Electronic Supplementary Information

Highly active and stable copper catalysts derived from copper silicate double-shell nanofibers with strong metal-support interaction for RWGS reaction

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Experimental

Synthesis of SiO$_2$ hollow nanofibers. The SiO$_2$ hollow nanofibers were prepared through a single capillary electrospinning method. 0.95 g of polyvinylpyrrolidone (PVP, M_n = 1300000) was completely dissolved in 10 mL of ethanol. After stirring for several minutes, 1.6 ml of tetraethylorthosilicate (TEOS) was slowly added to form a homogeneous solution. Then, the precursor was transferred into a plastic syringe for electrospinning under the voltage of 9.5 kV and the products were collected at a distance about 20 cm to the syringe tip. Finally, the composites of PVP/TEOS were calcined in the air at 550 °C for 2 h to obtain SiO$_2$ hollow nanofibers.

Synthesis of hierarchical double-shells CuSiO hollow nanofibers. The hierarchical double-shells CuSiO hollow nanofibers were prepared through a simple hydrothermal process. In brief, copper acetate monohydrate (0.2 mmol), ammonia chloride (2 mmol) and NH$_3$·H$_2$O (0.2 mL, 28%) were added to 10 mL distilled water and transferred into a 15 mL Teflon-lined autoclave after full mixing with as-prepared SiO$_2$ hollow nanofibers (0.02 g). The autoclave was sealed and maintained at 140 °C for 10 h, the

resulting light blue precipitates were collected and washed several times with distilled water and absolute ethanol. The final products were dried at 60 °C for 12 h.

Synthesis of CuSiO/CuO$_x$ hollow nanofibers. The CuSiO/CuO$_x$ hollow nanofibers were prepared through a simple hydrogen reduction process. The obtained products were placed in a porcelain boat, and then calcined at 350 °C for 2 hours in a tubing furnace under H$_2$/Ar (5% H$_2$, 95% Ar) mixed atmosphere. The final black products were CuSiO/CuO$_x$ hollow nanofibers. Conventional SiO$_2$/Cu and TiO$_2$/Cu catalysts were prepared by impregnation method. 0.85 g of fused SiO$_2$ or TiO$_2$ power was impregnated by soaking the powders in a solution of 0.57 g of Cu(NO$_3$)$_2$·3H$_2$O in a sealed vial, followed by drying. Then, the obtained powers were calcined at 350 °C for 2 hours in a tubing furnace under H$_2$/Ar mixed atmosphere, too. The surface composition of copper was determined to be 15 wt% from the XPS data.

Catalyst Evaluation for the RWGS Reaction. The RWGS reaction was conducted under atmospheric pressure in a quartz-tube fixed bed reactor (i.d. 4 mm). A 20 mg amount of the catalyst was used for one batch. A gas mixture of 4% Ar, 24% CO$_2$ and 72% H$_2$ was passed through the catalyst bed at a flow rate of 20 mL/min. The products were analyzed by an online gas chromatograph (Agilent 7820) equipped with a TCD detector. The outlet gas flow rate was determined by the inner standard method, in which the CH$_4$, CO, and CO$_2$ were calculated based on the flow rate of inner gas (Ar). CO$_2$ conversion was calculated from the measured CO$_2$ concentration using the formula CO$_2$ conversion = [(CO$_{2in}$ − CO$_{2out}$)/CO$_{2in}$], where CO$_{2in}$ and CO$_{2out}$ were the inlet and outlet CO$_2$ concentration, respectively.

