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Enhancing photoactivity for hydrogen generation by electron tunneling via flip-flop hopping over iodinated graphitic carbon nitride

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ABSTRACT

In this work, the significant electron tunneling over iodine-decorated graphitic carbon nitride (I-g-C_3N_4) was achieved by I_3^- and I_5^- clusters implanted. The flip-flop electron tunneling takes place via strong Rashba spin-orbit coupling in p orbitals of polyiodides. The electron tunneling and hopping bridged the easier transfer route between far-located carbon atoms of g-C_3N_4 through the polyiodides p orbitals. By taking the advantage of this tunneling, the conductivity of I-g-C_3N_4/Ag photocatalyst was remarkably increased and the lifetime of photogenerated charges was largely prolonged, evidenced by I–V characteristics and the photoluminescence (PL) spectra. With the help of these properties, the obtained I-g-C_3N_4/Ag photocatalyst presented high active for hydrogen generation under visible light irradiation and Ag NPs as active site for hydrogen formation. 104.3 μmol H_2 was evolved over I-g-C_3N_4/Ag photocatalyst in 3 h, about three time higher than that of un-iodinated g-C_3N_4/Ag, and no remarkable decay of activity was observed in 900 min reaction. The highest AQE value of 7.3% was achieved at 520 nm.

1. Introduction

Photocatalytic water splitting for hydrogen generation driven by sunlight irradiation is one of the most promising routes to store the solar energy [1–6]. Photocatalytic hydrogen evolution system usually contains a metal-based cocatalyst, a photosensitizer and a sacrificial electron donor [7]. In order to achieve high efficiency of hydrogen generation, many efforts have been done in searching excellent electron conductive material to improve the charge separation efficiency [8], broadening the photo response range [9] and utilizing highly active cocatalysts [10]. Among them, improving the charge separation efficiency is a critical factor to obtain an excellent hydrogen evolution activity.

The rapid electron transfer can enhance the charge separation and decrease carrier recombination probability. This objective required material holding good electrical conductivity to promise high electron transfer rate. Graphene and graphitic carbon nitride materials are potential candidates because they have adjacent carbon atoms with both σ bond and π bond. Although the σ electron is strongly restricted by the atom core, however, the π electron is relatively delocalized. The π bonds can build π ribbons, providing a tunneling route for the electron transfer [11], leading to better conductivity, and are beneficial for photocatalytic reaction [12–14].

Implanting semiconductor NPs and metal NPs on the surface of graphene [15,16] or graphitic carbon nitride [17,18] is an effective way to improve photocatalytic activity, such as incorporating graphene with Pt NPs [19], TiO_2 [20], $BiVO_4$ [21], etc., due to efficient charge separation and easier transfer from the conduction band of semiconductors or the exited dye to graphene, leading to a significant enhancement of H_2 evolution activity. Unfortunately, attempts to further improving their lower conductivity and mobility meet difficulties partially because of the effect of residual oxygen functional groups and vacancy defects [22,23]. Further enhancing the electrical conductivity of graphene and graphitic carbon nitride is urgent for achieving higher H_2 evolution activity.

Iodine has been widely applied in improving the electrical conductivity of polymer materials [24–26]. It is known that graphene and graphitic carbon nitride has a similar conjugate structure to conducting polymers. Density functional calculations and topological simulations confirmed that charge transfer occurred between iodine and the nanotube wall in the case of linear triiodide (I_3^-) and pentaiodide (I_5^-) intercalated molecules [27]. In addition, first-principle density-functional calculations revealed that graphene edges could provide decent adsorption sites for halogen atom combination [28]. In fact, many attempts had been devoted to improve the electrical conductivity of carbon materials by doping iodine

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species in fuel cells research. For example, Kalita et al. confirmed that iodine doping of graphene can enhance the electron transfer between atomic iodine and graphene surface by the aid of polyiodides (I_3^- and I_5^-) species [29,30]. Zhan et al. found the iodinated graphene exhibited higher reversible capacity, longer-term stability and more excellent performance at very high current density. With doping I_3^-, the positive charge density on the graphene was increased, leading to excellent electrochemical activity [31]. It was already confirmed that the I_3^- and I_5^- interacted with carbon atoms through a charge transfer process could reduce the resistance of carbon materials and improve the electron transfer rate [32,33]. However, less works have be devoted to understand the mechanism of charge transfer iodinated g-C_3N_4. For example, Wang et al. found that iodine existing in the lattice of conjugated polymers could increase their electrical conductivity [34]. Our recent work found that the exceptional electrical properties of I_3^- and I_5^- cluster decorated carbon materials might attribute to a larger Rashba spin-orbit coupling induced by heavy adatoms with active electrons living in p orbitals [35]. The tunneling opened by the polyiodides p orbitals could lead an electron hopping between two neighbor carbon atoms in graphene, which gave the superior charge transfer performance. Considering the similar property between graphene and graphitic carbon nitride, we deduce the I_3^- and I_5^- cluster can also induce an flip-flop electron tunneling bridge between far-located carbon atoms on g-C_3N_4 by strong Rashba spin-orbit coupling in p orbitals over polyiodides decorated g-C_3N_4.

