

Efficient cosensitization of graphene/Pt photocatalysts for solar hydrogen generation using graphene as an efficient electron transfer carrier

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1. Introduction

As an alternative strategy for efficiently utilizing solar energy, dye-sensitization of semiconductors has been considered as an effective route to harvest large part of the solar energy for enhancing the H₂ production and photoelectrical conversion efficiency.⁸⁻¹⁴ Recently, it has been reported that the panchromatic cosensitization of TiO₂ electrodes using multiple dyes having complementary visible light absorption is effective to improve the photoelectrochemical conversion efficiency of dye-sensitized solar cells (DSSCs),¹⁵⁻²⁰ as compared to individual dye-sensitized systems since the light absorption of the single dyes is rather limited. More importantly, in the dye photosensitized H₂ evolution systems, the photocatalytic efficiency is mainly hampered by the competing electron and oxidized dye species (dye⁺) recombination process, which reduces the efficient transfer of electrons from photoexcited dye to catalyst and prohibits the water or proton reduction. Therefore, to retard the recombination of the electron and dye⁺ species, the presence of an electron transfer carrier is essential.

Graphene is a zero-band gap semiconductor and exhibits nondispersive charge transport characteristics and possesses a superior electrical conductivity and higher work function in accepting and transporting electrons to CNTs. Additionally, the flexible atom-thin 2D feature and large surface area of graphene also make it to be an excellent support matrix to anchor inorganic nanoparticles such as semiconductors and metals for designing newly photo-functional nanomaterials with improved performance. Herein, we report the efficient cosensitization of graphene dispersed with Pt catalyst employing Eosin Y (EY) and Rose Bengal (RB) as cosensitizer that have distinct but complementary spectral absorption in visible region. By combining the EY and RB sensitizers we have observed a higher activity and stability for visible light H₂ production from water reduction compared to the individual dye-sensitized photocatalytic systems.

2. Experimental

Graphite oxide (GO) was prepared from natural graphite using a modified Hummers method. Photocatalytic experiments were performed in a sealed quartz flask (150 mL) with a flat window (an efficient irradiation area of 13.2 cm²) and a silicone rubber septum for sampling at ambient temperature. Eosin Y (EY), Rose Bengal (RB), and Eosin Y and Rose Bengal (EY/RB) sensitized graphene/Pt photocatalysts were prepared using the in situ photoreduction method. The light source was a 300-W tungsten halogen lamp, which equipped with either a 420 nm cutoff filter or various band-pass filters. Prior to light irradiation, the suspension of the catalysts was dispersed by ultrasonication and degassed by bubbling Ar gas for 40 min. The amount of hydrogen evolution was measured using gas chromatography (Agilent 6820, TCD, 13× column, Ar carrier). For the apparent quantum yield (AQY) measurements, the photon flux of the incident light was determined using a Ray virtual radiation actinometer.

The AQY was calculated from the ratio of the number of reacted electrons during hydrogen evolution to the number of incident photons. Photocurrent responses of photocatalyst samples were

measured on an electrochemical analyzer (CHI660A) in a homemade standard three-compartment cell. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Scientific ESCALAB210-XPS photoelectron spectrometer with an Mg (K α) X-ray resources. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtered Cu K α radiation operated at 40 kV and 40 mA. FTIR spectra were measured on a Nexus 870 FT-IR spectrometer from KBr pellets as the sample matrix. UV-vis spectra were obtained with a Hewlett-Packard 8453 spectrophotometer. Transmission electron microscopy (TEM) images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at accelerating voltage of 300 kV.

3. Results and Discussion

The X-ray photoelectron spectroscopy (XPS) survey and C1s scan analyses of resulting graphene powders indicate that the atomic ratio of C/O of the graphene is estimated to be about 8.9, which is greatly higher than that of GO sample (C/O=2.1), showing most of the oxygen-containing groups have been successfully removed from GO upon reduction. The results of X-ray diffraction patterns (XRD) and Fourier-transform infrared spectroscopy (FTIR) show the effective reduction of GO to graphene, which is in good agreement with the results of XPS analysis.

Sensitizers EY and RB employed in this study are typically halogenated xanthene dyes. The absorption spectra of EY, RB, and EY/RB mixed with graphene in aqueous TEOA solution show that the absorption spectrum of EY displays a low-energy visible band at 518 nm and exhibits a higher molar extinction coefficient ($\epsilon=74112$ M⁻¹ cm⁻¹) while the maximum absorption of RB appears at 550 nm with a ϵ of 56787 M⁻¹ cm⁻¹, due to π - π^* transitions of the conjugated molecules. Also, a shoulder band at about 485 nm for EY and 510 nm for RB is observed, which are characteristics of the aggregated xanthene dyes species. The absorbance of EY and RB cosensitizer exhibits both absorption features of individual dyes, resulting in an extended and enhanced photo-absorption from 430 to 590 nm and ensuring a good light harvesting efficiency for visible light induced H₂ evolution reaction.

