

## Supporting Information

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### **Cu<sub>2</sub>O/Reduced Graphene Oxide Composites for the Photocatalytic Conversion of CO<sub>2</sub>**

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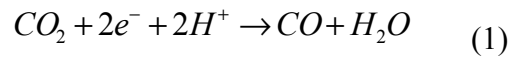
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## 1. Calculation of apparent quantum yield

Quantum yield is an important factor to evaluate the performance of photocatalysts, which is defined as the following equation:<sup>[1,2]</sup>

$$QY\% = \frac{\text{Number of reacted electron}}{\text{Number of incident photon}} \times 100$$

Assuming 2 electrons consumed per CO molecule evolved according to reaction (1), the number of reacted electrons can be substituted by twice the number of CO molecules evolved.



As a result, the initial quantum yield can be estimated by the equation:<sup>[3]</sup>

$$AQY\% = \frac{[CO] \times 2 \times N_A}{H \times A \times \frac{\lambda}{hc} \times t}$$

Where:

[CO] is the CO amount (mol) after 30 minutes (initial)

$N_A$  is the Avogadro's number ( $\text{mol}^{-1}$ )

H is the apparent light input at the photocatalyst ( $\text{W} \cdot \text{m}^{-2}$ )

A is the base reactor area ( $\text{m}^2$ )

$h$  is the Planck's constant ( $\text{J} \cdot \text{s}$ )

$c$  is the speed of light ( $\text{m} \cdot \text{s}^{-1}$ )

$\lambda$  is the light wavelength (m)

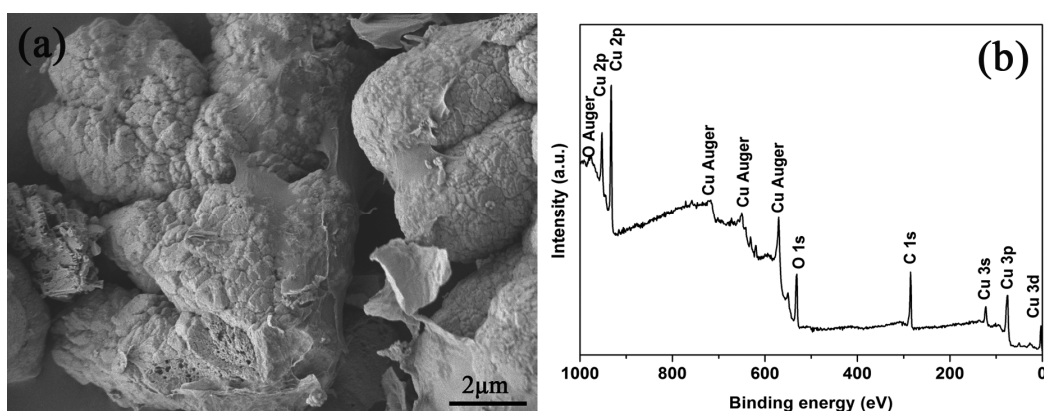
$t$  is the time (s)

The quantum yield for the CO production was measured using a similar experimental setup, with a band pass filter ( $\lambda=400$  nm). The spatial average light power density after the 400 nm band pass filter

and flat borosilicate glass was ca.  $540 \mu\text{W}\cdot\text{cm}^{-2}$ . For the photocatalytic reaction, 0.1 g  $\text{Cu}_2\text{O}/\text{RGO}$  photocatalysts were dispersed into 3 ml DI water with 0.7 M sodium sulphite. After the irradiation by a 150 W Xe lamp for 30 minutes, 1 mL of gas sample was analysed by a gas chromatograph.

