Supporting information (SI) for

Crumpled Reduced Graphene Oxide - Amine – Titanium Dioxide Nanocomposites for Simultaneous Carbon Dioxide Adsorption and Photoreduction

Yao Nie[1], Wei-Ning Wang[2], Yi Jiang[1], John Fortner[1], and Pratim Biswas[1*]

[1]Department of Energy, Environmental and Chemical Engineering
Washington University in St. Louis
St. Louis, MO 63130, USA
[2]Department of Mechanical and Nuclear Engineering, Virginia Commonwealth
University, Richmond, Virginia 23284, USA

Catalysis Science & Technology

*To whom correspondence should be addressed:

Pratim Biswas: Tel: +1-314-935-5548; Fax: +1-314-935-5464; E-mail:

pbiswas@wustl.edu

S1. UV-Vis absorption spectrum of TiO_2, CGO (at 200 °C), CGOTI (TiO_2/GO 20%, at 200 °C) and CGOATI (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C) (20mg/L).

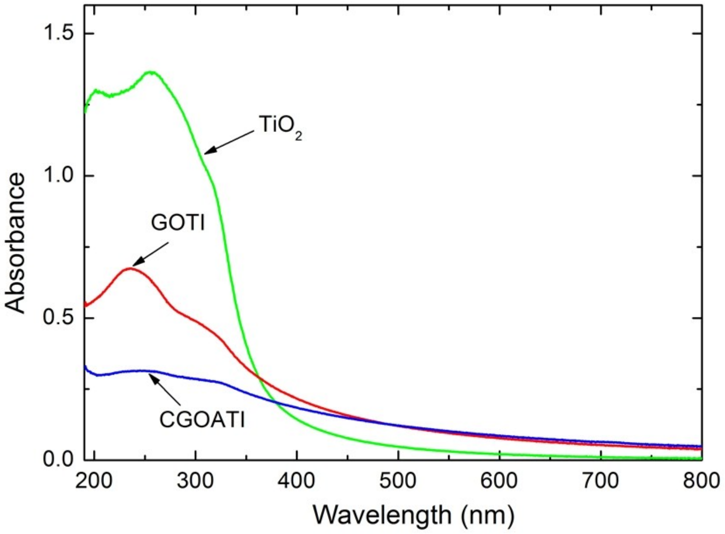

Figure S1. UV-Vis absorption spectrum of TiO_2, (at 200 °C), CGOTI (TiO_2/GO 20%, at 200 °C) and CGOATI (TiO2/GO 20%, EDA/GO 15:1, at 200 °C) (20mg/L).

From the figure above, an extended absorption range was observed when compared to bare TiO_2, which is due to the band gap narrowing of TiO_2 when participating in Ti-O-C interactions [1]. This extension makes the graphene-modified TiO_2 have an advantage over bare TiO_2 in the utilization of light.

S2. Light spectrum of the Xe lamp.

