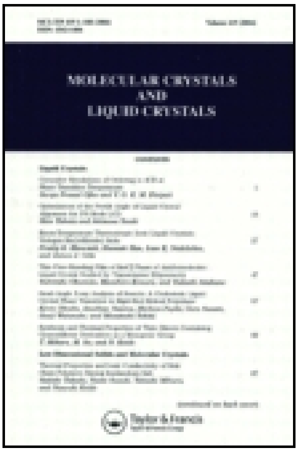

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Enhanced Photoelectrochemical Response of Graphene-Coated Al_2O_3-TiO_2 Nanocomposite Photoanodes

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Enhanced Photoelectrochemical Response of Graphene-Coated Al_2O_3-TiO_2 Nanocomposite Photoanodes

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Graphene-coated Al_2O_3 (GCA)-TiO_2 nanocomposite photoanodes were fabricated by dispersing the GCA (1, 3, and 5 wt.%) and TiO_2 nanoparticles. Photoelectrochemical (PEC) responses under the white light illumination were significantly enhanced with the increase of the GCA content and all of the GCA-TiO_2 films exhibited much better PEC responses than the electrode prepared from the TiO_2 alone. The significantly improved PEC response of the GCA-TiO_2 can be attributed to the enhanced electron transport.

Keywords Electron transport; graphene-coated Al_2O_3, TiO_2; nanocomposite; photoelectrochemical response

Introduction

Photoelectrochemical (PEC) systems are promising methods of producing H_2 gas using solar energy in an aqueous solution [1–5]. The photoelectrochemical properties of numerous metal oxides have been studied [1–6]. Among them, the PEC systems based on TiO_2 have been extensively studied [1,2]. The metal oxides absorb photons with energies larger than the bandgaps and generate electron-hole pairs. Taking into account that n-type semiconductors such as the TiO_2 are used as the photoanodes,

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the photogenerated electrons move to the counter electrode where water reduction occurs and the photogenerated holes move towards semiconductor/electrolyte interface where water oxidation takes place.

Nanoporous electrodes consisting of nanoparticles provide a large surface area, which increases the photoelectrochemical reaction sites [7]. However, it is well known that the nanoparticles don't develop a depletion layer (or space charge region), because those particle sizes are smaller than the depletion layer [7,8]. It indicates that no electric field exists at the interface between the nanoparticles and the electrolyte, leading to large back electron transfer (or recombination reaction) from the conduction band of the TiO_2 to the electrolyte.

The graphene is a zero band gap material and individual sheets of the graphene possess excellent electrical conductivity, due to the existence of an extended sp^2-bonded carbon network [9,10]. In this paper, the graphene-coated Al_2O_3 (GCA)-TiO_2 composite films were prepared for the photoelectrochemical cells. With increasing the GCA content into the nanocomposite electrodes, the PEC response was significantly enhanced. It can be attributed to the efficient charge separation (or reduced recombination rate) of the photogenerated electron-hole pairs caused by the improved electron transport through the GCA-TiO_2 to the transparent conducting oxide (TCO).

Experimental

The graphene-coated Al_2O_3 (GCA) nanoparticles were synthesized by the reverse route of the reaction below.

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3\ CO(g) \tag{1}$$

AlN powders were first prepared by calcining a (hydroxo)(succinato)Al(III) complex at 1300°C for 5 h under a flow of nitrogen [11]. The powders in an alumina crucible were set in an alumina tube and heated at a rate of 5°C/min to 1400°C in a gas mixture of argon and 10 vol % CO at a flow rate of 200 ml/min. The reverse reaction of Eq. (1) occurred at 1400°C so that the graphene-coated Al_2O_3 particles could be synthesized by calcining the AlN powders at 1400°C for 20 h under a flow of 10 vol % CO/Ar, the more detailed things of which were described elsewhere [12].

The GCA-TiO_2 composite films were prepared by simply dispersing the GCA (1, 3, and 5 wt.% over TiO_2) and commercial TiO_2 (P25) nanoparticles together in ethanol. The graphene-TiO_2 colloids were thoroughly dispersed using a conditioning mixer by adding ethyl cellulose as a binder and α-terpineol as a solvent for the GCA-TiO_2 pastes, followed by concentration using an evaporator. The 10 μm-thick, , mesoporous GCA-TiO_2 films were fabricated by doctor-blading the GCA-TiO_2 pastes on the FTO (F-doped SnO_2) TCO followed by calcination at 450°C for 30 min. For comparison, the 10 μm-thick, mesoporous TiO_2 film without the GCA was prepared using the similar preparation process.

