

Surface polarization enhancement: high catalytic performance of Cu/CuO_x/C nanocomposites derived from Cu-BTC for CO oxidation

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Computational methods: The Vienna AB-initio Simulation Package (VASP) code has been used for our calculations¹. This code solves the Kohn-Sham equations of density functional theory (DFT) using a plane-wave basis set and the projector augmented wave (PAW) method². The exchange and correlation effects were calculated by the generalized gradient approximation in the formulation of Perdew-Wang-91. To ensure the accuracy of the calculated results, the cutoff energy was set to 400 eV for the plane-wave expansion of the electronic wave function. All structures were optimized with a convergence criterion of 1×10^{-5} eV for the energy and 0.01 eV/Å for the forces.

Two models contain 4 layers of Cu (200) and an in-plane periodicity of (4*4) Cu₂O layer or CuO layer, which are built for representing the oxidized surface and in-situ obtained copper oxide according to our HRTEM image. The Gamma scheme with 5x5x1 K point mesh is used to represent the Brillouin zone.

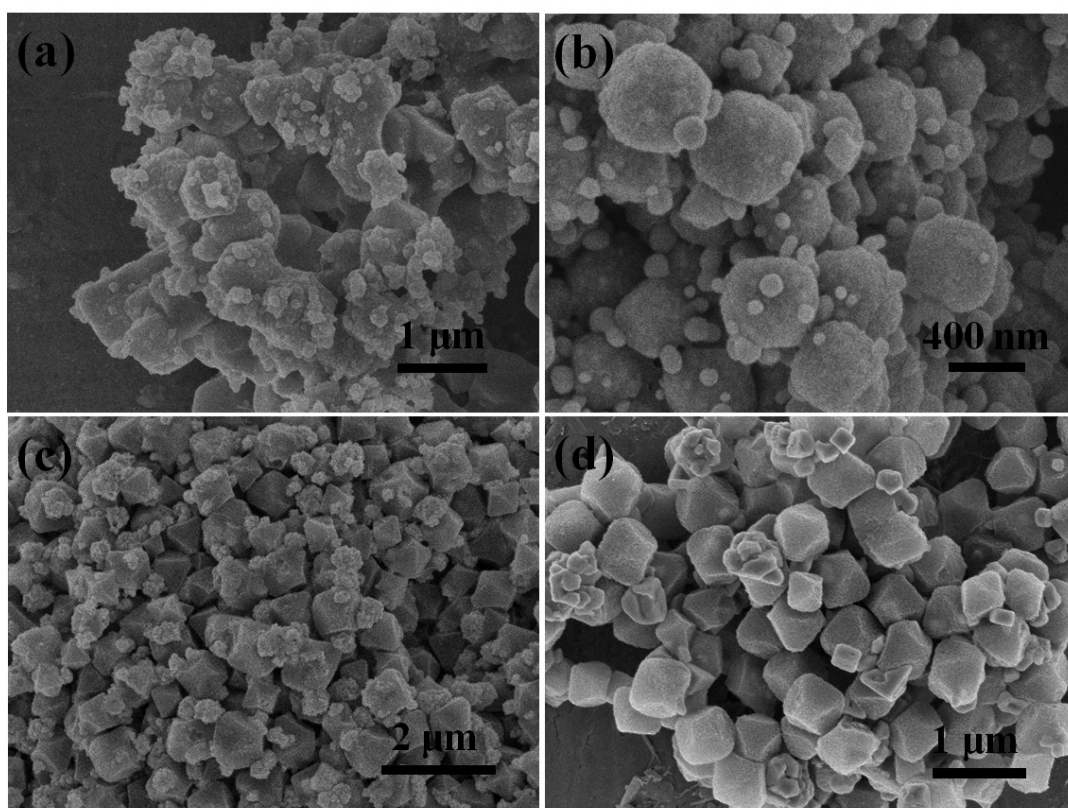


Fig. S1 SEM images of Cu-BTC annealed at: (a) 350 °C (b) 400 °C (c) 600 °C (d) 700 °C

