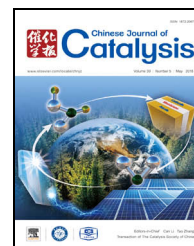


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## Article

# Enhancing the photocatalytic activity and photostability of zinc oxide nanorod arrays via graphitic carbon mediation

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## ABSTRACT

Low optical absorption and photocorrosion are two crucial issues limiting the practical applications of zinc oxide (ZnO)-based photocatalysts. In this paper, we report the fabrication of graphitic-carbon-mediated ZnO nanorod arrays (NRAs) with enhanced photocatalytic activity and photostability for CO<sub>2</sub> reduction under visible light irradiation. ZnO NRA/C-*x* (*x* = 0.05, 0.1, 0.2, and 0.3) nanohybrids are prepared by calcining pre-synthesized ZnO NRAs with different amounts of glucose (0.05, 0.1, 0.2, and 0.3 g) as a carbon source via a hydrothermal method. X-ray photoelectron spectroscopy reveals that the obtained ZnO NRA/C-*x* nanohybrids are imparted with the effects of both carbon doping and carbon coating, as evidenced by the detected C–O–Zn bond and the C–C, C–O and C=O bonds, respectively. While the basic structure of ZnO remains unchanged, the UV-Vis absorption spectra show increased absorbance owing to the carbon doping effect in the ZnO NRA/C-*x* nanohybrids. The photoluminescence (PL) intensities of ZnO NRA/C-*x* nanohybrids are lower than that of bare ZnO NRA, indicating that the graphitic carbon layer coated on the surface of the ZnO NRA significantly enhances the charge carrier separation and transport, which in turn enhances the photoelectrochemical property and photocatalytic activity of the ZnO NRA/C-*x* nanohybrids for CO<sub>2</sub> reduction. More importantly, a long-term reaction of photocatalytic CO<sub>2</sub> reduction demonstrates that the photostability of ZnO NRA/C-*x* nanohybrids is significantly increased in comparison with the bare ZnO NRA.

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## 1. Introduction

Photocatalysis using semiconductors and solar energy for water splitting to generate hydrogen and recycling CO<sub>2</sub> back to hydrocarbon fuels has attracted wide attention, in view of the global energy crisis and environment pollution issues [1–8]. Over the past four decades, tremendous efforts have been devoted to developing various semiconductor photocatalysts

[6–16], among which zinc oxide (ZnO) has been intensively studied because of its attractive photophysical properties and nontoxicity [17–20]. However, the practical application of ZnO as a photocatalyst has hardly been realized. This has been because of its low photostability that is caused by photocorrosion [21–24], in which the zinc ion is prone to oxidation by photo-generated holes upon light irradiation. ZnO is a wide band gap ( $E_g \approx 3.2$  eV) semiconductor, so it can only absorb ultraviolet

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(UV) wavelengths. UV wavelengths constitute only ~4% of the solar spectrum, so longer visible wavelengths are effectively wasted [25–27]. Previous studies have shown that doping with C, N, or S could extend the optical absorption range of ZnO into the visible region. Lin *et al.* [28] prepared hierarchically porous nanoarchitectures of C-doped ZnO by a facile and inexpensive wet-chemical method. Cho *et al.* [29] used vitamin C as a carbon source to synthesize C-doped ZnO as a visible light photocatalyst.

Efficient charge separation and transfer are essential for efficient photocatalytic activity [30,31]. How to suppress the recombination of photoinduced charge carriers (electron/hole pairs) has long been a challenge in photocatalysis [32,33]. A photocatalytic reaction is a surface-based process involving the separation and transport of photoinduced charge carriers, as the subsequent redox reactions mainly occur on the catalyst surface. One-dimensional (1-D) semiconductors have large surface-to-volume ratios and good charge carrier transport rates which benefit from the ballistic effect. Thus, 1-D semiconductors are expected to exhibit superior photocatalytic activity compared with conventional powder photocatalysts [34,35]. Coating a thin amorphous carbon layer on the surface of a semiconductor has been demonstrated to effectively improve charge carrier separation. In this context, many recent studies have reported the coating of 1-D ZnO with a carbon layer to suppress charge carrier recombination, and in turn improve the photocatalytic activity. Mu *et al.* [36] prepared ZnO–carbon nanofiber heteroarchitectures with high photocatalytic activity for degrading rhodamine B. Han *et al.* [37] reported the enhanced photocatalytic activity and anti-photocorrosion properties of ZnO by coupling with versatile carbon species. A microwave-assisted carbonization strategy was adopted by Guo *et al.* [38] to form a uniform carbon coating on ZnO nanorods, which enhanced their photocatalytic activity. Yu *et al.* [39] synthesized ZnO/carbon quantum dots by a one-step method, and the resulting material exhibited excellent photocatalytic ability for toxic gas degradation under visible light irradiation. Akir *et al.* [40] synthesized carbon-ZnO nanocomposites with enhanced visible light photocatalytic performance for degrading rhodamine B. Others have synthesized ZnO-nanoparticle/graphene-oxide or ZnO-nanorod/reduced-graphene-oxide composites for the photodegradation of methylene blue [41,42]. However, previous studies on carbon-modified ZnO have rarely focused on comprehensively improving the photostability, charge carrier separation, and photocatalytic CO<sub>2</sub> reduction [26].

