Graphene-induced spatial charge separation for selective water splitting over TiO₂ photocatalyst

Shixiong Min^{a,*}, Fang Wang^a, Gongxuan Lu^{b,*}

^a School of Chemistry and Chemical Engineering, Beifang University of Nationalities, Yinchuan, 750021, Ningxia Province, China.

^b State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China.

*Corresponding author.

Fax: 86-951-2067915; Tel: 86-951-2067917; E-mail: msxwf@163.com (S. Min).

Fax/Tel: 86-93-4968178. E-mail: gxlu@lzb.ac.cn, gxlu@ns.lzb.ac.cn (G. Lu).

Abstract: Here we report that separately decorating TiO_2 (P25) nanoparticles and CoO_x cocatalyst on single reduced graphene oxide (rGO) sheet results in an advanced photocatalyst, P25-rGO-Co, which exhibits enhanced photocatalytic performances for selective H_2 or O_2 evolution from water splitting. Characterization results show that rGO cannot only efficiently accept and transport photogenerated electrons but also shuttle holes to CoO_x cocatalyst simultaneously, achieving an efficient spatial charge separation on P25-rGO-Co, thus improving the half-reaction efficiency.

Keywords: reduced graphene oxide; TiO_2 ; spatial charge separation; water splitting

1. Introduction

Graphene, as a promising two-dimensional (2D) carbon nanomaterial, has been incorporated with the semiconductors to enhance the photocatalytic and photoelectrochemical performances of semiconductor-based composite materials [1,2]. For examples, nanocomposites of graphene with semiconductors have shown enhanced activity for H₂ or O₂ evolution reaction [3,4]. It has also been shown that the graphene can efficiently capture and shuttle the electrons from excited dye to decorated H₂-evolving cocatalysts [5-7], improving the H₂ evolution activity in dye sensitized systems. Among above-mentioned studies, it has been generally accepted that the graphene mainly offers a rapid 2D electron transportation pathway to achieve an efficient separation of photogenerated charge carriers due to its excellent electron accepting and transporting properties. However, the role of graphene for transporting photogenerated holes has not been sufficiently addressed in the field of photocatalytic water splitting, although it has been demonstrated by Gemi et al. [1] that holes have almost identical mobility to electron on graphene sheets. In addition, above studies only showed the applications of anchoring single-nanoparticle components on graphene for H₂ evolution, but decorating two even more (co)catalyst components on a single graphene sheet that can carry out selective catalytic reactions with enhanced performances at separated active sites has not been explored [8,9].

Herein, we report an advanced P25-rGO-Co photocatalyst prepared by separately decorating TiO₂ (P25) and CoO_x species on a single reduced graphene oxide (RGO) sheet *via* a two-step hydrolysis-hydrothermal method. Experimental results reveal that the presence of rGO not only provides an ideal 2D matrix for spatially anchoring P25 and CoO_x cocatalyst with high dispersion, but also offers a rapid transportation pathway for both photogenerated electrons and holes, thus a efficient spatial charge separation and an enhanced photocatalytic H₂ and O₂ evolution activity are achieved on P25-rGO-Co photocatalyst.

2. Experimental

2.1 Photocatalyst preparation

The P25-rGO-Co photocatalyst was synthesized by separately decorating CoO_x species and P25 nanoparticles on rGO sheets using two-step hydrolysis-hydrothermal method (Fig.S1). Typically, 20 mg of GO was dispersed in 35 mL of ethanol, to which 2.0 mL of 10 mg/mL $\text{Co}(\text{Ac})_2$ aqueous solution was added to form GO-Co^{2+} complex. Next, 0.5 mL of 30 % NH_4OH was added to hydrolysis Co^{2+} to form CoO_x species on GO sheets at 353 K. After stirring for 10 h, 1.0 g of TiO_2 (P25) was added into above mixture and sonicated for 15 min and the reaction mixture was hydrothermally heated at 423 K for 3 h. The products were collected by centrifugation and washed with ethanol and water, and dried in air. The obtained sample was denoted as P25-rGO-Co. P25-Co and P25-rGO photocatalysts were prepared under the same experimental conditions without adding GO and Co salt, respectively.