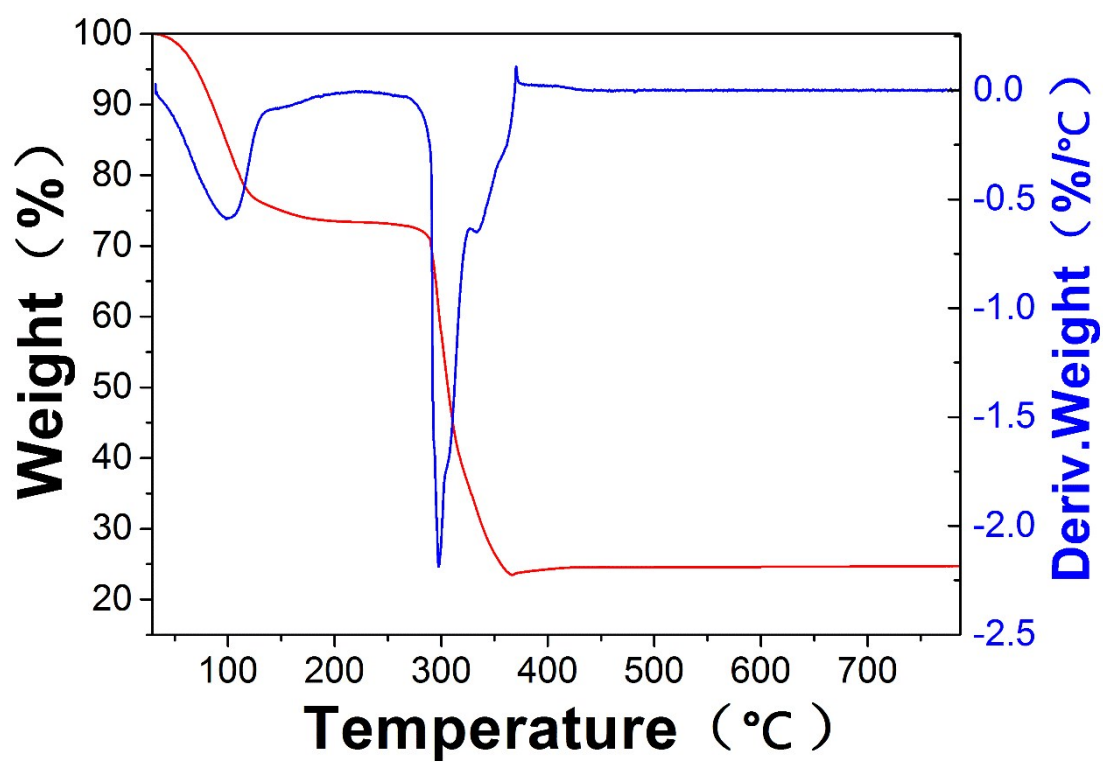


Fig. S2 TG-DTA curves of Cu-BTC under a flow of N₂ with a heating rate of 20°C min⁻¹.

