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Research Article

Photocatalytic Reduction of CO_2 Using TiO_2-Graphene Nanocomposites

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TiO_2-graphene (TiO_2-RGO) nanocomposites were prepared *via* a simple chemical method by using graphene oxide (GO) and TiO_2 nanoparticles as starting materials. The morphologies and structural properties of the as-prepared composites were characterized by X-ray diffraction, Raman spectroscopy, N_2 adsorption-desorption measurements, and transmission electron microscopy. TiO_2-RGO nanocomposites exhibited great photocatalytic activity toward reduction of CO_2 into CH_4 (2.10 μmol g^{-1} h^{-1}) and CH_3OH (2.20 μmol g^{-1} h^{-1}), which is attributed to the synergistic effect between TiO_2 and graphene.

1. Introduction

The past few decades have witnessed the problem of global warming, which is dominantly caused by carbon dioxide emissions from fossil fuel consumption. Therefore, seeking for any alternative to minimize CO_2 emission has attracted increasing attention all over the world. The traditional method used to solve this problem is carbon capture and storage, but in fact this problem has never been solved radically because CO_2 does not convert into other substances [1]. The photocatalytic reduction of CO_2 into hydrocarbon fuels was found to be a prospective way [2].

TiO_2 is one of the most promising semiconductor materials used in the photocatalysis due to its excellent stability, nontoxicity, and low price [3]. Graphene, one atomic sp^2-bonded planar carbon nanosheet, is a nearly ideal 2D nanoscale carbon material [4]. Due to the unique structure and excellent electronic, thermal, and mechanical properties, graphene is expected to be catalyst supports [5, 6]. The combination of graphene with TiO_2 can create composites with both the outstanding characters and functions of two components and lead to some additional novel properties. Thus, graphene-based photocatalyst possesses numerous opportunities for the photocatalytic CO_2 reduction field [7].

In the previous researches, Wang et al. prepared TiO_2-RGO composite *via* a single-step aerosol approach, and they also investigated the role of synthesis temperature and TiO_2/GO ratio in CO_2 photoreduction [8]. Tu et al. developed a simultaneous reduction-hydrolysis technique to fabricate TiO_2-graphene hybrid nanosheets for the reduction of CO_2 into CH_4 and C_2H_6 [9]. Tan et al. reported a series of noble metal nanoparticles supported on reduced graphene oxide/TiO_2 *via* a solvothermal method, which exhibited enhanced photocatalytic activities toward the photoreduction of CO_2 into CH_4 gas [10]. Sim et al. reported rapid thermal reduced graphene oxide/Pt-TiO_2 nanotube arrays for enhanced photocatalytic reduction of CO_2 into CH_4 [11]. Kuai et al. achieved a CdS/reduced graphene oxide/TiO_2 core-shell nanostructure, which yielded greater improvements in the photoreduction of CO_2 [12]. Hasan et al. showed the photoelectrocatalytic reduction of CO_2 to CH_3OH and HCOOH using a Cu-RGO-TiO_2 photoelectrocatalyst [13]. Xing et al. coupled boron-doped graphene nanosheets with TiO_2 nanoparticles for enhancing CO_2 photoreduction [14].