In the view of above, we developed a route of fabrication of iodinated g-C_3N_4 photocatalyst by in situ AgI NPs decomposition using light irradiation method. The structure and chemical states of iodine species were characterized through XPS and XRD spectroscopy. The results suggested that I species were in the forms of I_3^- and I_5^-. I–V curves showed the I_3^- and I_5^- decorated g-C_3N_4 exhibited better electrical conductivity and could enhance electron transfer properties, which remarkably reduced the recombination of electron and hole, and prolonged the lifetime of photogenerated charges. The iodinated g-C_3N_4 photocatalyst performed higher activity and long-term stability for hydrogen generation. About 104.3 μmol H_2 was generated over I-g-C_3N_4/Ag photocatalyst in 3 h, about three time higher than that of un-iodinated g-C_3N_4/Ag. No remarkable decay of activity was observed during 900 min reaction. The highest AQE value of 7.3% was achieved at 520 nm.

2. Experimental

2.1. Preparation of the g-C_3N_4 photocatalyst

Typically, 20 g of urea powder was put into a crucible with a cover and then heated to 550 °C within 30 min in a muffle furnace under the protection of nitrogen and maintained at this temperature for 3 h. The resultant powder was cooled to room temperature, washed with ultrapure water, collected by filtration and finally dried at room temperature.

2.2. Photocatalytic H_2 evolution activity and AQE measurements

Photocatalytic experiments were performed in a sealed Pyrex flask (150 ml) with a flat window (an efficient irradiation area of 14 cm^2) and a silicone rubber septum for sampling at ambient temperature. In a typical reaction system, 20 mg g-C_3N_4 was added into 100 ml 10% (v/v) TEOA aqueous solution. After 30 min ultrasonic treatment, 1 ml 0.1 M $AgNO_3$ aqueous solution was added into the suspension drop by drop and then the 1 ml 0.1 M KI aqueous solution was added in the same way. This suspension was stirred for 30 min. Subsequently, 70 mg EY was added into the suspension. Prior to irradiation, the suspension was degassed by bubbling Ar gas for 30 min. The light source was a300-W Xe lamp, which equipped with either a 420 nm cut-off filter or various band-pass filters. Photon flux of the incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum, 400–700 nm; sensitivity, 10–50 μV μmol^{-1} m^{-2} s^{-1}). The amount of H_2 was measured using gas chromatography (Aglient 6820, TCD, 13 × column, Ar carrier), and the AQE was calculated from the ratio of the number of reacted electrons during oxygen evolution to the number of incident photons by the follow equation:

$$\mathrm{AQE}[\%] = 2 \times \text{number of evolved } H_2\text{molecules/number of incident photos} \times 100$$

2.3. Working electrode preparation and photoelectrochemical measurements

Photocurrent responses of catalyst samples were measured on an electrochemical analyzer (CHI660E) in a homemade standard three-compartment cell, consisting of an organic glass enclosure with a quartz window and a 1.2 cm diameter opening opposite the window to the work electrode was clamped. The working electrodes were prepared by drop-coating sample suspensions directly onto the precleaned indium tin oxide glass (ITO glass) surface by microsyringe with an infrared heat lamp to speed drying. The surface of working electrode exposed to the electrolyte was a circular film with the geometrical surface areas of 1 cm^2. Platinum foil was used as a counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The supporting electrolyte was 10% TEOA aqueous solution mixed with 0.1 M Na_2SO_4 aqueous solution. A 300-W Xe lamp with an optical cutoff filter ($\lambda \geq 420$ nm) was used for excitation light source. The unbiased anodic photocurrent was investigated with an amperometric current-time technique.

2.4. Characterizations

Transmission electron microscopy (TEM) images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at accelerating voltage of 300 kV. The X-ray diffraction patterns (XRD) of the samples were recorded on a Rigaku B/Max-RB X-ray diffractometer with a nickel-filtrated Cu Kα radiation. The accelerating voltage and current were 40 kV and 30 mA, respectively. XPS analysis was performed using a VG ScientificESCALAB210-XPS photoelectron spectrometer with a Mg KRX-ray resource. FT-IR spectra were measured on a Nexus 870 FT-IR spectrometer from KBr pellets as the sample matrix. UV–vis Diffuse Reflectance Spectra were obtained with a Shimadzu UV-3600 UV-vis-near-IR spectrophotometer. $BaSO_4$ was used as a reflectance standard. The fluorescence decay times and PL spectra were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulse sat 460 nm with 1 MHz repetition rate was used as an excitation source. Light-scattering Ludox solution was used to obtain the instrument response function (prompt). The time ranges are 0.055 ns/channel in 4096 effective channels. Horiba Jobin Yvon DAS6 fluorescence decay analysis software was used to fit the model functions to the experimental data. The I–V curves of the specimens were measured by the 2-probe method on a Keithley 4200 semiconductor characterization system (electrode contact area of 2.56×10^{-6} m^2) at room temperature in air environment.

3. Results and discussion

The mechanism of formation of the Ag NPs, I_3^- and I_5^- on the surface of g-C_3N_4 is illustrated in Scheme 1. The g-C_3N_4 suspension was dispersed by ultrasound in 10% (v/v) TEOA solution to