Research Article

Photocatalytic Reduction of CO₂ Using TiO₂-Graphene Nanocomposites

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†TiO₂–graphene (TiO₂–RGO) nanocomposites were prepared via a simple chemical method by using graphene oxide (GO) and TiO₂ nanoparticles as starting materials. The morphologies and structural properties of the as-prepared composites were characterized by X-ray diffraction, Raman spectroscopy, N₂ adsorption-desorption measurements, and transmission electron microscopy. TiO₂–RGO nanocomposites exhibited great photocatalytic activity toward reduction of CO₂ into CH₄ (2.10 μmol g⁻¹ h⁻¹) and CH₃OH (2.20 μmol g⁻¹ h⁻¹), which is attributed to the synergistic effect between TiO₂ 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 CO₂ 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 CO₂ does not convert into other substances [1]. The photocatalytic reduction of CO₂ into hydrocarbon fuels was found to be a prospective way [2].

TiO₂ 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 sp²-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 TiO₂ 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 CO₂ reduction field [7].

In the previous researches, Wang et al. prepared TiO₂–RGO composite via a single-step aerosol approach, and they also investigated the role of synthesis temperature and TiO₂/GO ratio in CO₂ photoreduction [8]. Tu et al. developed a simultaneous reduction-hydrolysis technique to fabricate TiO₂–graphene hybrid nanosheets for the reduction of CO₂ into CH₄ and C₂H₆ [9]. Tan et al. reported a series of noble metal nanoparticles supported on reduced graphene oxide/TiO₂ via a solvothermal method, which exhibited enhanced photocatalytic activities toward the photoreduction of CO₂ into CH₄ gas [10]. Sim et al. reported rapid thermal reduced graphene oxide/Pt-TiO₂ nanotube arrays for enhanced photocatalytic reduction of CO₂ into CH₄ [11]. Kuai et al. achieved a CdS/reduced graphene oxide/TiO₂ core-shell nanostructure, which yielded greater improvements in the photoreduction of CO₂ [12]. Hasan et al. showed the photoelectrochemical reduction of CO₂ to CH₃OH and HCOOH using a Cu-RGO-TiO₂ photoelectrocatalyst [13]. Xing et al. coupled boron-doped graphene nanosheets with TiO₂ nanoparticles for enhancing CO₂ photoreduction [14].
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\(_3\)OH).

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 into 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 K\(_\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)).

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
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 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$^\circ$ 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 slightly 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
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$_3$OH by using pure TiO$_2$ sample (Cat-1). With the addition of graphene amount of photocatalysts, CO$_2$ can be photoreduced to CH$_3$OH and CH$_4$. It is obvious that Cat-3 (2.20 μmol g$^{-1}$ h$^{-1}$ CH$_3$OH 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$_3$OH and 1.34 μmol g$^{-1}$ h$^{-1}$ CH$_4$). The CH$_3$OH 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$_3$OH 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$_3$OH and CH$_4$ by using TiO$_2$-RGO samples as photocatalysts. The yields of CH$_4$ and CH$_3$OH 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.

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