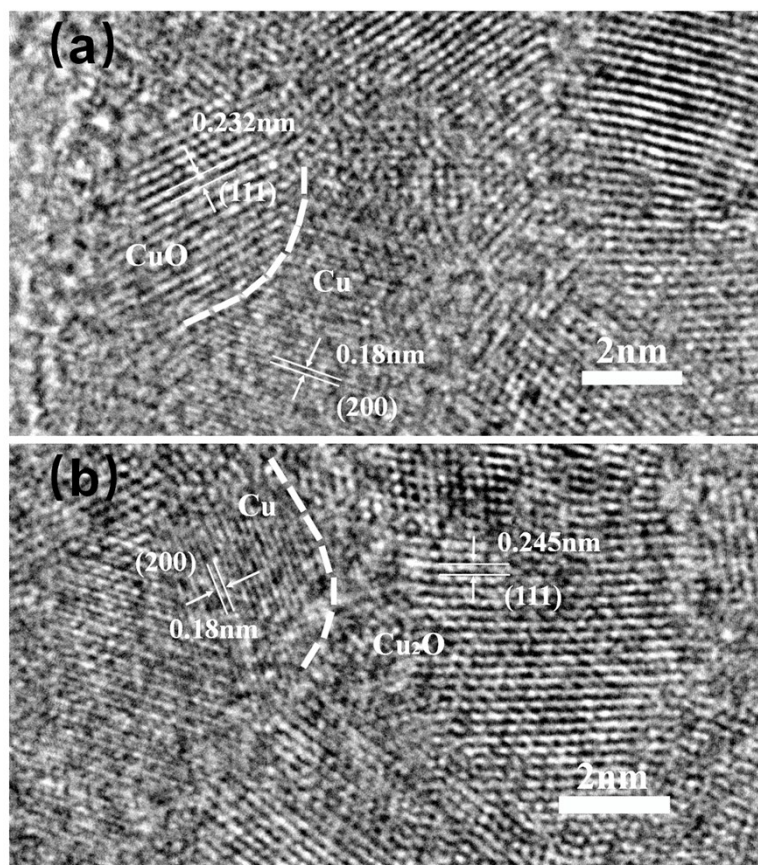


Fig. S3 HRTEM images of (a) Cu-CuO interface; (b) Cu-Cu₂O interface

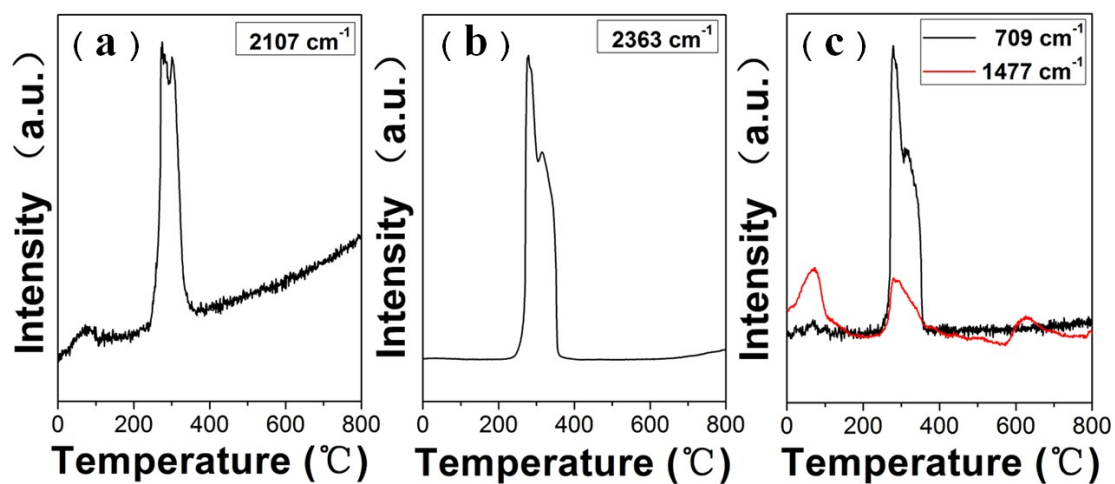


Fig. S4 IR absorbance variation of (a) CO, (b) CO₂, (c) C₆H₆ as a function of temperature.