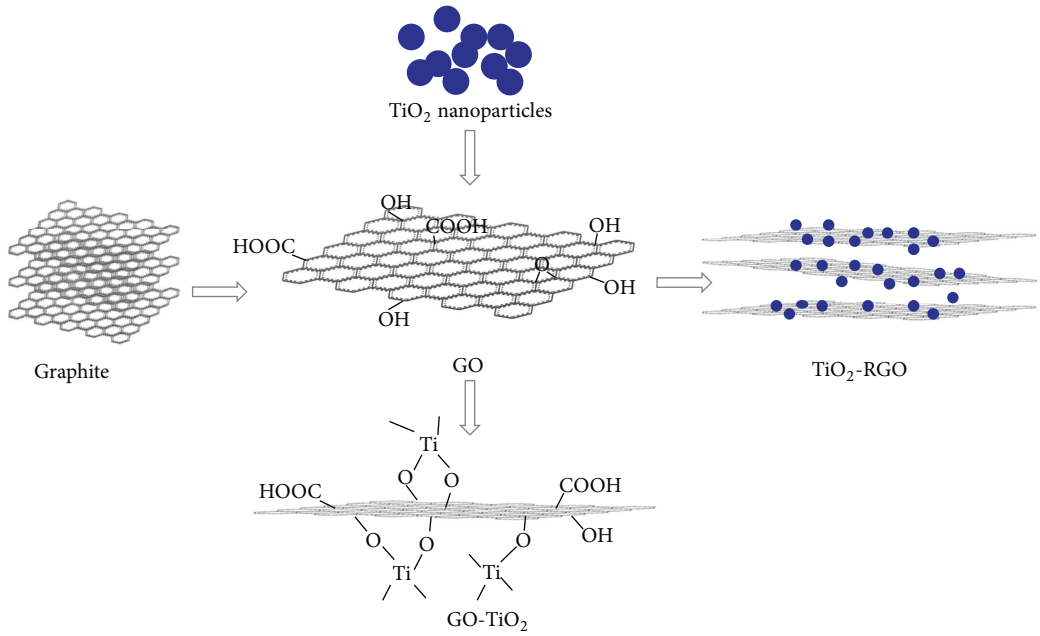

Figure 1: Illustration of the preparation of TiO_2-RGO nanocomposites.

Cheng et al. provided a photoelectrocatalytic technique for reduction of CO_2 into chemicals [15]. Liang et al. demonstrated greater improvements in the photoreduction of CO_2 by a graphene-TiO_2 nanocomposite with low graphene defect densities [16].

Herein, we present a simple and relatively general approach for synthesis of TiO_2-RGO nanocomposites using GO and TiO_2 nanoparticles as starting materials. It is important that the procedure for preparing TiO_2-RGO nanocomposites can be carried out under ambient conditions. The high photocatalytic activity of TiO_2-RGO nanocomposites is confirmed by photocatalytic conversion of CO_2 to reusable hydrocarbons (CH_4 and CH_3OH).

2. Experimental

2.1. Synthesis of TiO_2-RGO Nanocomposites. GO was prepared according to the modification of Hummers methods as described previously [17]. Typically, 0.05 g as-prepared GO dissolves in the 250 mL water in the 500 mL round-bottom flask, yielding an inhomogeneous yellow-brown dispersion. This dispersion was sonicated 20 min using an ultrasonic bath cleaner (Fisher Scientific KQ5200) until it became clear with no visible particulate matter. TiO_2 nanoparticles (0.10 g) were then added into the flask, and the mixture was stirred for 24 h at room temperature. Then hydrazine monohydrate (3.00 mL, 50%) was then added to the above as-prepared product (TiO_2-GO), and the suspension was heated in an oil bath at 100°C under a water-cooled condenser for 24 h, where the RGO sheets gradually precipitated out as a black solid and gradually form the TiO_2-RGO. This product (Cat-2) was isolated by filtration over a medium fritted glass funnel, washed copiously with water and methanol, and dried under vacuum at 60°C. Cat-3 was synthesized using a similar approach and only changed the amount of GO to 0.1 g. Pure TiO_2 was marked as Cat-1.

2.2. Materials Characterization. The samples were characterized by Raman spectrometer (JobinYvon HR 800). Transmission electron microscope (TEM) micrographs were obtained on a Tecnai G20 (Philip) electron microscope. Brunauer-Emmett-Teller (BET) surface area of the catalysts was analyzed by N_2 adsorption and desorption isotherms with a micromeritics ASAP 2020™ physisorption system. X-Ray diffraction (XRD) analysis was recorded on a XRD-6000 X-ray diffractometer (Shimadzu) with Cu Kα radiation (λ = 1.5406 Å).