2.2 Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G²-F30 field emission transmission electron microscope. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtrated $\text{Cu K}\alpha$ radiation operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a K-Alpha-surface Analysis (Thermon Scientific) using X-ray monochromatization. Steady-state and time-resolved photoluminescence spectra were recorded with a Horiba Scientific FluoroMax-4 spectrofluorometer.

2.3 Photocatalytic experiments

Photocatalytic experiments were performed in a sealed quartz flask (150 mL) with a flat window and a silicone rubber septum for sampling. The light source was a 250-W high pressure mercury lamp. For H_2 evolution experiments, 50 mg of the photocatalyst was dispersed in 80 mL of 20% (v/v) CH_3OH aqueous solution. For O_2 evolution experiments, 50 mg of the photocatalyst was dispersed in 80 mL of 0.05 M AgNO_3 solution containing 0.2 g La_2O_3 . The reaction mixture was sonicated for 5 min and degassed by bubbling Ar gas for 40 min prior to light irradiation. The amount of H_2 and O_2 evolution was analysed using Agilent 6820 gas chromatography (TCD, 13X column, Ar).

2.4 Photoelectrochemical measurements

Photoelectrochemical measurements were carried out with an electrochemical analyser (CHI660A) in a standard three-compartment cell. Pt foil was used as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The supporting electrolyte was 0.5 M Na₂SO₄ solution. A 250 W high pressure mercury lamp was used as light source. The working electrodes were prepared by drop-coating 0.2 mL of sample suspensions (3.57 mg/mL) directly onto the conductive surface (1.6 cm²) of ITO glass.

3. Results and discussions

Fig. 1a shows the TEM image of the P25-rGO-Co photocatalyst, in which the P25 nanoparticles (NPs) are decorated throughout rGO sheets and no Co species are observable on its surface. High-resolution TEM in Fig. 1b reveals that no crystalline Co species could be observed on rGO surface, but HAADF image and EDX mappings in Fig. 1c reveal that the Co species distribute throughout rGO sheets. This result suggests that the loaded Co species is most likely amorphous and highly dispersed on rGO sheets, which is further confirmed by the EDX profiles in Fig. 1d. EDX profile recorded at the middle of the rGO sheet (spot 1) only shows C, O, and Co signals, while EDX profile collected at aggregated P25 NPs (spot 2) presents strong C, O, and Ti signals but without Co signals, suggesting the spatial anchoring of Co species and P25 NPs on single rGO sheets. The P25-rGO-Co, P25-Co, and P25-rGO exhibit similar XRD patterns (Fig. S2) to P25 and there are no extra diffraction peaks for the rGO and Co species. XPS confirms the reduction of GO to rGO with ~4 at. % N doping (Fig. S3a and b). Co2p XPS spectra (Fig. S3c) show two major peaks at 796.7 and 780.9 eV, corresponding to Co2p_{1/2} and Co2p_{3/2} of the Co³⁺ and Co²⁺ oxidation states, respectively, with a weak satellite peak at 790.7 eV related to the Co²⁺ components [10]. These results reveal that the loaded Co species contains both Co²⁺ and Co³⁺ oxides (referred to as CoO_x hereafter). Therefore, above results strongly confirm that the rGO serves as an ideal matrix to spatially anchor P25 NPs and CoO_x species on single 2D rGO sheet.

The photocatalytic H₂ evolution activities of various photocatalysts were displayed in Fig. 2a and b. P25 NPs alone has a low rate of H₂ evolution, while the incorporation of rGO leads to a ~2.5-fold