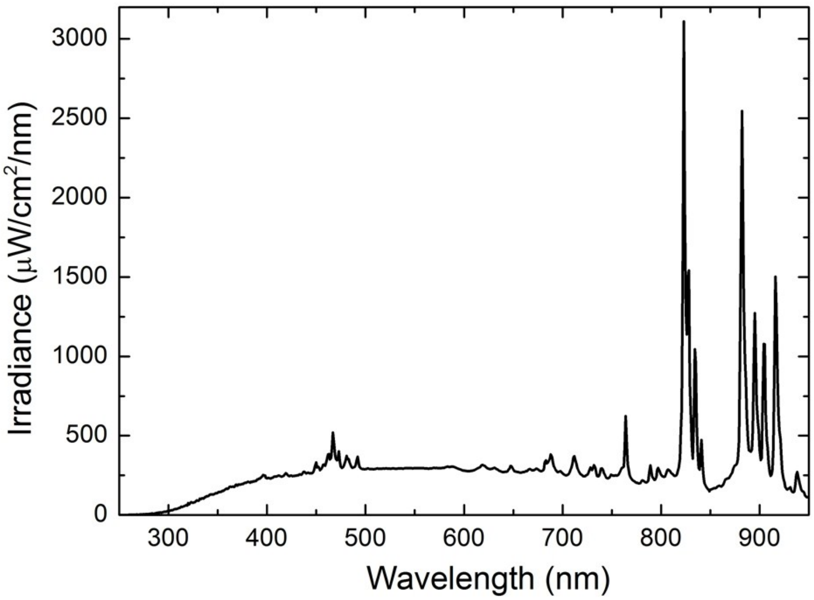

Figure S2. Light spectrum of the Xe lamp.

For TiO_2 nanoparticles with a bandgap of 3.2 eV, the effective UV range is 250 – 388 nm. By integration, the accumulated intensity in this effective UV range was calculated to be 11.5 mW/cm^2.

S3. Calculation of the average distance between two TiO_2 NPs in a typical CGOATI nanocomposite

By assuming the TiO_2 NPs are spherical with average size 22±6 nm (calculated from TEM images), the number of TiO_2 NPs in a typical nanocomposite (480nm) with an 85% void factor can be estimated using the following equation

$$n_{TiO_2\,NPs} = \frac{V_{measured,TEM} \times (1 - void\ \ factor\%)}{V_{TiO_2\,NPs}} = \frac{(D_{measured,TEM})^3 \times (1 - void\ \ factor\%)}{(D_{TiO_2\,NPs})^3},$$

where $V_{measured,TEM}$, $V_{TiO2,NPs}$ are the volumes of the typical nanocomposite and TiO_2 NP, and $D_{measured,TEM}$, $D_{TiO2,NPs}$ are the diameters of the typical nanocomposite and the TiO_2 NP measured from TEM images respectively.

In this specific condition, the number of TiO_2 NPs encapsulated in the typical nanocomposite is about 1550. With the assumption that all the TiO_2 NPs are evenly distributed inside the nanocomposite, the average distance between two TiO_2 NPs can be calculated as

$$d = \Big(\frac{V_{measured,TEM}}{n_{TiO_2\,NPs}\,{}^{\pi}\!/\!{}_{6}}\Big)^{1/3} - D_{TiO_2\,NPs} = \Big(\frac{(D_{measured,TEM})^3}{n_{TiO_2\,NPs}}\Big)^{1/3} - D_{TiO_2\,NPs}.$$

The average distance between two TiO_2 NPs is calculated to be around 20 nm, which indicates the TiO_2 NPs (22±6 nm) are well separated.

S4. Background testing of CGOATI nanocomposites (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C) with light on, where nitrogen (N_2) was the source gas.

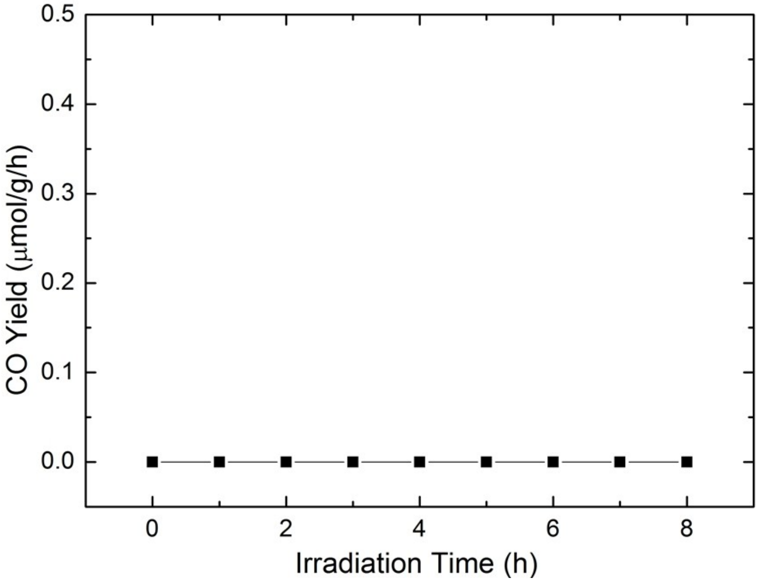

Figure S3. Background testing of CGOATI nanocomposites (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C), where nitrogen (N_2) was the source gas. CO was either not produced or was below our detection limit during this process.