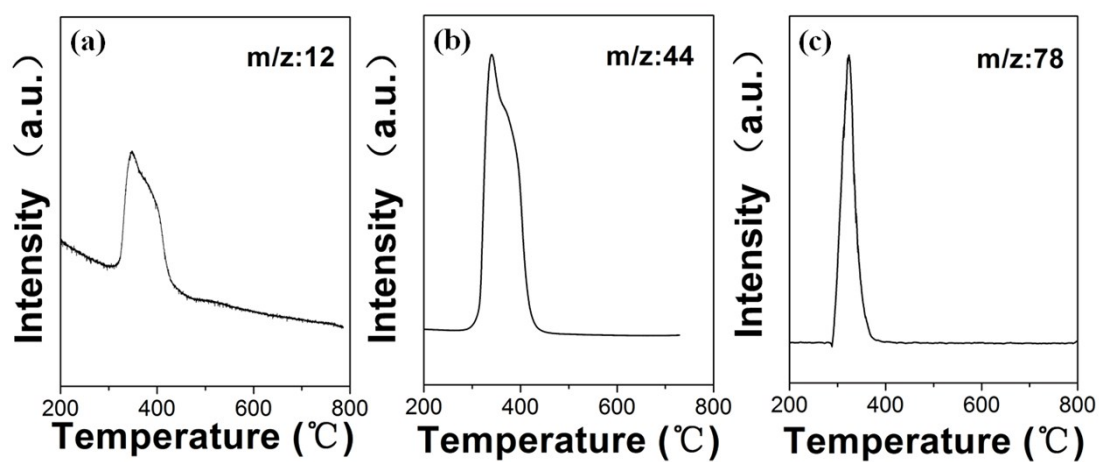


Fig. S5 MS intensity variation of (a) CO, (b) CO₂, (c) C₆H₆ as a function of temperature.