enhancement in H₂ evolution rate for P25-rGO. Without rGO but loading CoO_x, P25-Co shows a much higher H₂ evolution rate because CoO_x can facilitate the charge separation by efficiently capturing photogenerated holes [10]. Notably, after loading CoO_x on rGO, the rate of H₂ evolution on P25-rGO-Co is further enhanced, which is even 1.6 times higher than P25-Co. On the other hand, the photocatalytic O₂ evolution activities for above four photocatalysts were compared in Fig. 2c and d, where the P25-rGO-Co also shows the highest rate of O₂ evolution. **Note that the rGO itself is inactive for both H₂ and O₂ evolution reactions.** For comparison, a photocatalyst of Co-P25-rGO was prepared, in which ~1.5 nm CoO_x was first loaded on P25 NPs (Co-P25) and then the Co-P25 was decorated on rGO sheets (Fig. S4). The Co-P25-rGO shows H₂ and O₂ evolution rates inferior to that of P25-rGO-Co (Fig. S5). These results indicate that the spatial anchoring of CoO_x and P25 NPs on rGO sheets seems to be crucial for achieving enhanced photocatalytic performances on P25-rGO-Co.

In order to clarify the essential roles of rGO and CoO_x in enhancing the photocatalytic activity of P25-rGO-Co, the transient photocurrent responses for photocatalysts were measured under UV light irradiation at zero bias, as shown Fig. 3a. It is clear to see that the P25 shows a very low photocurrent. With CoO_x loading, the photocurrent of P25-Co doubles as compared to P25 because the loading of CoO_x reduces the amount of holes accumulated and thus prohibits the surface charge recombination [10]. Furthermore, when P25 is decorated on rGO sheets, the photocurrent is further enhanced. Note that loading of CoO_x leads to much less pronounced enhancement in photocurrent of P25 as compared to rGO, suggesting that although the capturing of photogenerated holes of P25 by CoO_x species is feasible, the lower electron mobility of CoO_x ($5.0\sim7.0\times10^{-5}$ cm²/Vs) than rGO (2.0×10^6 cm²/Vs) increases the recombination between the electrons in P25 and the holes in CoO_x, resulting in much lower photocurrent for P25-Co. Notably, P25-rGO-Co exhibits a remarkably enhanced photocurrent, which is 20, 10, and 4 times higher than that of P25, P25-Co, and P25-rGO, respectively. Given that the decorated P25 NPs on rGO sheets were spatially separated from CoO_x, the clearly enhanced photocurrent of P25-rGO-Co indicates that the rGO not only provides a fast transfer pathway for electrons [8], but also can shuttle

holes to loaded CoO_x efficiently, resulting in a spatial charge separation in P25-rGO-Co. To further support this point, the steady-state (Fig. 3b) and time-resolved photoluminescence (Fig. 3c) spectra of photocatalysts were performed. The results show that the PL intensity for both P25-rGO-Co and P25-rGO is much weaker than that of P25-Co and P25, indicating that the direct charge recombination can be greatly suppressed. Meanwhile, the emission decay of the P25-rGO-Co and P25-rGO is slower than that of P25-Co and P25, suggesting that the enhanced charge separation is related to the prolonged lifetime of accumulated electrons and holes in P25-rGO-Co and P25-rGO [11].

In addition, the electrochemical activities of these photocatalysts were investigated, as shown in Fig. 3d. During the cathodic polarization process, the presence of rGO, CoO_x , or both rGO and CoO_x does not make a difference on the cathodic current density in the potential range of 0 to -1.0 V vs. SCE. This result implies that, in the case of P25-rGO-Co, the rGO is just an electron acceptor while the CoO_x cocatalyst only act as a spectator for the hole transfer and a oxidation cocatalyst for electron donor, *i.e.*, they are not involved in the reduction processes. On the other hand, during the anodic polarization process, the anodic current densities of P25-rGO-Co and P25-Co are nearly the same, but are obviously greater than those of P25-G and P25, unambiguously demonstrates that the loading of CoO_x cocatalyst can greatly promote the hole transfer processes of P25 *via* rGO. In addition, the presence of rGO has a negligible effect on the anodic current density of P25 or P25-Co, indicating that the rGO involves in the oxidation processes just as a media for the hole transfer from the P25 to CoO_x rather than an active sites for O_2 evolution.