Characterization. Siemens D5005 Diffractometer was used to record the X-ray diffraction (XRD) patterns. Transmission electron microscopic (TEM) images and high angle annular dark field STEM (HAADF-STEM) image were obtained on a JEM-2100F microscope. Scanning electron microscopy (SEM) images were obtained on XL30 ESEM FEG microscope. Elemental analysis was performed with a TJAPOEMS spectrometer. X-ray photoelectron spectroscopy (XPS) was analyzed on Thermo ESCALAB 250 XPS instrument. The Brunauer-Emmett-Teller (BET) surface area of the samples was performed on Micromeritics Tristar 3000 analyzer at 77.4 K.
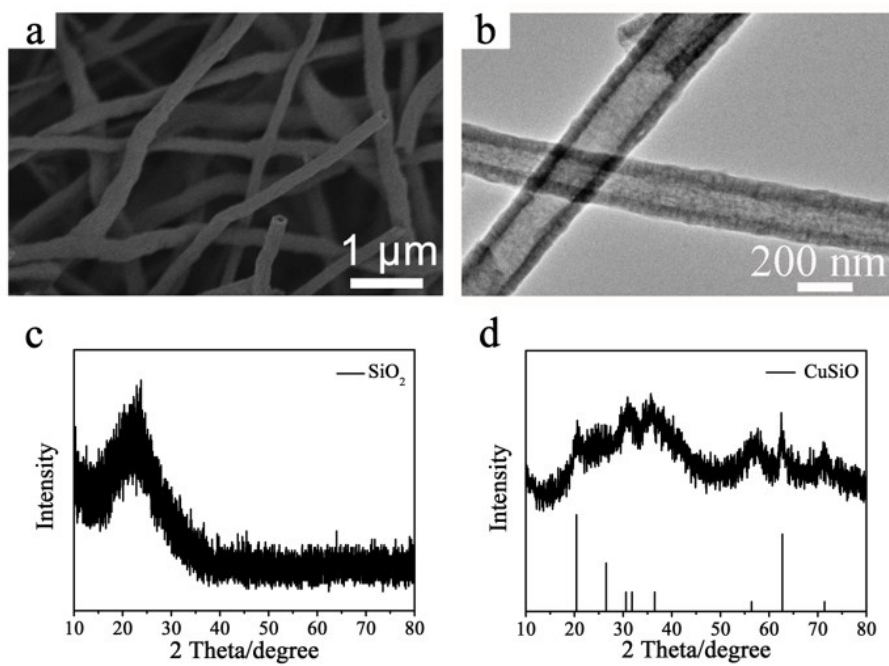
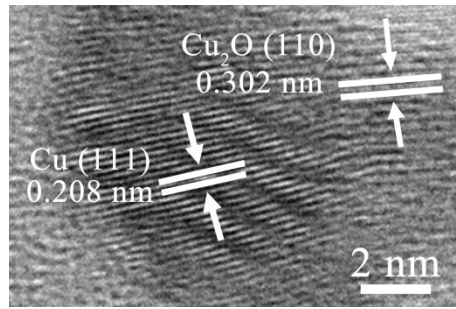Fig. S1 Typical SEM (a) and TEM (b) images of SiO$_2$ nanofibers; XRD patterns of (c) SiO$_2$ and (d) CuSiO nanofibers.
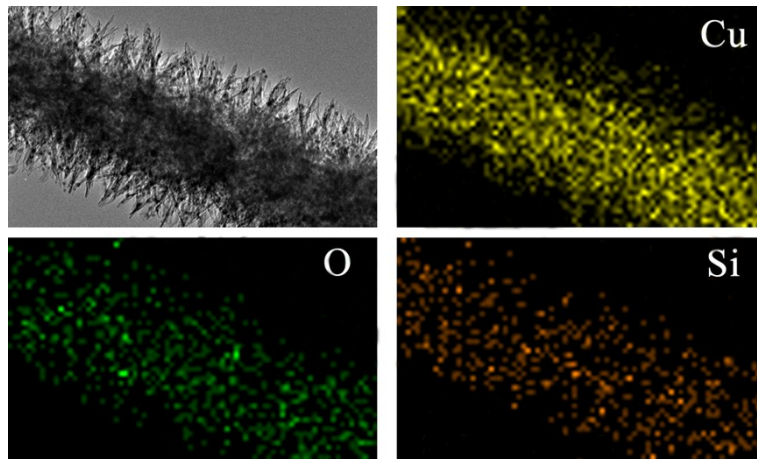
Fig. S2 HRTEM image of the CuO$_x$ nanoparticles.

