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_o, which is the ratio of the gravitational force to the surface tension force.

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

where $\Delta\rho$, a, d_p, and σ 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 4×10^{-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.

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

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), ΔT the temperature different (K), and λ the latent heat of water (kJ/kg). As from **Table 1**, the solvent evaporation rate increased with increasing synthesis temperature, from 6.79×10^{-8} g/s at 400°C to 1.77×10^{-7} g/s at 1000°C, indicating that a higher synthesis temperature causing a higher evaporation rate.

Photocatalytic Pathways for CO_2 Reduction

Step 1: Photoexcitation (*e-h* Generation/Recombination)

Photocatalyst + $h\nu \rightarrow e^- + h^+$ **(1)**

$e^- + h^+ \rightarrow$ heat **(2)**

Step 2: CO_2 Reduction Pathways

As explained before, to reduce CO_2, the semiconductor is required to have its conduction band electrons with higher energy compared to the CO_2 reduction potential while the holes in the valence band to be able to oxidize water to O_2.

Valence Band (Photooxidation)

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

Conduction Band (Photoreduction)

Most of the researchers agree that the CO_2 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 CO_2 in aqueous medium with multi-electron transfer are shown as follows.

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

$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$ **(5)** **= - 0.52 V**

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ **(6)** **= - 0.48V**

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ **(7)** **= - 0.38 V**

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ **(8)** **= - 0.24 V**

1 **$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$ (9)** **= - 0.16 V**

2 Although the formation of methane, methanol and ethanol is thermodynamically favorable, it requires
3 more electrons and protons. These products are more likely produced in CO_2 photoreduction in aqueous
4 solutions, since more protons can be produced by water.[12,18]

Figure S1. XRD Patterns of TiO_2-SiO_2 composite particles prepared at different temperatures.