Based on the above analysis, a mechanism was proposed, as shown in Fig. 4. The conduction band minimum and valence band maximum of P25 are -0.29 and 2.9 V vs NHE, respectively, while the location of Femi level of rGO can be roughly estimated to ~0 V vs NHE [11]. As a result, when the P25 and CoO_x are separately decorated on rGO, a large energy offset between VB of P25 and rGO will form at the interface, while the energy offset between CB of P25 and rGO is relatively smaller. Once the electrons and holes are photogenerated in the P25, they will most likely separately transfer to the rGO

owing to the formed energy band offsets [11], leading to a spatial charge separation on P25-rGO-Co, thus resulting in enhanced efficiencies for H₂ and O₂ evolution reactions.

4. Conclusions

An efficient photocatalyst, P25-rGO-Co, has been developed by spatially decorating P25 NPs and CoO_x cocatalyst on single rGO sheet. Due to its high electron and hole mobility, the presence of rGO hardly involved in catalytic reactions but can significantly enhance the charge separation efficiency of TiO₂ by capturing electrons and simultaneously transferring holes to CoO_x on rGO sheets; as a result, the photocurrent response and photocatalytic activity of P25-rGO-Co towards H₂ or O₂ evolution was greatly enhanced as compared to reference samples.

Acknowledgments

This work is supported by the National Science Foundation of China (21463001, 21173242, 21263001), the Natural Science Foundation of the Ningxia Hui Autonomous Region (NZ15102), the Key project (2014XZZ02) and General project (2014XYZ02) of Beifang University of Nationalities, and the cultivation project of National Natural Science Foundation (2014QZP04).

References

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* 306 (2004) 666-669.
- [2] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, A. Govindaraj, *Angew. Chem. Int. Ed.* 48 (2009) 7752-7777.
- [3] Q. J. Xiang, J. G. Yu, M. Jaroniec, *Chem. Soc. Rev.* 41 (2012) 782-796.
- [4] X. Huang, X. Y. Qi, F. Boeyab, H. Zhang, *Chem. Soc. Rev.* 41 (2012) 666-686.
- [5] S. X. Min, G. X. Lu, *J. Phys. Chem. C* 115 (2011) 13938-13945.
- [6] S. X. Min, G. X. Lu, *J. Phys. Chem. C* 116 (2012) 25415-25424.
- [7] S. X. Min, G. X. Lu, *Int. J. Hydrogen Energy*. 37 (2012) 10564-10574.

- [8] I. V. Lightcap, T. H. Kosel, P. V. Kamat, *Nano Lett.* 10 (2010) 577-583.
- [9] P. V. Kamat, *J. Phys. Chem. Lett.* 1 (2010) 520-527.
- [10] F. X. Zhang, A. Yamakata, K. Maeda, Y. Moriya, T. Takata, J. Kubota, K. Teshima, S. Oishi, K. Domen, *J. Am. Chem. Soc.* 134 (2012) 8348–8351.
- [11] Y. Lin, K. Zhang, W. F. Chen, Y. D. Liu, Z. G. Geng, J. Zeng, N. Pan, L. F. Yan, X. P. Wang, J. G. Hou, *ACS Nano* 4 (2010) 3033-3038.

Figure Captions

Fig. 1. (a) TEM image of P25-rGO-Co. (b) HRTEM image of selected area (blue rectangle) in panel a. (c) HAADF image and corresponding EDX element mappings. (d) EDX profiles recorded at selected spot 1 and 2 in panel c.

Fig. 2. (a, b) H_2 and (c,d) O_2 evolution activities over P25, P25-rGO, P25-Co, and P25-rGO-Co.

Fig. 3. (a) $I-t$ profiles of photocatalyst electrodes in 0.5 M Na_2SO_4 solution under chopped UV light irradiation. (b) Steady-state (excitation wavelength: 280 nm) and (c) time-resolved photoluminescence spectra (excitation wavelength: 280 nm; detection wavelength: 410 nm) of P25, P25-rGO, P25-Co, and P25-rGO-Co. (d) Linear sweep voltammetries (LSVs) of photocatalyst electrodes in 0.5 M Na_2SO_4 aqueous solution. The scan rate was 1 mV/s.

Fig. 4. Proposed mechanism for selective H_2 or O_2 evolution from water splitting over P25-rGO-Co photocatalyst.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Graphical Abstract