2.3. Evaluation of Photocatalytic Activity. The photocatalytic activity of the prepared TiO_2-RGO nanocomposites was studied in a double-wall cylindrical quartz reactor at ambient condition with continuous gas flow. Briefly, 0.1 g catalyst was dispersed in 100 mL distilled water containing KOH (0.2 mol L^{-1}). Before the reaction, CO_2 was bubbled into the solution for 30 min to remove any excess air and achieve the adsorption-desorption equilibrium. High pressure mercury lamp was used as the light source (250 W). CH_4 was detected as the sole product in the outlet gas based on gas chromatograph analysis. Methanol was detected by ultraviolet visible spectrophotometer.

3. Results and Discussion

3.1. Characterization of TiO_2-RGO Nanocomposites. Figure 1 shows a schematic procedure for fabricating TiO_2-RGO nanocomposites. In this straightforward procedure, GO was firstly prepared from graphite powder, followed by chemical

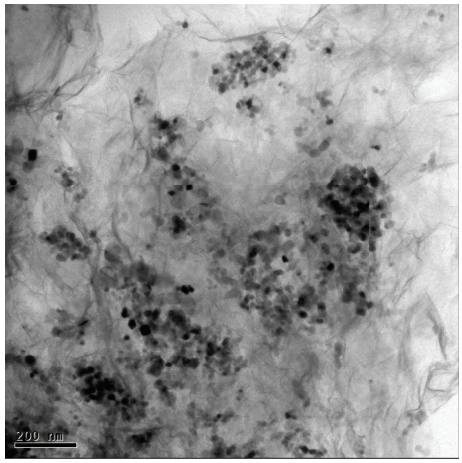

Figure 2: TEM image of TiO_2-RGO nanocomposites.

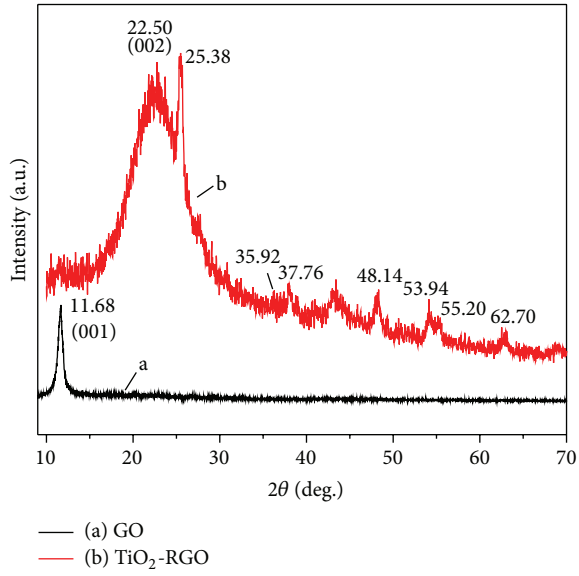

Figure 3: XRD patterns of (a) GO and (b) TiO_2-RGO.

deposited TiO_2 nanoparticles onto GO sheet; the as-prepared materials were reduced through a hydrothermal reaction to obtain TiO_2-RGO nanocomposites.

Figure 2 shows the TEM images of the as-formed TiO_2-RGO nanocomposites. As seen from Figure 2, many nanoparticles adhered to the graphene sheets with little agglomeration, which confirms the successful immobilizing TiO_2 nanoparticles on the graphene sheet. The reason for the effective assembly is that TiO_2 nanoparticles can interact with functional groups such as epoxides, hydroxyl, and carboxylic acids on the GO sheets.