Herein, we report a modified hydrothermal method for fabricating graphitic-carbon-mediated visible-light-responsive ZnO nanorod arrays (NRAs). The resulting carbon-containing NRAs exhibit enhanced photocatalytic activity and photostability for CO<sub>2</sub> reduction, compared with the NRA containing no carbon. By calcining pre-synthesized ZnO NRAs coated with different amounts of glucose as a carbon source at a suitable hydrothermal temperature, we obtain ZnO NRA/C-*x* nanohybrids on zinc foil. The ZnO NRA/C-*x* nanohybrids are imparted with the effects of both carbon doping and carbon coating, so they exhibit increased absorption ability and photostability

compared with the ZnO NRA. The graphitic carbon layer coated on the surface of the ZnO NRA significantly enhances charge carrier separation and transport and thus enhances the photocatalytic activity of the ZnO NRA/C-*x* nanohybrids. This study provides a method involving graphitic carbon mediation for fabricating a highly stable and active ZnO-based photocatalyst for CO<sub>2</sub> reduction.

## 2. Experimental

### 2.1. Sample preparation

The ZnO nanorod array was directly grown on zinc foil (2.0 cm × 3.0 cm) via a hydrothermal method at 180 °C for 4 h, in a solution containing 25 mL of H<sub>2</sub>O, 2 g of NaOH, and 3.6 mL of 30% H<sub>2</sub>O<sub>2</sub>. The surface of the zinc foil was pretreated using hydrochloric acid for 20 s. After rinsing with deionized water several times, the synthesized ZnO NRA on the zinc foil was dried at room temperature. A typical procedure for coating carbon on the ZnO NRA was as follows. Different amounts of glucose (0.05, 0.1, 0.2, 0.3 g) were first dissolved in 30 mL of deionized water, into which the ZnO NRA was added; the resulting solution was then heated to 180 °C for 4 h, followed by cooling to room temperature. After washing with deionized water several times, the samples were dried in an oven at 80 °C for 1 h. Finally, the samples were placed in a tube furnace and calcined at 800 °C with a heating rate of 5 °C/min for 3 h in an argon gas atmosphere, to obtain the resulting samples ZnO-NRA/C-*x* (where *x* = 005, 01, 02, and 03, and denotes added glucose amounts of 0.05, 0.1, 0.2, and 0.3 g, respectively). For comparison, zinc foil coated with graphitic carbon (denoted as Zn/C foil) was also prepared following a similar procedure as mentioned above.

### 2.2. Characterization

The crystal structures of the synthesized samples were determined using a powder X-ray diffractometer (XRD; Cu K<sub>α</sub> radiation, D8 Advanced, Bruker, Germany). Microstructures were observed using a field-emission scanning electron microscope (FESEM; JOEL-S4800, Japan) and a transmission electron microscope (TEM; FEI Tecnai G2 F20, USA), both equipped with an energy dispersive X-ray spectrometer. Raman scattering spectra were recorded using a Raman spectroscope (XploRA PLUS, HORIBA Scientific, NJ, USA). The optical properties of the samples were characterized by measuring their ultraviolet-visible (UV-Vis) diffuse reflectance spectra with a spectrophotometer (UV-2700, Shimadzu, Japan) and photoluminescence (PL) spectra with a fluorescence spectrophotometer (Fluorolog-3, HORIBA Scientific, NJ, USA), respectively. The valence states of near-surface elements were measured by X-ray photoelectron spectroscopy (XPS; Escalab 250, Thermo Scientific, MA, USA). XPS spectra were calibrated using the C 1s peak (284.8 eV) as the reference.

### 2.3. Evaluation of photoelectrochemical (PEC) and photocatalytic activities

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