S5. Background testing of CGOATI nanocomposites (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C) with light on, where nitrogen (N_2) was the source gas.

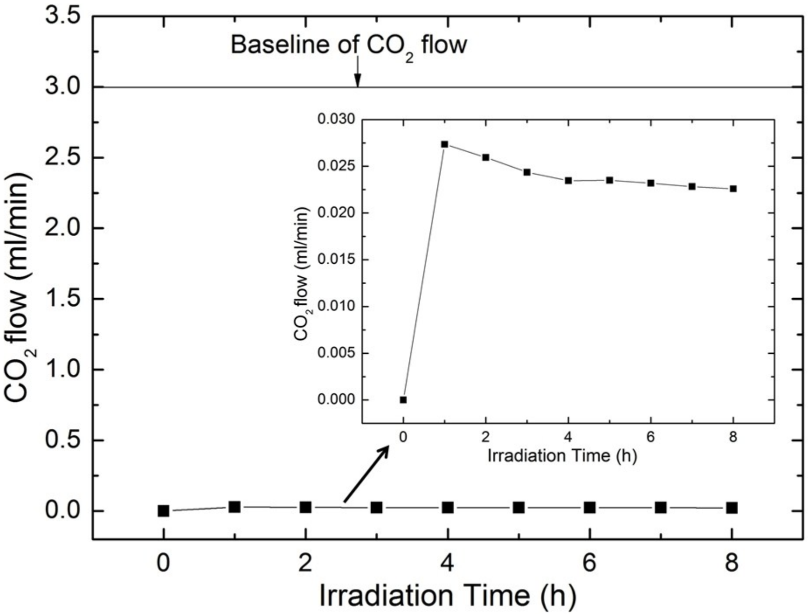

Figure S4. Background testing of CGOATI nanocomposites (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C), where nitrogen (N_2) was the source gas. The baseline of CO_2 flow means the flow in the actual CO_2 photoreduction analysis (not control experiments). The ratio of produced CO_2 to the baseline CO_2 is about 0.01.

S6. Isotope experiments

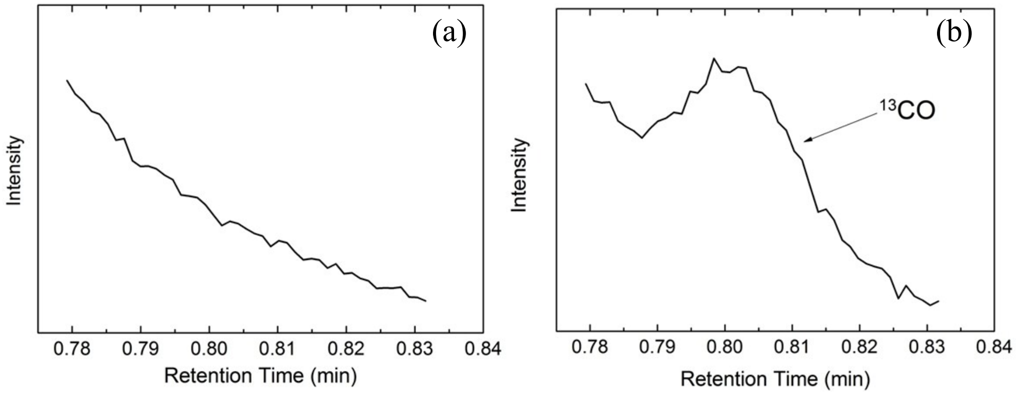

Figure S5. The mass chromatography spectra of ^{13}CO (m/z=29), (a) before UV-irradiation; (b) generated from UV-irradiated CGOATI nanocomposites (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C) after 2h.