## 2. Morphology and survey XPS spectrum of $\text{Cu}_2\text{O}/\text{RGO}$ composites

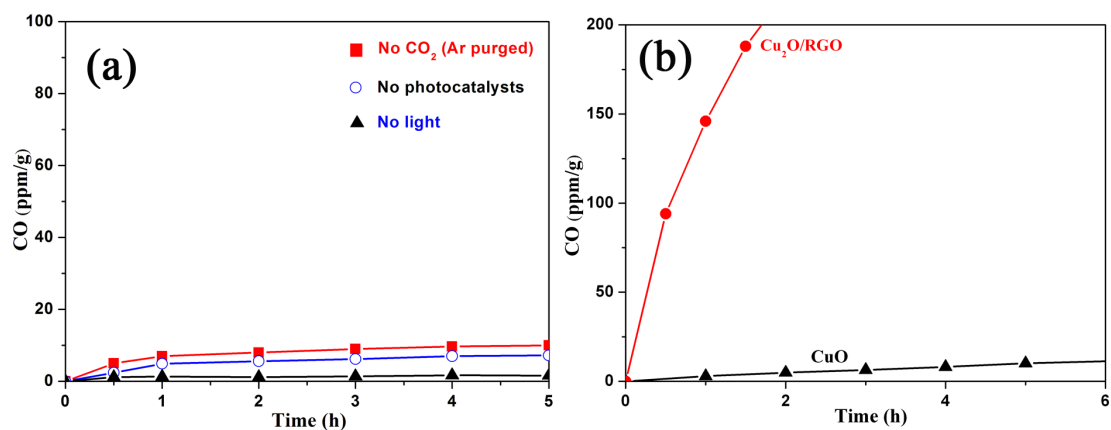
As displayed in Figure S1, only signals of Cu, O and C elements are detected in the survey XPS spectrum of  $\text{Cu}_2\text{O}/\text{RGO}$  composites.



**Figure S1** Survey XPS spectrum of  $\text{Cu}_2\text{O}/\text{RGO}$  composites.

## 3. Photocatalytic reduction of $\text{CO}_2$ under different conditions

Series of control experiments were carried out and the results are shown in Figure S2a. A similar microwave-assisted hydrothermal method was used to synthesize  $\text{CuO}$  nanomaterial.<sup>[4]</sup> In a 80 mL reactor, 25 mL of 0.1 M  $\text{Cu}(\text{NO}_3)_2$  was mixed with 25 mL of 0.5 M urea aqueous solution. After stirring for 30 minutes, the solution was heated with stirring in the microwave system at  $150 \text{ }^\circ\text{C}$  for 30 minutes. Its activity was tested and found nearly negligible.

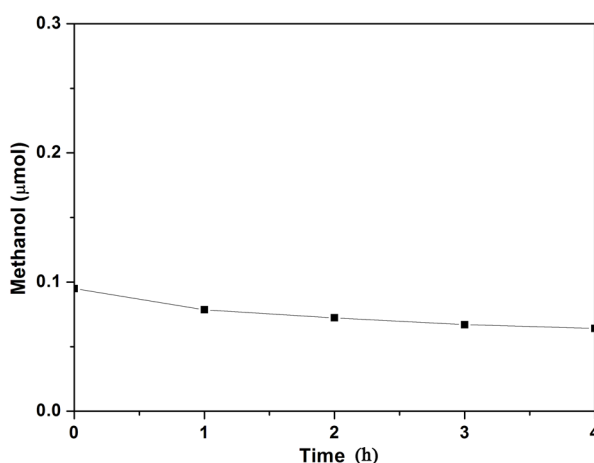


**Figure S2** (a) Amount of CO detected under different conditions; (b) Photocatalytic production of CO by CuO.

#### 4. Analysis of products in the liquid solution

In order to clarify the possible formation of other hydrocarbon products in the reaction solution, liquid samples during photocatalytic reaction were also collected and analyzed. After a certain time interval, 0.2 mL of the reaction solution was collected by a syringe. 0.5  $\mu\text{L}$  of the filtered sample was analyzed by gas chromatograph fit with a flame ionization detector (FID, connected to Shimadzu QP-2010SE GC-MS, Plot-Q capillary column).

