Supporting information (SI) for
Crumpled Reduced Graphene Oxide - Amine – Titanium Dioxide Nanocomposites for Simultaneous Carbon Dioxide Adsorption and Photoreduction

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

Figure S1. UV-Vis absorption spectrum of TiO₂, (at 200 °C), CGOTI (TiO₂/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 TiO₂, which is due to the band gap narrowing of TiO₂ when participating in Ti-O-C interactions [1]. This extension makes the graphene-modified TiO₂ have an advantage over bare TiO₂ 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

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

where $V_{measured,TEM}$, $V_{TiO_2,NPs}$ are the volumes of the typical nanocomposite and TiO$_2$ NP, and $D_{measured,TEM}$, $D_{TiO_2,NPs}$ 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

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

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$_2$O 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), $\phi$, 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].

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

(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:

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

(2)

where $N_A$ is the Avogadro’s constant.

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

$$
E = \frac{hc}{\lambda}
$$

(3)

where $h$, $c$ and $\lambda$ 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: $6.85 \times 10^{-19}$ J
- Yield of CO: 65 μmol/g/h
Mass of the catalyst used: 1.0 mg

Based on Eq. (1), the $\phi$ 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

