Reduction of CO$_2$ to Methanol on Photocatalysts of ZnO/rGO in Isopropanol

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Keywords: ZnO nanoparticles, Graphene, Hydrothermal synthesis, Photocatalytic reduction, CO$_2$, Methanol.

Abstract. The hydrothermal synthesis procedure was used to prepare the photocatalysts of ZnO nanoparticles (NPs) anchored on graphene (Gr). The activity enhancement of pristine ZnO NPs by anchored on graphene was evaluated for photocatalytically reducing CO$_2$. The experimental results showed that the graphene could significantly improve the photocatalytic activity, where ZnO NPs anchored on 30wt% Gr showed the best photocatalytic performance for achieving the highest yield of methanol up to 2772.9 µmol/h·g$_{cat}$. The enhanced photocatalytic could be attributed to the following reasons. The first one was that the light was harvested on the 2D graphene dispersed ZnO NPs uniformly. And the second one was the combination of ZnO NPs and graphene in ZnO NPs/Gr photocatalysts could transfer charge to separate photogenerated electron and hole efficiently, which was confirmed by the photoluminescence analysis.

Introduction

With the development of economy, so many industries have come into being that excess emission of CO$_2$ is resulting in global warming. Reducing CO$_2$ in atmosphere has become the most urgent environmental issue in recent decades[1,2]. In 1972 Fujishima et al[3] firstly reported splitting water into oxygen and hydrogen in the presence of the TiO$_2$ electrode under irradiation. At the present, more and more photocatalysts have been found. Among of them ZnO is a wide band gap semiconductor and a promising photocatalyst due to its non-toxic safety, low price, easy preparation, good chemical stability and so on[4]. By now variety of morphologies and synthesis approaches of ZnO have been reported and applied dominantly as photocatalysts for degradation of pollutants and reduction of CO$_2$[4-6]. However, the pristine ZnO is restricted as photocatalyst because of its wide band gap for ultraviolet absorption and quick recombination of electron and hole. Although many efforts have been paid to improve the photocatalytic performance of ZnO[7-9], its photocatalytic activity is still unsatisfactory.

Graphene is a kind of carbonaceous two-dimensional material composed of single-layer carbon atoms[10] due to its advantages of high specific surface area, excellent electronic conductivity and high transparency. The graphene combined with photocatalysts of semiconductors has been proved to effectively enhance the performance of photocatalysts[11]. We combine ZnO and graphene to prospect making a significant enhancement in photocatalytic reduction of CO$_2$ comparing to pure ZnO and graphene. Yokomizo et al. prepared graphene–ZnO nanoparticles with good performance of photocatalytic reduction by the irradiation of UV light[12]. However, no research have been reported that the combine ZnO with graphene exhibits their excellent characteristics to effectively enhance the activity of photocatalytic reduction of CO$_2$.

Experimental

Synthesis of ZnO/Gr Composites

The graphite powders were oxidized to form graphite oxide (GO) by a modified Hummers' method[13,14]. 1.387 g (0.01 mol) of ZnCl$_2$ powder and 0.80 g (0.02 mol) of NaOH were dissolved in two 100 mL C$_6$H$_{12}$O$_4$ respectively under the help of 1 h sonication to accelerate dissolution. The prepared two solutions were mixed, which then was heated to 90°C and refluxed for 3 h under
stirring and further heated to 120 °C for keeping 2 h. The finally formed slurry was centrifuged and washed several times with ethanol and deionized water. The precipitate was dried at 80 °C for 10 h to obtain the white powder of ZnO. Before centrifugation in the above procedure the ZnO precursor was obtained and would be used to synthesize ZnO/Gr. The different amounts of the ZnO precursor were mixed under stirring with the 1 mg/mL GO. Then the mixture was transferred into a Teflon-lined autoclave and at 120°C kept for 3 h. The obtained ZnO/Gr composites was centrifuged, washed three times with ethanol and deionized water and dried overnight under vacuum at 60°C.

**Photocatalytic Reduction of CO**2

The photocatalytic reactor was homemade and sealed with a quartz window for transmitting the light from a 250W high pressure mercury lamp. The reaction temperature was maintained at 20°C. For each batch of evaluation 20 mg photocatalyst and 20 mL isopropanol were added into the reactor, CO₂ was passed through the isopropanol in reactor for 30 min to purge the air. Turned on the light and the reaction was carried out for 10 h. The obtained liquid products were analyzed by a gas chromatograph (BRUKER, 456-GC) using hydrogen flame detector (FID) and N₂ as carrier gas.

