



Short communication

# Graphene-induced spatial charge separation for selective water splitting over TiO<sub>2</sub> photocatalyst

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## ABSTRACT

Here we report that separately decorating TiO<sub>2</sub> (P25) nanoparticles and CoO<sub>x</sub> cocatalyst on a single reduced graphene oxide (rGO) sheet results in an advanced photocatalyst, P25-rGO-Co, which exhibits enhanced photocatalytic performances for selective H<sub>2</sub> or O<sub>2</sub> evolution from water splitting. Characterization results show that rGO can not only efficiently accept and transport photogenerated electrons but also shuttle holes to CoO<sub>x</sub> cocatalyst simultaneously, achieving an efficient spatial charge separation on P25-rGO-Co, thus improving the half-reaction efficiency.

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## 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 H<sub>2</sub> or O<sub>2</sub> evolution reaction [3,4]. It has also been shown that the graphene can efficiently capture and shuttle the electrons from excited dye to decorated H<sub>2</sub>-evolving cocatalysts [5–7], improving the H<sub>2</sub> 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 H<sub>2</sub> 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 TiO<sub>2</sub> (P25) and CoO<sub>x</sub> 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<sub>x</sub> cocatalyst with high dispersion, but also offers a rapid transportation pathway for both photogenerated electrons and holes, thus an efficient spatial charge separation and an enhanced photocatalytic H<sub>2</sub> and O<sub>2</sub> 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<sub>x</sub> species and P25 nanoparticles on rGO sheets using a 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 Co(Ac)<sub>2</sub> aqueous solution was added to form GO-Co<sup>2+</sup> complex. Next, 0.5 mL of 30% NH<sub>4</sub>OH was added to hydrolysis Co<sup>2+</sup> to form CoO<sub>x</sub> species on GO sheets at 353 K. After stirring for 10 h, 1.0 g of TiO<sub>2</sub> (P25) was added into the 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 the 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.

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## 2.2. Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Tecnai-G<sup>2</sup>-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 filtered 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<sub>2</sub> evolution experiments, 50 mg of the photocatalyst was dispersed in 80 mL of 20% (v/v) CH<sub>3</sub>OH aqueous solution. For O<sub>2</sub> evolution experiments, 50 mg of the photocatalyst was dispersed in 80 mL of 0.05 M AgNO<sub>3</sub> solution containing 0.2 g La<sub>2</sub>O<sub>3</sub>. 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<sub>2</sub> and O<sub>2</sub> evolution was analysed using Agilent 6820 gas chromatography (TCD, 13X column, Ar).