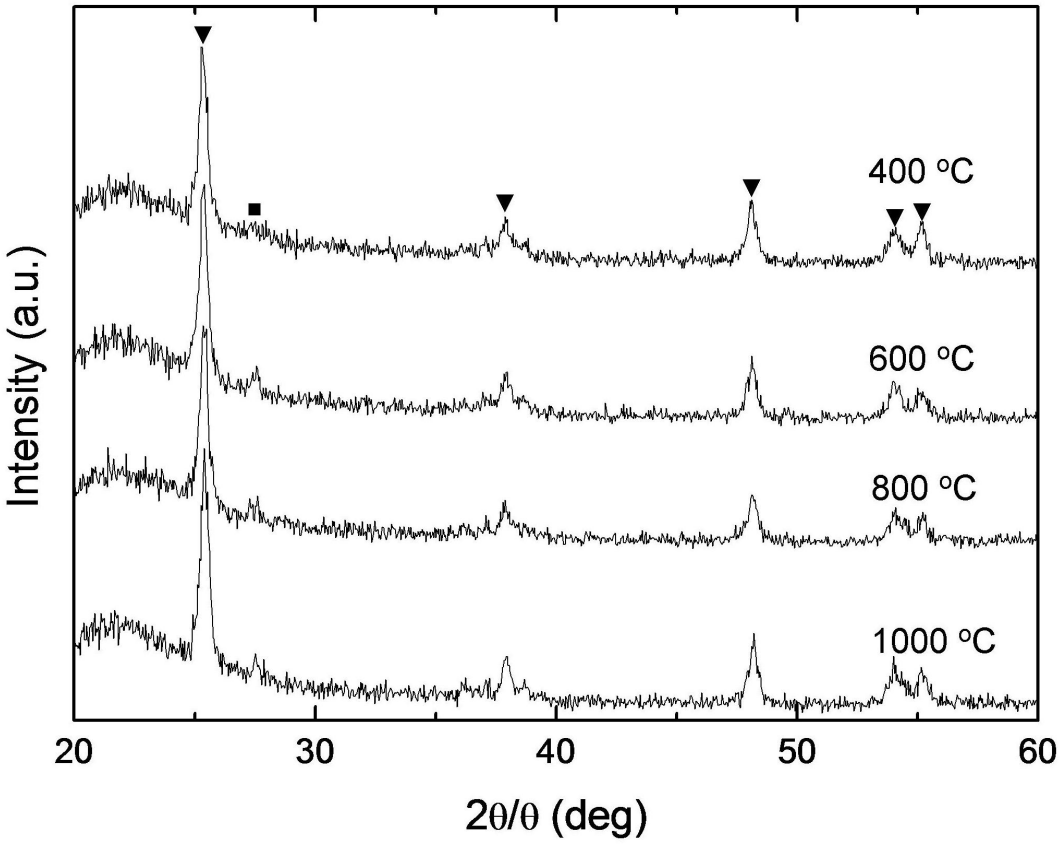
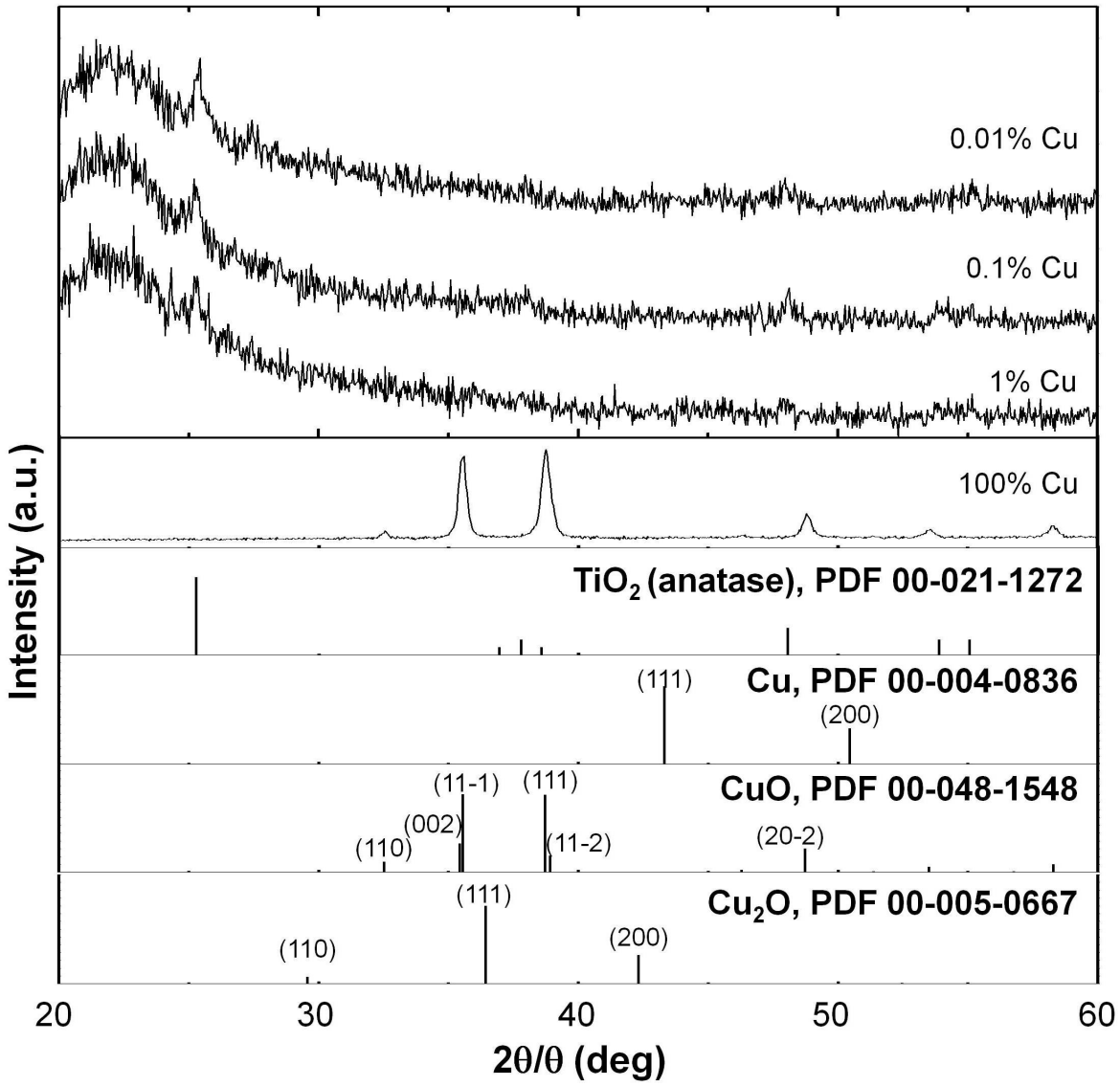


Fig. S1 reveals the XRD patterns of the catalyst particles prepared at different temperatures. Major crystal peaks are assigned to TiO_2 anatase phase according to the Joint Committee on Powder Diffraction Standards reference (JCPDS No. 21-1272) with trace rutile (JCPDS No. 21-1276) phase appeared. All 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.