XRD characterization was conducted to determine the crystal structural about GO and TiO_2-RGO, and the results are shown in Figure 3. The pure GO showed a sharp peak at $2\theta = 11.68^\circ$, corresponding to the GO (001) plane with an interlayer spacing of 0.83 nm. It can be found that the interlayer spacing of GO is larger than that of the natural graphite powder because of the introduction of oxygen-containing

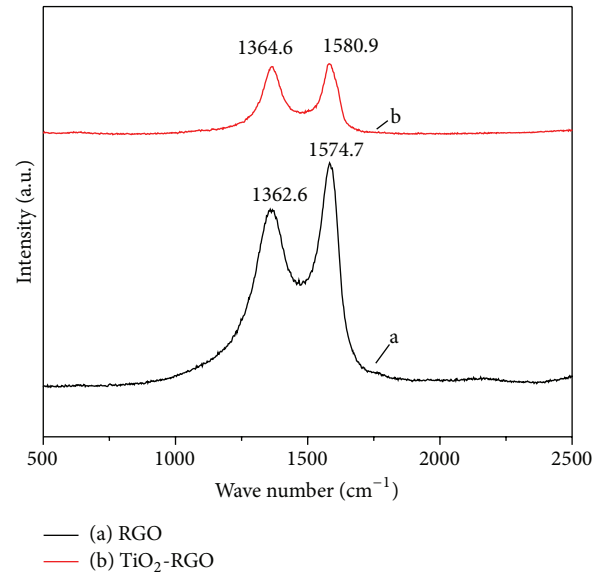

Figure 4: Raman spectra of (a) RGO and (b) TiO_2-RGO.

functional groups onto the surface of carbon sheet. As for TiO_2-RGO, the feature peak of the GO has disappeared and a very broad peak at $2\theta = 22.50^\circ$, corresponding to graphene (002) plane with an interlayer spacing of 0.40 nm, was observed, which confirms the reduction of GO to graphene in the hydrothermal environment. However, there was a small amount of residual oxygen-containing functional groups in the as-formed TiO_2-RGO nanocomposites due to the incomplete reduction of GO sheet to graphene [18]. The same phenomenon was observed in previous studies [19]. The reflection peaks at $2\theta = 25.38$, 35.92, 37.76, 48.14, 53.94, 55.20, and 62.70° can be indexed to (101), (103), (004), (200), (105), (211), and (204) crystal planes of anatase TiO_2. The XRD analysis further confirms the successful preparation of TiO_2-RGO nanocomposites.

Raman spectroscopy was utilized to examine the information about structural changes during the fabrication process. As shown in Figure 4(a), the Raman spectra of RGO exhibited a D-band peak at 1362.6 cm^{-1} and a G-band peak at 1574.7 cm^{-1}. In contrast, the G-band shifts by 6.2 cm^{-1} to a high frequency at 1580.9 cm^{-1} for TiO_2-RGO nanocomposites (Figure 4(b)), which suggests the occurrence of charge transfer between the GO sheet and TiO_2 nanoparticles. It is well known that the intensity ratio of D-band to G-band (I_D/I_G) is characteristic of the extent of disorder present within the material [20]. In our case, I_D/I_G was 0.96 for TiO_2-RGO, and it increased compared to that of the RGO (I_D/I_G = 0.91), exhibiting a greater sp^2 character. Besides, the ratio of the intensities for TiO_2-RGO is slight increased, which confirms the presence of donor molecules on graphene.

To further investigate the specific surface area of TiO_2-RGO, the N_2 adsorption-desorption measurements were carried out at 77 K. Figure 5 shows that the nitrogen adsorption isotherm is a typical IV type curve. Additionally, the loop observed is ascribed as type H3 loops confirming the presence of a mesoporous structure. The specific BET surface

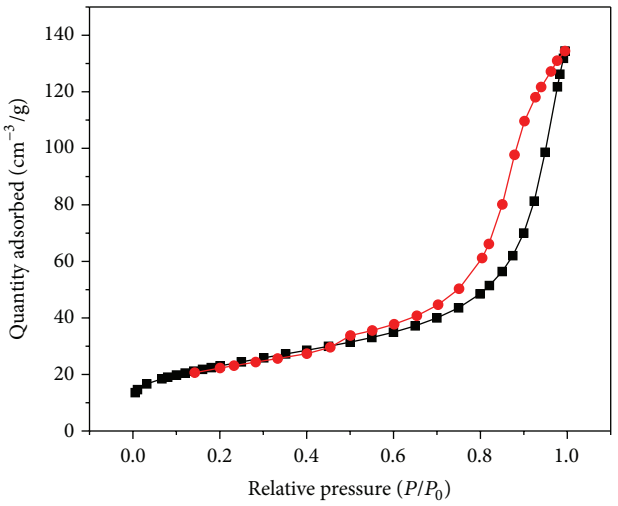

Figure 5: Typical nitrogen adsorption-desorption isotherm of TiO_2-RGO.

