

One-Step Synthesis of Nanostructured Graphene Nanocomposites for CO₂ Capture and Photoreduction

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Introduction:

As knowledge of the effect that carbon emissions have on the ecosystem increases, greater attention is being drawn to decreasing carbon dioxide (CO₂) production [1]. Carbon capture and sequestration (CCS) is one method of reducing carbon emissions, often realized with amine adsorption [2], and followed by CO₂ underground storage [1]. CCS is energy intensive and has unknown associated risks [1]. An alternative process, carbon capture and conversion (CCC), can improve CCS using solar energy to reduce CO₂ to useable products, eliminating CO₂ storage risks while meeting energy needs with an available source [1]. CCC can be realized using semiconductor photocatalysis to absorb solar energy and produce electron-hole pairs supporting reduction and oxidation mechanisms [1].

We sought to improve the CCC catalyst by synthesizing a ternary-structured nanoball consisting of ethylenediamine functionalized reduced graphene oxide-titanium dioxide (EDA/rGO-TiO₂) using a one-step furnace aerosol reactor (FuAR) method. TiO₂ was used to provide a suitable semiconductor [1]; rGO provided a conductive support with high surface area and morphology to increase charge transfer and reduce agglomeration [3]; EDA functionalization provided surface groups to increase CO₂ adsorption [2]; FuAR synthesis allowed for fast, relatively inexpensive production that supports bulk implementation [3]. EDA/rGO-TiO₂ was tested as a CCC photocatalyst to determine its effectiveness.

Experimental:

EDA/rGO-TiO₂ was synthesized employing the FuAR system shown in Figure 1. We prepared a precursor solution by mixing 37.6 μ L TiO₂ suspension (40 wt%), 10 mL EDA solution ($\geq 99.5\%$), 50 mL GO suspension (1.4 wt%), and 140 mL deionized water in a covered beaker stirring magnetically at 4000 rpm for 24 hours. The solution was loaded into a Collision Nebulizer and the furnace was set to 200°C. Compressed nitrogen gas entered through a valve at a pressure of 14 psi, traveled into the Collision Nebulizer and atomized the solution into micrometer-sized droplets. The droplets flowed through the furnace wherein the droplet water evaporated, particles formed and passed through a diffusion dryer absorbing excess water before collection on a filter.

We repeated the procedure varying the furnace synthesis temperature to 150, 300, 400, 500, 600 and 800°C, and at 200°C furnace synthesis temperature varying the volumetric ratio of EDA to GO in solution from 10/50 to 15/50, 20/50, 25/50 and 30/50 EDA/GO. The rGO and rGO-TiO₂ particles were synthesized similarly at furnace temperatures of 200°C, 400°C and 600°C from solutions of 50 mL GO (1.4 wt%) and 150 mL deionized water, the latter incorporating 37.6 μ L TiO₂ (40 wt%). TiO₂ particles were obtained by drop-casting 10 mg TiO₂ onto a filter. EDA/rGO-TiO₂ was characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy.

We tested EDA/rGO-TiO₂ as a catalyst in CO₂ photoreduction employing the reactor depicted in Figure 2. EDA/rGO-TiO₂ was placed on deionized water-dampened glass wool inside the reaction chamber. Compressed CO₂ was set to maximum flow (> 42 mL/min) into a water bubbler using a mass flow controller to generate a mixture and flow into the chamber to purge the system. After one hour, the ultraviolet lamp was turned on illuminating EDA/rGO-TiO₂. The CO₂ flow rate was lowered to 3 mL/min. The reaction duration was 12 hours during which gas concentrations were recorded after passing through the chamber using gas chromatography (GC).

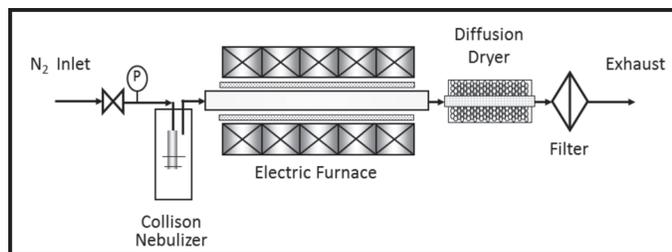


Figure 1: Furnace aerosol reactor.