S7. Reaction stoichiometry

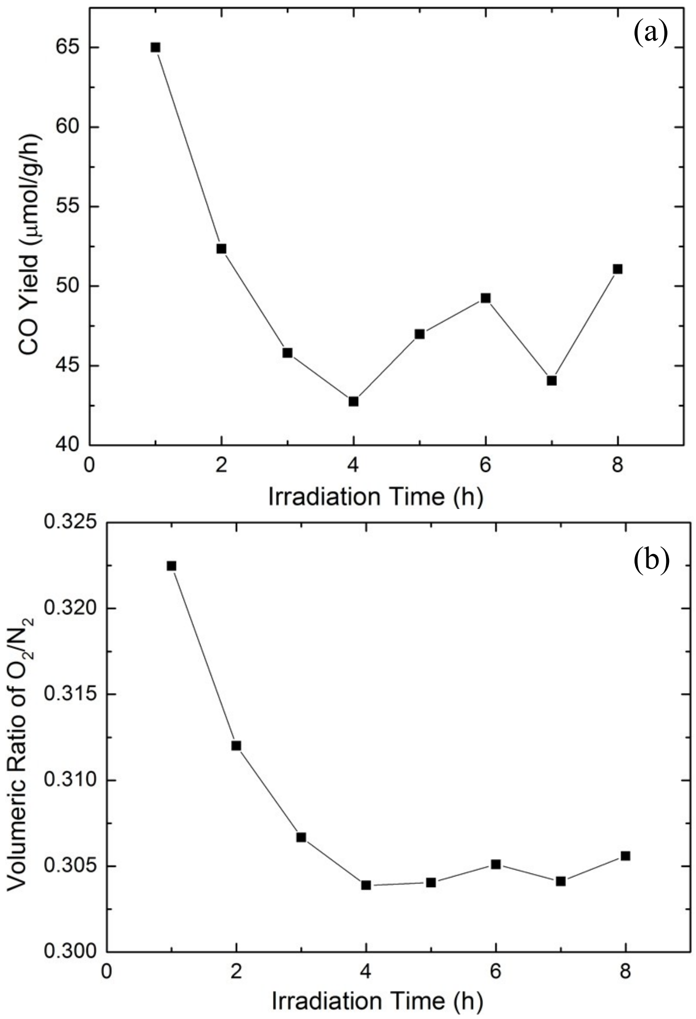

Figure S6. (a) The CO yield, (b) volumetric ratio of O_2/N_2, as a function of irradiation time, with CGOATI nanocomposites (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C) as the catalyst.

The concentrations of O_2 and N_2 in the effluent gas were also monitored during the CO_2 photoreduction experiments using CGOATI. There was background O_2 detected in the reactor effluent gas at the beginning of the test, possibly because the reactor was not well vacuumed out before purging it with the CO_2-H_2O mixture and possibly because of the low concentration impurity gases in the CO_2 cylinder. Hence, a better indicator of O_2 production from the photocatalytic reaction is the volumetric ratio of O_2/N_2 in the effluent gas. As shown in the figures below, the time dependence of the O_2/N_2 ratio is well correlated with that of CO production, which implies the ratio of oxidation and reduction products meets stoichiometry.

S8. Apparent quantum efficiency calculation

The photoreduction performance can be characterized by the photochemical apparent quantum efficiency (quantum yield), ϕ, which is defined as a measure of the molar fraction of incident photons that result in CO_2 reduction products [2]. For the case that CO is the product, apparent quantum efficiency can be calculated by the following equation, as two electrons are required to convert one CO_2 molecule to one CO molecule [3].

$$\phi(\%) = \frac{2 \times CO\ yield\ (mol)}{incident\ photon\ (mol)} \times 100\% \qquad (1)$$

The highest CO yield within the 8 hours UV irradiation was taken for calculation of quantum efficiency. The moles of incident photon were calculated using the following equation:

$$incident\ photon\ (mol) = \frac{total\ incident\ energy}{average\ photon\ energy \times N_A} \qquad (2)$$

where N_A is the Avogadro's constant.