The PEC measurements were performed in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface [13]. The GCA-TiO_2 nanocomposite films (active area: 0.25 cm^2) were used as the working electrodes. A Pt sheet (area: 10 cm^2) and a Ag/AgCl electrode (with saturated KCl) were used as the counter and reference electrodes, respectively. A 1-M KOH basic aqueous solution was used as the electrolyte. The PEC responses were measured using a Xe lamp (150 W) with a light intensity of 100 mW/cm^2, measured by a photodiode power meter. The current-voltage performances under the chopped light on/off illumination were measured with a scan rate of 5 mV/s during the potential sweep.

Results and Discussion

Figure 1 shows the HR-TEM image of the graphene sheets in the graphene-coated Al_2O_3 (GCA). The particle size of the GCA was in a range of 20 to 40 nm. Two or three parallel dark fringes were observed at the edge of GCA and the spacing between neighboring fringes is 0.34 nm, which is in a good agreement with the spacing between the (002) planes of graphite. More detailed description on the GCA is described elsewhere [12].

The GCA-TiO_2 nanocomposite, mesoporous films were fabricated by dispersing the GCA (1, 3, and 5 wt% over TiO_2) and TiO_2 nanoparticles. Figure 2(a) shows the current-voltage curves of the TiO_2 (sample 1) and the GCA-TiO_2 nanocomposite electrodes measured under the chopped light on/off illumination, where the 1, 3, and 5 wt.%-GCA-TiO_2 films are referred to as the samples 2, 3, and 4, respectively. In order to confirm whether the photocurrent was specifically generated only by the absorbed photons without any dark current contribution, the photoelectrochemical responses were measured under light on/off illumination. The dark current under light-off conditions hardly changed across the potential range, when compared to the photoresponse under light-on conditions, indicating that the photocurrents of the GCA-TiO_2 films were generated only by the absorbed photons under light illumination without the contribution of the dark current. The photosensitivity (μA/W)

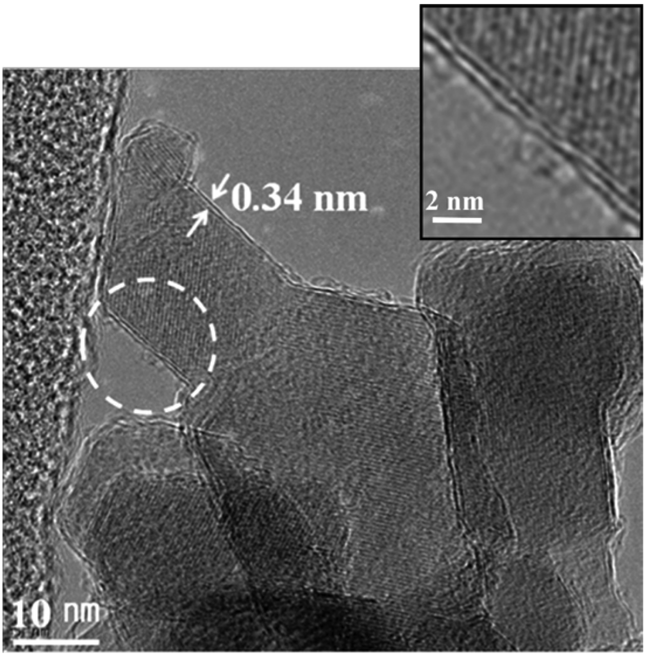

Figure 1. HR-TEM images of the synthesized graphene-coated Al_2O_3 particles.