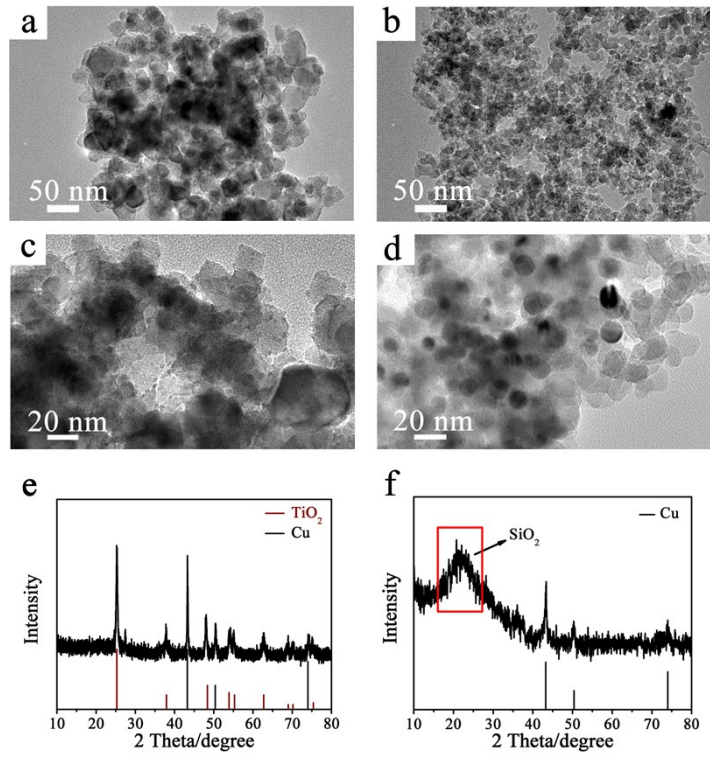Fig. S3 Mapping of elements by EDX analysis of CuSiO/CuO$_x$

Fig. S4 Typical TEM images of (a, c) TiO_2/Cu and (b, d) SiO_2/Cu; XRD patterns of (e) TiO_2/Cu and (f) SiO_2/Cu.

Table S1 Catalytic activities of the $CuSiO/CuO_X$ compared with reported conventional catalysts toward the RWGS

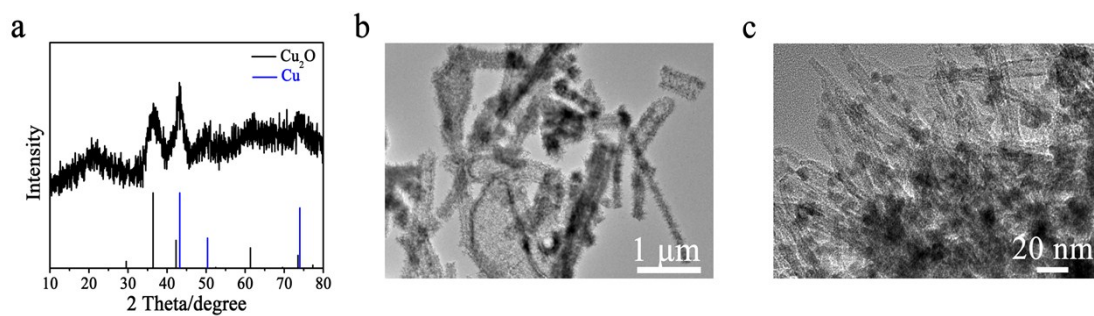| Catalyst	Temperature (°C)	Activity (10^{-5} $mol_{CO2}/g_{cat}/s$)	References
$CuSiO/CuO_X$	500	3.18	This work
TiO_2/Cu	500	1.78	This work
SiO_2/Cu	500	1.11	This work
Cu/Al_2O_3	500	0.9	1
Cu/Al_2O_3	600	3.1	2
CuO_x/CeO_2	550	1.23	3
$Cu-CeO_2$	400	2.23	4
$Cu/\beta-Mo_2C$	500	1.64	5
Cu/mesoporous silica	400	0.167	6
Cu/SiO_2	500	3.34	7
Cu/SiO_2	600	1.49	8
Fe/SiO_2	600	0.744	8
$CuFe/Al_2O_3$	400	2.67	9
Ni/Ce-Zr-O	550	2.17	10
In_2O_3	500	2.38	11
CeO_2	500	1.34	11
$In_2O_3-CeO_2$	500	2.98	11

Fig. S5 XRD (a) patterns and TEM (b, c) images of CuSiO/CuO$_x$ catalysts after stability test.

References

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