**Results and Discussion**

**The XRD Analysis**

Figure 1 showed the XRD patterns of the prepared pure ZnO and different mass percents of graphene in ZnO NPs/Gr. All of the peaks were consistent with JCPDS card number 36-1451, which proved the prepared ZnO being hexagonal wurtzite structure. The diffractive peak of Gr was shown at 13.29°. However, the intensity of Gr was too weak to observe the obvious change in different mass percents. According to the formula of Scherrer, the average particle sizes of ZnO in ZnO NPs/Gr were about 17 nm and well dispersed on Gr, which could be observed on the image of TEM.

**The SEM and TEM Analyses**

The typical morphologies and microstructures of the samples were observed by SEM and TEM and shown in Figure 2 Figure 2 (a) showed ZnO NPs had uniform sizes but poor dispersion and agglomeration. In Figure 2 (b) the ZnO NPs anchored on graphene to form ZnO NPs/Gr, in which the sizes of ZnO NPs were obviously reduced compared to pure ZnO NPs. Meanwhile the graphene efficiently inhibited the aggregation of ZnO NPs in ZnO NPs/Gr. The HRTEM images of Figure 2(c) exhibited a lattice spacing of 0.28 nm, corresponding to the crystal face (100) of ZnO in ZnO NPs/Gr. For the selected region EDX spectrum of ZnO NPs/Gr in Figure 2(d) illustrated that the sample did consist of three elements: C, Zn and O, without any impurities.
The UV-Vis DRS Spectrometer Analysis

Figure 3 displayed the UV-Vis Diffuse Reflectance Spectroscopy (DRS) of pure ZnO NPs and different ZnO/Gr composites. Because of the interaction between ZnO nanoparticles and graphene, as for ZnO/Gr composites, the peak had a slight offset\cite{15,16}. And the absorption of ZnO/Gr composites was stronger than pure ZnO nanoparticles when the wavelength was longer than 400 nm due to the introduction of graphene. It can be also seen the bandgaps of pure ZnO and ZnO/Gr composites were estimated through the formula of Kubelka-Munk\cite{17}. The bandgaps energy of ZnO/30\%Gr composites was changed to 2.68 eV compared to the value of pure ZnO nanoparticles 3.1 eV.

The Photoluminescence Emission Spectrum Analysis

Figure 4 showed the peak strength of ZnO nanoparticles was much higher than those of the ZnO NPs/Gr which was mainly due to excitation recombination among photo-electrons and holes\cite{18}. Moreover, the PL intensity of ZnO/Gr composites decreases obviously compared to pure ZnO nanoparticles, indicating that in the samples of ZnO/Gr composites the separation efficiency of electrons and holes showed better result.

The Activities of the ZnO NPs/Gr Photocatalysts

Figure 5 showed the average generation rate of methanol in 10h. The methanol formation rate of the pure ZnO NPs was 763.9 $\mu$mol/h·g$_{cat}$. With the percentage variance of the graphene, the photocatalysts showed different photocatalytic activities. When ZnO NPs anchored on 30wt\% graphene its photocatalytic activity was up to the highest value of 2772.9 $\mu$mol/h·g$_{cat}$. It can be also seen that the ZnO NPs/Gr exhibited much higher photocatalytic activities than that of the pure ZnO NPs because of the graphene transferring electron in time. Due to the high electronic conductivity
of graphene, which accelerated the transfer of the photogenerated carriers on ZnO NPs, simultaneously suppressed the recombination of electron and hole. The prolonged lifetime of photoelectrons finally improved the activity of photocatalyst.

![Figure 4. PL spectra of ZnO, various contents of ZnO NPs/Gr.](image)

![Figure 5. Rates of methanol over ZnO NPs/rGO with different amounts of graphene.](image)

**Conclusions**

In this paper ZnO NPs/Gr were prepared, characterized and evaluated. The ratio of graphene to ZnO affected the light absorbance and photocatalytic activities of ZnO NPs/Gr obviously, and the ZnO NPs/30%Gr approach to the highest photocatalytic activity at the methanol formation rate of 2456.79 µmol/h·g<sub>cat</sub>. The graphene in ZnO NPs/Gr composites promoted the timely transformation of photo-generated electrons, inhibited the recombination of electron and hole and enhanced the activity of photocatalytic reduction of CO<sub>2</sub>. In addition, the reaction mechanism of photocatalytic reduction of CO<sub>2</sub> to form CH<sub>3</sub>OH in (CH<sub>3</sub>)<sub>2</sub>CHOH was proposed by comprehensive analysis.

**Acknowledgement**

We genuinely appreciate financial support by the National Natural Science Foundation of China (NSFC, No. 21176192 and 21776220).

**Reference**