Platinum nanoparticles (Pt NPs) as hydrogen evolution catalyst were decorated on the surface of graphene nanosheets by in-situ photoreduction of H₂PtCl₆ during photocatalytic reaction. TEM images clearly demonstrate that many small Pt NPs with narrow size distribution uniformly disperse on the graphene sheets. The particle size of the Pt nanocrystals is estimated to be ~3-5 nm. The good distribution of Pt NPs on graphene sheets and strong interaction guarantees the efficient electron transport properties of graphene/Pt, and also possibly improve the photocatalysis performance of catalysts. The d-spacings of adjacent fringe for Pt is 2.27 Å that can be indexed to as the {111} plane of face-centered cubic (fcc) Pt lattice. These results indicate that Pt NPs have been directly and tightly decorated on the surface of graphene sheets, forming a hybrid with the combined merits of 2D supports with large surface areas and the highly dispersed NPs, which can be an exciting material for use in photocatalysis.

H₂ evolution activity of the dye-sensitized photocatalytic systems constructed with various combinations of dyes, graphene, and Pt catalyst under visible-light irradiation ($\lambda \geq 420$ nm) indicated that no H₂ evolution was observed using graphene either with or without Pt in absence of a dye sensitizers. Significantly, the introduction of graphene can greatly improve the activity of EY and EY/RB sensitized graphene/Pt (G/Pt), while the RB sensitized system show moderately increased activity. These results clearly indicate that the synergy of a photosensitizer, graphene, and Pt is indispensable for improving the photocatalytic activity of these photosensitized

systems. The EY and RB (EY/RB=1/1) cosensitized G/Pt shows a remarkably high H₂ evolution activity of 36.7 $\mu\text{mol}\cdot\text{h}^{-1}$, corresponding to an apparent quantum yield (AQY) of 9.4% at $\lambda \geq 420$ nm. This value exceeds that of EY-G/Pt (16.8 $\mu\text{mol}\cdot\text{h}^{-1}$, 4.3%) and RB-G/Pt (23.6 $\mu\text{mol}\cdot\text{h}^{-1}$, 6.0%) systems by a factor of 2.2 and 1.6 under same conditions, respectively, showing the superior performance to the individually dye sensitized systems due to the enhancement of light harvesting capability, even though the respective concentration of EY and RB in cosensitization system is lower than that of individual dye systems.

The photocatalytic H₂ evolution on EY/RB-G/Pt and RB-G/Pt proceeds with gradually decrease in the activity for longer than 60 h irradiation while the EY-G/Pt shows dramatically decreased activity after first 10 h and maintain its low activity for subsequent four runs with slight decrease, which can be attributable to the different dehalogenated degradation behaviors of these dyes. It is also found that the amount of hydrogen evolved on EY/RB-G/Pt is about 1812 μmol for 62 h, which greatly beyond the amount of dye used (24 μmol). The turnover number (TON) is beyond 75, confirming that the photosensitized H₂ evolution reaction proceeds photocatalytically.

The transient photocurrent responses of EY, RB, and EY/RB sensitized G/Pt coated on ITO glass were investigated for several on-off cycles of intermittent irradiation (20 s). Each systems show a notably and reversibly anodic photocurrent under visible light irradiation while their corresponding reference systems without Pt have no photocurrent response under same conditions, which clearly indicates that the enhanced photocurrent generation is due to the synergy of the dyes, graphene, and the Pt nanoparticles and evidences the directional electron transfer from excited dye to Pt through graphene carrier. The good dispersion together with the favorable work function of graphene could make it effective for transferring electrons from excited dyes to the Pt catalyst and spatial separation of the oxidized dye radicals (dye^{•+}) and photoexcited electrons, thus restraining the recombination process and resulting in higher performance of graphene based photosensitized systems for H₂ evolution.

To confirm the enhanced light harvesting capability by cosensitization, two-beam visible light irradiation experiments were performed at the respective maximum absorption of EY (520 nm) and RB (550 nm). The total quantum yield efficiency (TAQY) for H₂ evolution in the photosensitized systems using EY, RB or EY/RB as sensitizers further demonstrated the advantage of cosensitization. EY/RB cosensitized G/Pt system shows higher TAQY of 37.3% due to expanded visible light absorption, resulting in a significant enhancement in activity. Under same conditions, the TAQY of individual dyes sensitized systems are 13.9% and 21.7%, using EY and RB, respectively, showing inferior performance as compared to the cosensitized system.

4. Conclusions

In conclusion, we have demonstrated that dye-cosensitized graphene with dispersed Pt catalyst can exhibit very high photocatalytic activity and stability for H₂ evolution from water reduction under visible light irradiation. The complementary absorption of two dyes in visible region result in an extended light response and a higher efficiency than that of individual dyes systems. The graphene sheets provide an efficient electron transfer carrier from photoexcited sensitizers to Pt catalyst, leading to an efficient retardation of recombination process, thus resulting in an enhancement in photocatalytic activity. The present study shows the potential advantages of using dye cosensitization with graphene as electron transfer carrier to enhancing the efficiency of photosensitized systems.

Acknowledgement. This work has been financially supported by 973 program, 863 program of Department of Sciences and Technology of China (2007CB613305, 2009CB220003, and 2009AA05Z117) and Solar Energy Project of Chinese Academy of Sciences(KGCX2-YW-390-1 and KGCX2-YW-390-3).

5. References.

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