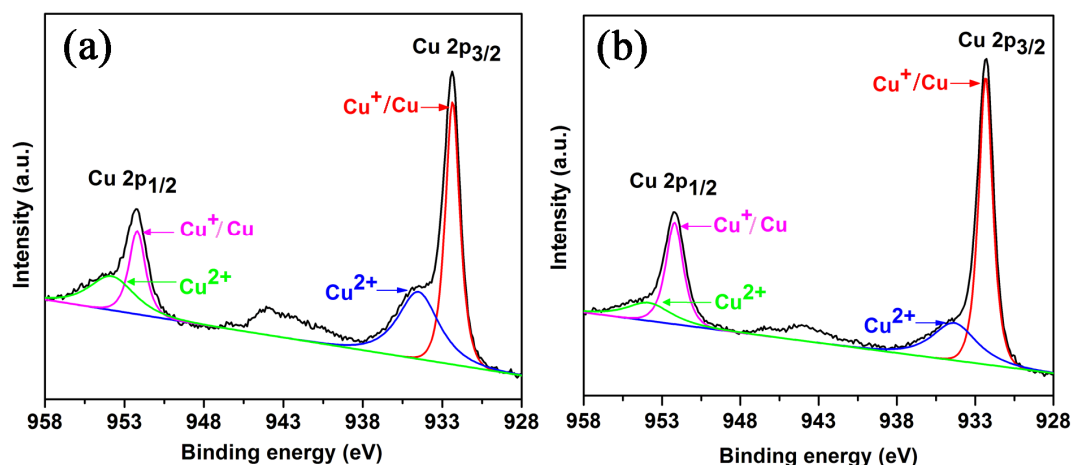
As shown in Figure S3, trace amount of methanol was detected before photocatalytic reaction, which might be ascribed to the contaminant adsorbed on the photocatalyst surface. However, its amount decreases with time under light irradiation, which confirms there is no methanol formed as a reduction product. It is reasonable that the kinetic drawback makes methanol formation more difficult than carbon monoxide in the absence of any cocatalyst, as more electrons are required.<sup>[5]</sup> In addition, methanol is widely used as a hole quencher in the photocatalytic reaction. It is generally believed that methanol is not stable, which can be easily oxidized into  $\text{CO}_2$  and  $\text{CO}$ .<sup>[6]</sup>



**Figure S3** Amount of methanol detected in the reaction solution.

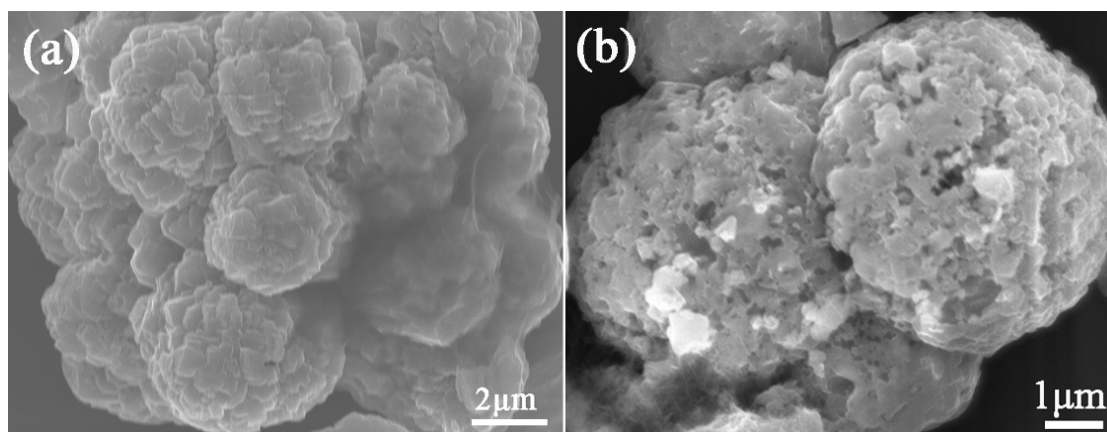
#### 5. Stability study of photocatalysts

To study the change of oxidation states of Cu elements during photocatalytic reaction, photocatalysts collected after 20 hours of reaction were characterized by XPS. As displayed in Figure S4a, the peaks assigned to  $\text{Cu}^{2+}$  obviously increase, compared to those in Figure 3c. It indicates formation of larger amount of CuO during photoreduction reaction. However, only slight change is seen for  $\text{Cu}_2\text{O}/0.5\%$  RGO composite in Figure S4b. Therefore, blank  $\text{Cu}_2\text{O}$  photocatalyst suffer serious photocorrosion.