Results and Discussion:

TEM, given in Figure 3, and SEM showed the GO sheets crumpled into nanoballs without agglomeration and dispersed with TiO_2 , which indicates EDA/rGO- TiO_2 maintained high surface area for CO_2 adsorption, amine functionalization and charge transfer with TiO_2 intercalation. FTIR and Raman spectra in Figure 4 allowed for surface functional group characterization of EDA/rGO- TiO_2 . EDA/rGO- TiO_2 FTIR and Raman spectra contained characteristic TiO_2 peaks indicating successful TiO_2 incorporation. EDA/rGO- TiO_2 FTIR spectra displayed a C = C graphene peak indicating that GO was reduced; characteristic C-N, N-H and CH_2 peaks evidenced successful EDA functionalization. EDA/rGO- TiO_2 Raman spectra showed characteristic D and G bands of rGO. The greater D/G band intensity ratio indicates a greater number of surface functional groups and defects in the nanoballs and provided evidence of EDA incorporation and remaining GO oxide groups. Spectral analysis of varying parameters showed that synthesis temperature and solution composition effected particle composition. EDA and reduction evidence became more intense and showed consistency at temperatures greater than 200°C and as the EDA/GO ratio increased, which indicated better EDA functionalization and GO reduction with greater temperature and EDA concentration.

Spectra comparison over periods of time showed EDA/rGO- TiO_2 maintained similar surface functional groups over 10 days and exhibited numerous variations after 40 days. This indicated EDA/rGO- TiO_2 has relatively stable surface composition over short periods of time, but significantly alters over extended periods of time. GC measurements using EDA/rGO- TiO_2 synthesized at 200°C with a 10/50 EDA/GO ratio showed carbon monoxide production indicating that the particles are functional catalysts for CO_2 reduction. Repeating the experiment with the same particles showed positive CO_2 reduction results indicating that the particles can be regenerated for reuse.

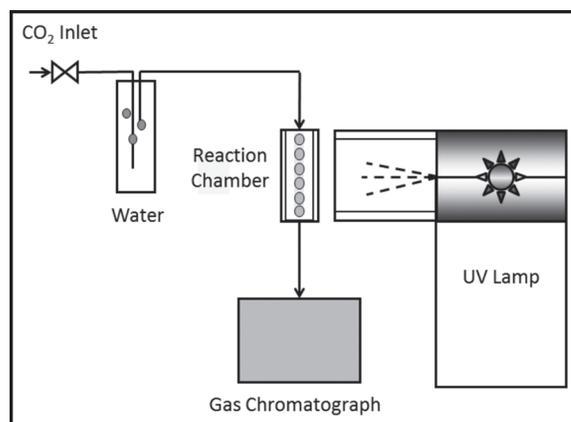


Figure 2: CO_2 photoreduction reactor.

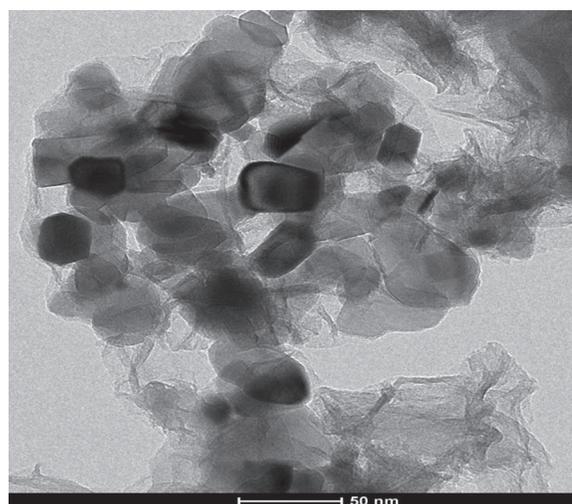


Figure 3: TEM image of EDA/rGO- TiO_2 .

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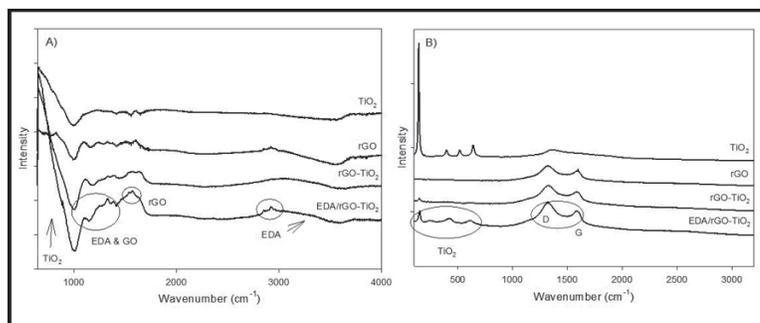


Figure 4: a) FTIR and b) Raman spectra varying particle composition.

References:

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