Supporting Information

Rapid Synthesis of Nanostructured Cu-TiO$_2$-SiO$_2$ Composites for CO$_2$

Photoreduction by Evaporation Driven Self-assembly

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Structural Stability of Micrometer-sized Droplets

The structural stability of droplets can be predicted from the Bond number, $B_0$, which is the ratio of the gravitational force to the surface tension force.

$$B_0 = \frac{\Delta \rho a d_p^2}{\sigma} \quad (1)$$

where $\Delta \rho$, $a$, $d_p$, and $\sigma$ are the density difference between droplet and surrounding fluids (air in this work) (kg/m$^3$), acceleration (m/s$^2$), droplet radius (m), and surface tension of droplets (N/m), respectively. Taking a water droplet of 4 µm in diameter as an example, the Bond number at room temperature was estimated to be around $4 \times 10^{-6}$, much smaller than 1, indicating their perfect spherical shape.

Evaporation Rate Calculation for Micrometer-sized Droplets

The solvent, i.e. water in this work, evaporation rates of a single micrometer-sized droplet at different synthesis temperature could be simply calculated according to the follow equation.

$$N_c = \frac{h_c A (\Delta T)}{\lambda} \quad (2)$$

where $N_c$ is the evaporation rate (g/s), $h_c$ the convective heat transfer coefficient (W/m$^2$K), $A$ the droplet surface area (m$^2$), $\Delta T$ the temperature different (K), and $\lambda$ the latent heat of water (kJ/kg). As from Table 1, the solvent evaporation rate increased with increasing synthesis temperature, from $6.79 \times 10^{-8}$ g/s at 400°C to $1.77 \times 10^{-7}$ g/s at 1000°C, indicating that a higher synthesis temperature causing a higher evaporation rate.
Photocatalytic Pathways for CO₂ Reduction

Step 1: Photoexcitation (\(e^-h^+\) Generation/Recombination)

Photocatalyst + \(hv\) → \(e^- + h^+\) \((1)\)
\(e^- + h^+\) → heat \((2)\)

Step 2: CO₂ Reduction Pathways

As explained before, to reduce CO₂, the semiconductor is required to have its conduction band electrons with higher energy compared to the CO₂ reduction potential while the holes in the valence band to be able to oxidize water to O₂.

Valence Band (Photooxidation)

\(2H_2O + 4h^+ \rightarrow O_2 + 4H^+\) \((3)\)

Conduction Band (Photoreduction)

Most of the researchers agree that the CO₂ photoreduction process is multi-electron transfer instead of single electron transfer as the electrochemical potential of -2.0 V for a single electron process does not support it. \(^{36}\) The possible reactions that can occur in the reduction of CO₂ in aqueous medium with multi-electron transfer are shown as follows.

\(CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H\) \((4)\) \(E_{\text{redox/NHE}} = -0.61\text{V}\)

\(CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O\) \((5)\) \("= -0.52\text{V}\)

\(CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O\) \((6)\) \("= -0.48\text{V}\)

\(CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O\) \((7)\) \("= -0.38\text{V}\)

\(CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O\) \((8)\) \("= -0.24\text{V}\)
Although the formation of methane, methanol and ethanol is thermodynamically favorable, it requires more electrons and protons. These products are more likely produced in CO₂ photoreduction in aqueous solutions, since more protons can be produced by water.¹²,¹⁸

$$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \quad (9) \quad = -0.16 \, \text{V}$$
**Figure S1.** XRD Patterns of TiO$_2$-SiO$_2$ composite particles prepared at different temperatures.

![XRD Patterns](image)

**Fig. S1** reveals the XRD patterns of the catalyst particles prepared at different temperatures. Major crystal peaks are assigned to TiO$_2$ anatase phase according to the Joint Committee on Powder Diffraction Standards reference (JCPDS No. 21-1272) with trace rutile (JCPDS No. 21-1276) phase appeared. All XRD patterns look very similar indicating their little influence on the CO$_2$ photoreduction.
Figure S2. XRD patterns of Cu-TiO$_2$-SiO$_2$ composite particles with different Cu molar percentages at 800°C with a fixed TiO$_2$ molar percentage of 2%, and the particles prepared from pure Cu(NO$_3$)$_2$ at the same condition.

The above XRD results showed that there are some possibilities of CuO particle formation when using the Cu(NO$_3$)$_2$ aqueous solution as the precursor at the present experimental conditions, which was also considered as one of the reasons for the deteriorated performance when using increased copper molar percentages.