**Figure S4** (a) Cu 2p spectrum of  $\text{Cu}_2\text{O}$  after 20 hour photocatalytic reaction; (b) Cu 2p spectrum of  $\text{Cu}_2\text{O}/\text{RGO}$  composite after 20 hour photocatalytic reaction.

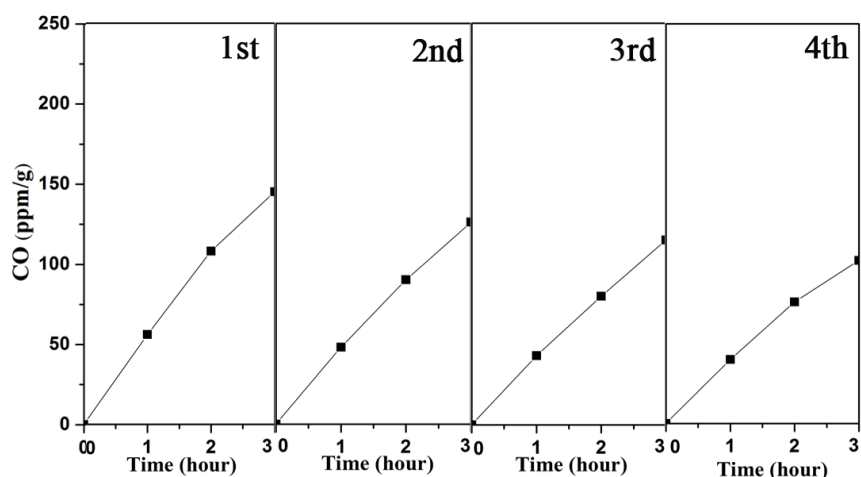
To study the morphological change of the photocatalysts,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}/\text{RGO}$  composite after photoreduction reaction were collected and characterized by SEM. As shown in Figure S5a, the morphology of  $\text{Cu}_2\text{O}/\text{RGO}$  composite hardly changed after the reaction of 20 hours. However,  $\text{Cu}_2\text{O}$  particles in Figure S5b become porous due to serious photocorrosion, good agreement with XPS and XRD measurement. It further confirms that the photostability of  $\text{Cu}_2\text{O}$  can be significantly improved by coupling with RGO.



**Figure S5** (a) SEM image of Cu<sub>2</sub>O/RGO composites after photoreduction reaction; (b) Cu<sub>2</sub>O after photoreduction reaction.

To study the effect of photocorrosion on the leaching of copper ions, leaching experiments were carried out. Typically, 0.2 g photocatalysts was dispersed in 10 ml of CO<sub>2</sub> saturated DI water. After purging by CO<sub>2</sub> for 5 minutes, the reactor was irradiated with a 150 W Xe lamp for 3 hours. Then, 0.2 mL of the reaction solution was collected by a syringe with 0.2 μm filter. The diluted solution was analysed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Varian Vista-pro). To exclude the influence of surface adsorbate and copper ions from other pathways, another 0.2 g photocatalysts dispersed in 10 mL CO<sub>2</sub> saturated DI water was stirred in the dark for 3 hours. The leaching of copper caused by photocorrosion was calculated by subtracting the value measured in the dark reaction.

The reuse of Cu<sub>2</sub>O/RGO composites was also tested. In each run, 0.2 g of the recycled photocatalysts was used and recycled again after the photocatalytic reaction. To make up the loss of catalysts, powders collected from the parallel experiments was combined for the next run. The activity of the composite is stable and reproducible within four cycles. The activity of recycled photocatalysts is equal to the average CO production rate mentioned above.



**Figure S6** Cycling test of Cu<sub>2</sub>O/RGO photocatalysts for CO<sub>2</sub> reduction.

## References

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