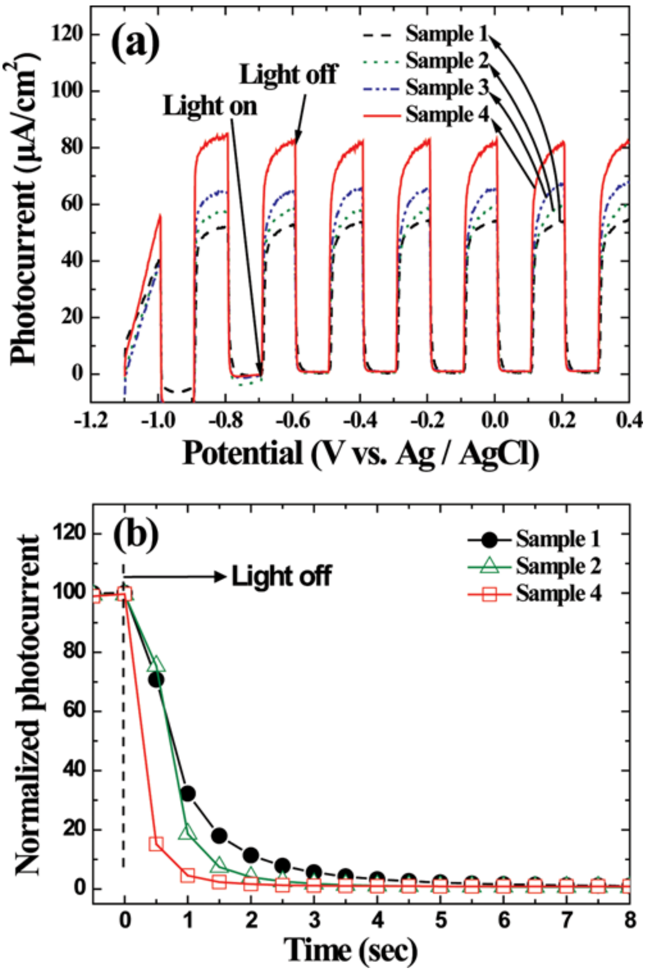

Figure 2. (a) Current-voltage curves of the the TiO_2 (sample 1) and the 1, 3, and 5 wt.%-GCA-TiO_2 nanocomposites (denoted as samples 2, 3, and 4, respectively) measured under the chopped light on/off illumination (b) Normalized photocurrent transients of the samples 1,2, and 4 measured at 0 V when the light is switched off.

values estimated at 0.2 V were 538, 597, 670, and 809 μA/W for the samples 1, 2, 3, and 4, respectively. All of the GCA-TiO_2 films exhibited better PEC responses than the TiO_2 film and the PEC response was significantly enhanced with the increased GCA incorporation. For the comparison of the carrier transport, the photocurrent transients were measured at 0 V when the light was switched off and normalized, as shown in Figure 2(b). The response of the 5 wt.% GCA-TiO_2 film was much faster than that of the 1 wt.% GCA-TiO_2, indicating faster carrier transport with the increased GCA content. All of the GCA-TiO_2 films exhibited faster response time than the TiO_2 film. This suggests that the GCA-TiO_2 films provided superior carrier transport, due to the excellent electron mobility in the graphene.

Figure 3 shows the ac impedance Nyquist plots of the samples 1, 2, and 4, respectively, measured at 0 V under the light illumination. The frequency range was 0.1 Hz to 0.1 MHz and the amplitude of the sinusoidal voltage signal was

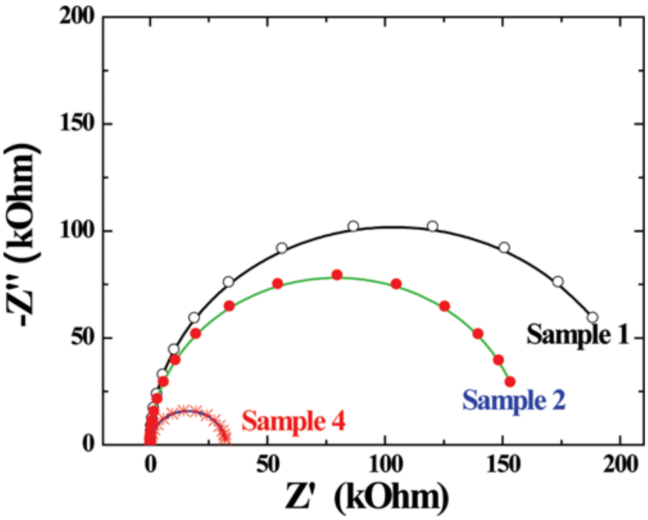

Figure 3. Nyquist plots of the samples 1, 2, and 4, respectively, measured at 0 V under the light illumination.

30 mV. Through an approximate comparison between the semicircles, the value of R_{ct} (charge-transfer resistance) significantly reduced with the increase of the GCA content in the TiO_2 mesoporous films, indicating the acceleration of the electron transfer process in the photoanode, which is corresponding well to the fast response time in Figure 2(b). Therefore, the significantly improved PEC responses of the GCA-TiO_2 nanocomposite films are attributed to superior carrier transport through the GCA-TiO_2 to the TCO.

Conclusions

The GCA-TiO_2 nanocomposite electrodes were prepared by dispersing the CGA (1, 3, and 5 wt.% over TiO_2) and the TiO_2 particles. The TiO_2 mesoporous films incorporated by the GCA exhibited much superior electron transport, compared to the TiO_2 film without the GCA, leading to the reduced recombination rate between the photogenerated electrons and holes and significantly enhanced photoelectrochemical responses. We expect that the GCA-TiO_2 composites should provide good insight on the electrodes for the different applications such as the photoelectrochemical water-splitting cells, the dye-sensitized solar cells, and the batteries.

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