improve the adsorption capability of TiO_2 toward EY dye by the formation of multidentate complexation. Liu et al. [15] reported that EY sensitized SiW_{11}/TiO_2 exhibits an average quantum efficiency of 11.4% during irradiation ($\lambda > 420$ nm) of 20 h. SiW_{11} as an excellent electron relay greatly facilitates the electron transfer from the reduced dye species $EY^{\cdot-}$ to conduction band (CB) of TiO_2 and suppresses the decomposition of $EY^{\cdot-}$.

Notably, carbon dots can increase the light absorbance and improve the solar-hydrogen conversion efficiency as a novel environmentally friendly sensitizer [16,17]. Many research groups have widely focused on designing some new nanocomposites such as carbon dots/ZnO [18], carbon dots/Fe_2O_3 [19], carbon dots/Ag_3PO_4 [20], carbon dots/TiO_2 [21] to enhance the photocatalytic activity. As for carbon dots/Ag_3PO_4 [20], carbon dots can not only protect Ag_3PO_4 from dissolution in aqueous solution but also act as both electron acceptors and donors to improve the charge transfer properties. Inspired by light absorption and resonance energy transfer processes of chlorophyll, Ma et al. [22] introduced carbon dots into the conventional dye-sensitized semiconductor systems, which show significantly higher photoelectric conversion efficiency, as much as 7 times that without carbon dots. Carbon dots could act as a one-way electron transfer intermediary for effective bridging of Rh B molecules and TiO_2 substrate, thereby developing highly efficient photoelectric devices. The findings also give us the idea of combining carbon dots with dye to construct electrode for solar-hydrogen conversion.

As stated above, both carbon dots and Eosin Y can improve the performance of TiO_2 electrode for water splitting. However, to the best of our knowledge, there is little research on co-sensitization of TiO_2 electrode with carbon dots and Eosin Y dye. During co-sensitization process, first and foremost, it needs the matched energy levels of the sensitizers. In Souza's group work [23], when N719 dye is anchored between TiO_2 and CdSe quantum dots, CdSe/N719/TiO_2 electrode exhibits the cell efficiency of 2.64%. While CdSe quantum dots are sandwiched between TiO_2 and N719 dye, the cell efficiency of N719/CdSe/TiO_2 electrode is only 1.16%. It is attributed to charge transfer effectively in a stepwise structure formed by the re-organization of energy levels. Therefore, when choosing carbon dots and Eosin Y as the co-sensitizers, it should clarify the effects of the charge transfer route in co-sensitization systems on the photoelectrochemical water splitting performances.

In our previous work [24], we have obtained the better preparation condition of carbon dots via electrochemical ablation of graphite rods and investigated the photoelectrochemical hydrogen activities of the carbon dots/TiO_2 nanotube arrays (TiO_2 NT) electrodes. Herein, we focus on fabricating the TiO_2 NT electrodes co-sensitized with carbon dots and Eosin Y to further improve the photoelectrochemical performances. More efforts are to analyze the interfacial properties and the electron transport kinetic parameters of the co-sensitized TiO_2 NT electrode. During the preparation, the sensitization sequence of carbon dots and Eosin Y is investigated. Accordingly, the possible charge transfer routes in as-prepared samples are discussed.

Experimental

Materials

Titanium foils (0.25 mm thickness, 99.5% purity) were supplied by Alfa-Aesar Chemical Technology Co. Ltd. Phosphate acid (H_3PO_4, ≥85% in water), triethanolamine(TEOA, ≥99% in water), sodium fluoride (NaF, ≥98%) and sodium sulfate (Na_2SO_4, ≥98%), were purchased from Tianjin Chemical Reagent Company. Ethanol (AR) and acetone (AR) were purchased from Beijing Chemical Corporation. All solutions were prepared using high-purity deionized water. Alcohol-soluble Eosin Y ($C_{20}H_8Br_4O_5$) was acquired from Sigma Aldrich Co. Ltd.

Preparation of carbon dots solution

Two graphite rods (99.99%, Tianjin Ai Da technology Co. Ltd) were perpendicularly inserted in a 100 ml beaker containing a mixture of deionized water and ethanol with 0.4 g NaOH [25,26], and they were used as anode and cathode with a separation of 3.5 cm, respectively. A direct current (DC) power supply was applied to provide the potential of 40 V between the two electrodes for 5 h. During the process, the solution quickly changes from colorless to yellow and finally to dark brown. Afterwards, the solution was filtrated to remove impurities and large particles, resulting in carbon dots solution.

Preparation of TiO_2 NT electrodes

TiO_2 nanotube array (TiO_2 NT) electrode was prepared by anodic oxidation method according to our previous report [27]. The anodization of Ti foil was carried out in an aqueous solution of 0.5M H_3PO_4 and 0.14 M NaF for in ultrasonication irradiation (Kunshan Ultrasonic Instrument Co. Ltd., KQ-100DE). The platinum gauze (20 mm × 30 mm) was counter electrode and 20 V DC voltage was supplied by DC power (Maynuo M8812, 0–2 A, 0–75 V) at room temperature for 1 h. After anodization, samples were properly washed with deionized water immediately to remove absorbed ions, and annealed at 450 °C for 4 h in air.

Preparation of carbon dots sensitized TiO_2 NT electrodes

The carbon dots were directly grown on the TiO_2 NT electrodes surfaces by impregnation method [24]. The experimental process is as follows: the prepared TiO_2 NT electrodes were immersed into carbon dots solution for 18 h, followed by rinsing with deionized water to remove the remaining carbon dots solution from the electrodes surface, and finally dried in

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