The photon energy at a certain wavelength can be calculated by:

$$E = \frac{hc}{\lambda} \qquad (3)$$

where h, c and λ are Planck constant, speed of light and wavelength of light, respectively. The average photon energy can be estimated by averaging the photon energy from 250 to 388 nm.

The constants that were used for the calculations are listed as below:

Light intensity in the effective light range:	11.5 mW/cm^2
Deposited film diameter (circle):	4.2 cm
Average photon energy:	6.85×10^{-19} J
Yield of CO:	65 µmol/g/h

Mass of the catalyst used: 1.0 mg

Based on Eq. (1), the ϕ was calculated to be 0.0094%.

S9. FTIR analysis of CGOTI and CGOATI samples in the range 650-2000 cm^{-1}.

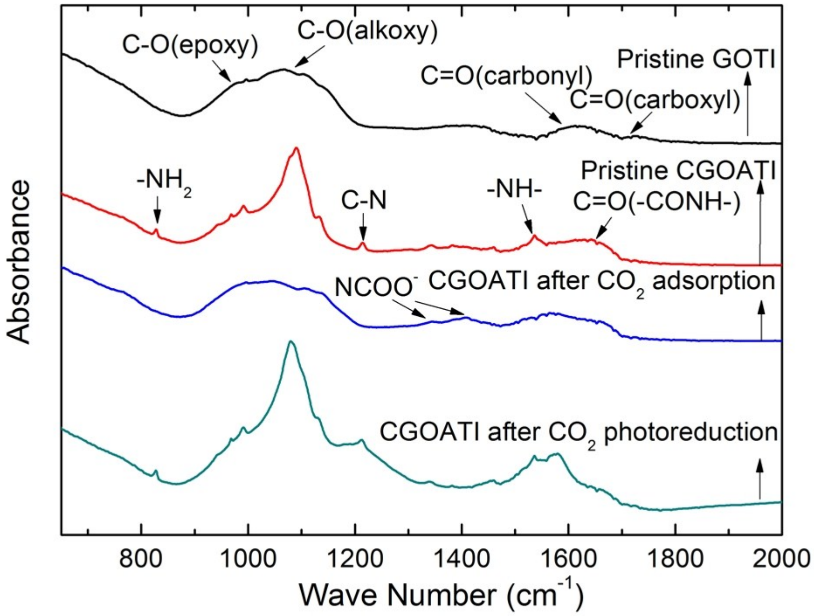

Figure S7. FTIR analysis of pristine CGOTI (TiO$_2$/GO 20%, at 200 °C), pristine CGOATI (TiO$_2$/GO 20%, EDA/GO 15:1, at 200 °C). Also shown are the spectra for the samples, CGOATI after CO$_2$ adsorption (only) and CO$_2$ adsorption and photoreduction.

S8. The I_D/I_G ratio and resistivity of CGOTI (TiO_2/GO 20%) samples with different synthesis temperatures