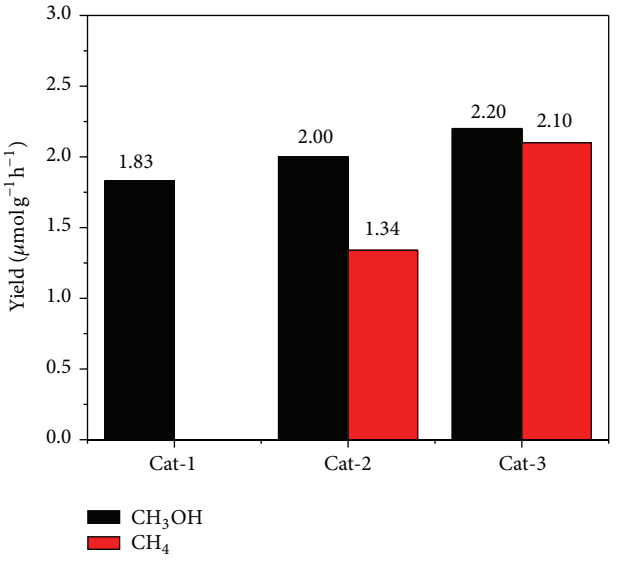

Figure 6: Comparison of photocatalytic activity of samples Cat-1, Cat-2, and Cat-3.

area of the as-prepared TiO_2-RGO was measured to be 80.18 m^2 g^{-1}.

3.2. Photocatalytic Properties of TiO_2-RGO Composites under Ultraviolet Light Irradiation. To evaluate the photocatalytic activity of TiO_2-RGO samples, the photocatalytic CO_2 conversion in the presence of KOH solution was investigated. Figure 6 shows that CO_2 can be photoreduced to CH_3OH by using pure TiO_2 sample (Cat-1). With the addition of graphene amount of photocatalysts, CO_2 can be photoreduced to CH_3OH and CH_4. It is obvious that Cat-3 (2.20 μmol g^{-1} h^{-1} CH_3OH and 2.10 μmol g^{-1} h^{-1} CH_4) exhibits much higher activity than Cat-2 (2.0 μmol g^{-1} h^{-1} CH_3OH and 1.34 μmol g^{-1} h^{-1} CH_4). The CH_3OH yield with TiO_2 was 1.83 μmol g^{-1} h^{-1}. The results demonstrated that the photocatalytic efficiency increased with the increases of graphene amount. With the graphene amount increased from 0 to 50%, the yields of CH_4 and CH_3OH increased simultaneously. It is attributed to the increasing separation efficiency of the photogenerated electrons, because the existence of graphene could offer more active adsorption sites and photocatalytic reaction centers [21]. Furthermore, the yield efficiency increased with the increase of dispersion degree.

4. Conclusions

In conclusion, we present a simple and relatively general approach for synthesis of TiO_2-RGO nanocomposites under ambient conditions by using GO and TiO_2 nanoparticles as starting materials. The results show that CO_2 can be photoreduced to CH_3OH and CH_4 by using TiO_2-RGO samples as photocatalysts. The yields of CH_4 and CH_3OH can reach 2.10 μmol g^{-1} h^{-1} and 2.20 μmol g^{-1} h^{-1}. It is hoped that our current work could pave a way toward the fabrication of TiO_2-RGO hybrid materials and facilitate their significant applications in various fields.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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