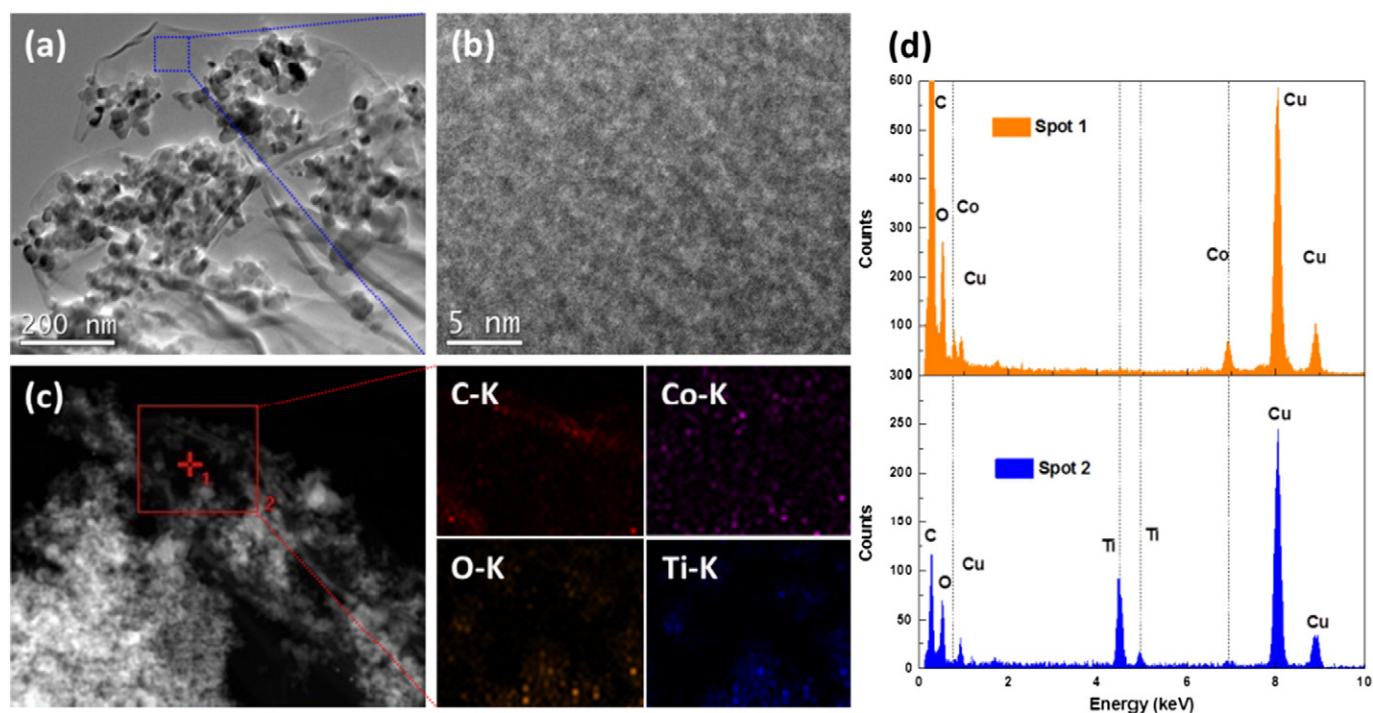
## 2.4. Photoelectrochemical measurements

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 a 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. A 250 W high pressure mercury lamp was used as a 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 cm<sup>2</sup>) 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). Co 2p XPS spectra (Fig. S3c) show two major peaks at 796.7 and 780.9 eV, corresponding to Co 2p<sub>1/2</sub> and Co 2p<sub>3/2</sub> of the Co<sup>3+</sup> and Co<sup>2+</sup> oxidation states, respectively, with a weak satellite peak at 790.7 eV related to the Co<sup>2+</sup> components [10]. These results reveal that the loaded Co species contains both Co<sup>2+</sup> and Co<sup>3+</sup> oxides (referred to as CoO<sub>x</sub> hereafter). Therefore, above results strongly confirm that the rGO serves as an ideal matrix to spatially anchor P25 NPs and CoO<sub>x</sub> species on a single 2D rGO sheet.

The photocatalytic H<sub>2</sub> evolution activities of various photocatalysts were displayed in Fig. 2a and b. P25 NPs alone have a low rate of H<sub>2</sub> evolution, while the incorporation of rGO leads to an ~2.5-fold enhancement in H<sub>2</sub> evolution rate for P25-rGO. Without rGO but loading CoO<sub>x</sub>, P25-Co shows a much higher H<sub>2</sub> evolution rate because CoO<sub>x</sub> can facilitate the charge separation by efficiently capturing photogenerated holes [10]. Notably, after loading CoO<sub>x</sub> on rGO, the rate of H<sub>2</sub> evolution on P25-rGO-Co is further enhanced, which is even 1.6 times higher than P25-Co. On the other hand, the photocatalytic O<sub>2</sub> evolution activities for above four photocatalysts were compared in Fig. 2c and d, where the P25-rGO-Co also shows the highest rate of O<sub>2</sub> evolution. Note that the rGO itself is inactive for both H<sub>2</sub> and O<sub>2</sub> evolution



**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.

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