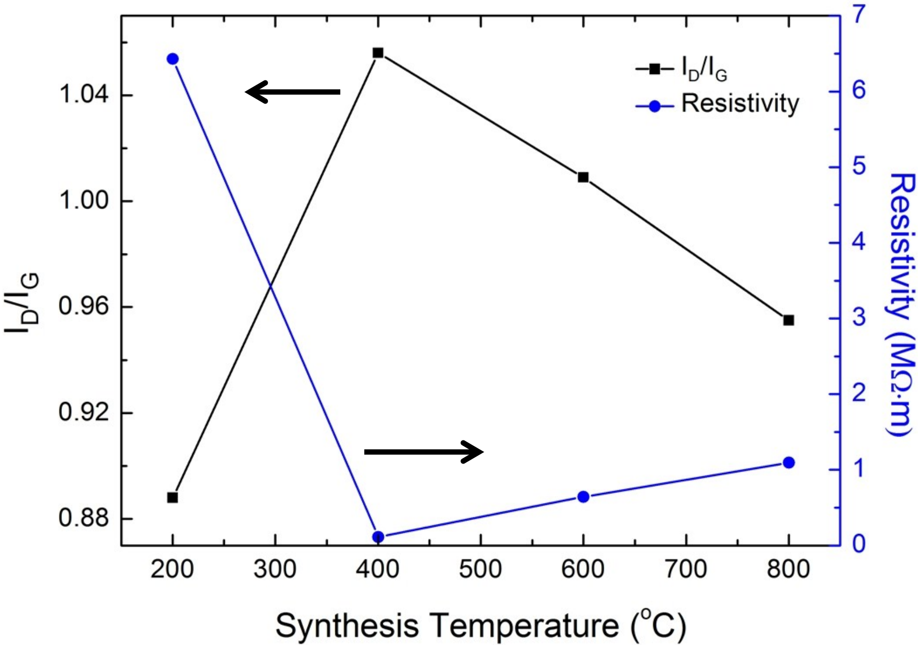

Figure S8. The I_D/I_G ratio and resistivity of CGOTI samples (TiO_2/GO 20%) with different synthesis temperatures.

S9. CO_2 photoreduction of CGOATI (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C) nanocomposites after two cycles.

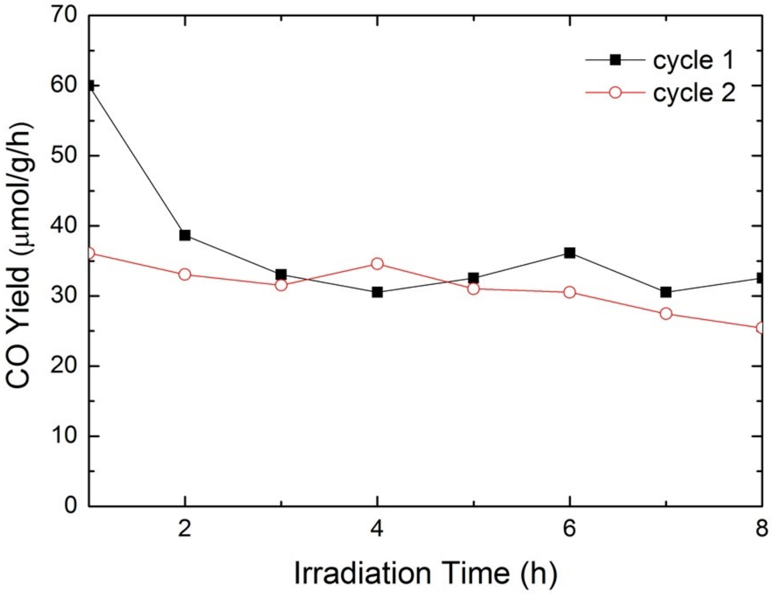

Figure S9. CO_2 photoreduction of CGOATI (TiO_2/GO 20%, EDA/GO 15:1, at 200 °C) nanocomposites after two cycles.

References

1. Sakthivel, S.; Kisch, H., Daylight photocatalysis by carbon-modified titanium dioxide. *Angewandte Chemie International Edition* **2003,** *42*, (40), 4908-4911.
2. Morris, A. J.; Meyer, G. J.; Fujita, E., Molecular approaches to the photocatalytic reduction of carbon dioxide for solar fuels. *Accounts of Chemical Research* **2009,** *42*, (12), 1983-1994.
3. Li, Y.; Wang, W.-N.; Zhan, Z.; Woo, M.-H.; Wu, C.-Y.; Biswas, P., Photocatalytic reduction of CO 2 with H 2 O on mesoporous silica supported Cu/TiO 2 catalysts. *Applied Catalysis B: Environmental* **2010,** *100*, (1), 386-392.