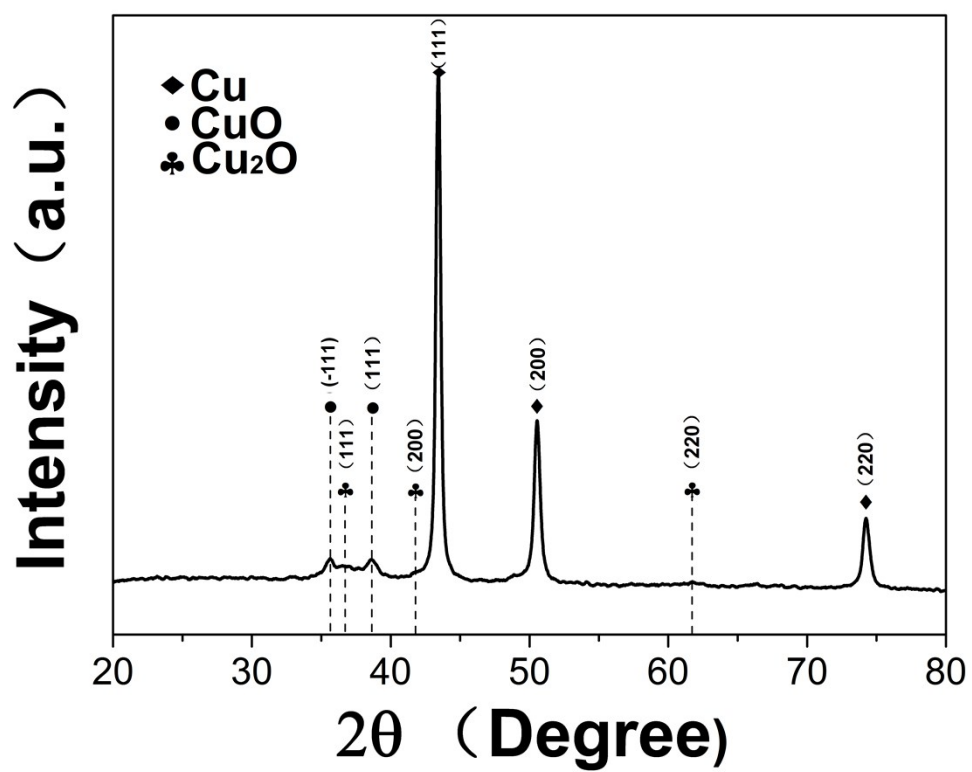


Fig. S6 XRD patterns of the as-prepared sample obtained at 500°C

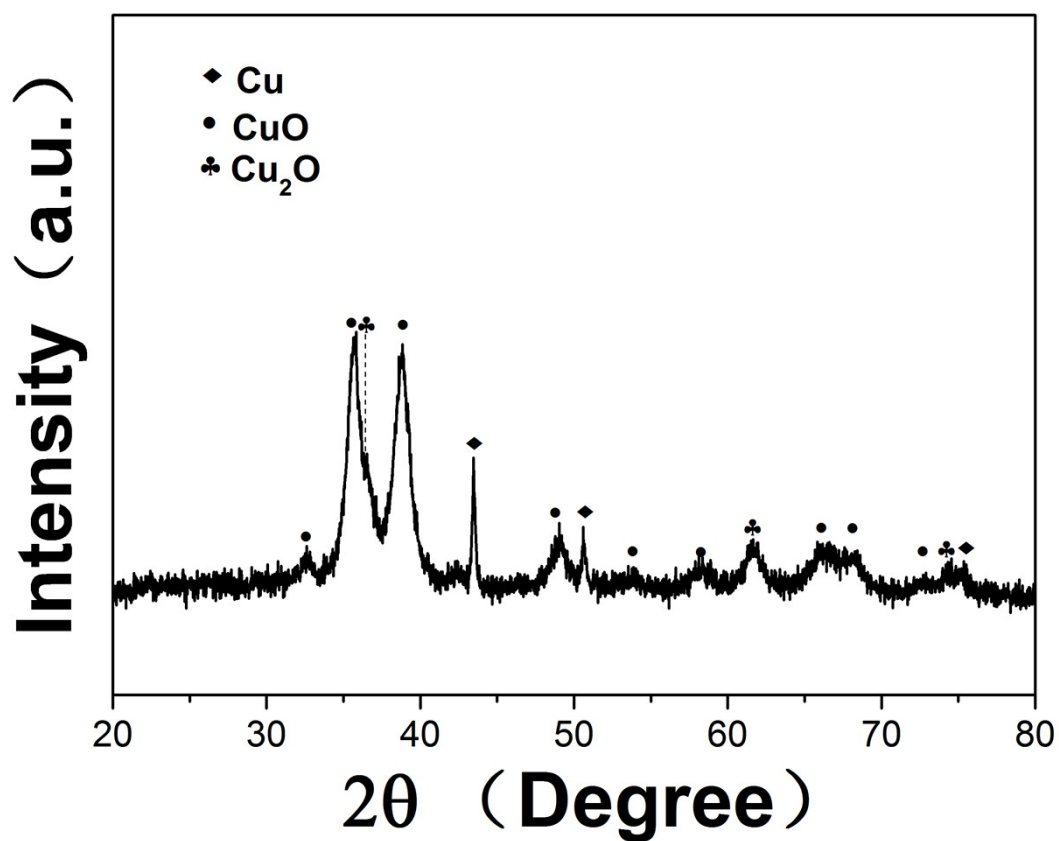


Fig. S7 XRD patterns of the as-prepared sample after being tested in 1% CO with space velocity of 36,000 mL g⁻¹ h⁻¹ at the temperature of 155°C for 48h

Table 1 Performance of S-500 and reported literatures

Catalyst	CO/%	T ₁₀₀ /°C	Ref.
Cu ₂ O	1	>240	<i>Angew. Chem. Int. Ed.</i> , 2011, 50 , 12294–12298
Cu ₂ O	1	>220	<i>J. Mater. Chem. A</i> , 2013, 1 , 282–287
CuO	4	>183	<i>J. Mater. Chem. A</i> , 2015, 3 , 3627–3632
Cu ₂ O/CuO composite	3.7	>240	<i>J. Mater. Chem. A</i> , 2015, 3 , 5294–5298
S-500	1	155	This work
S-500	5	155	This work

XPS

Deconvolution of the original Cu LMM peaks were performed, obtaining three symmetrical peaks centered at near 916.7, 917.8 and 919.8 eV, corresponding to Cu^+ , Cu^{2+} and Cu^0 species, respectively.³⁻⁶ The deconvolution results were listed in Table 2.

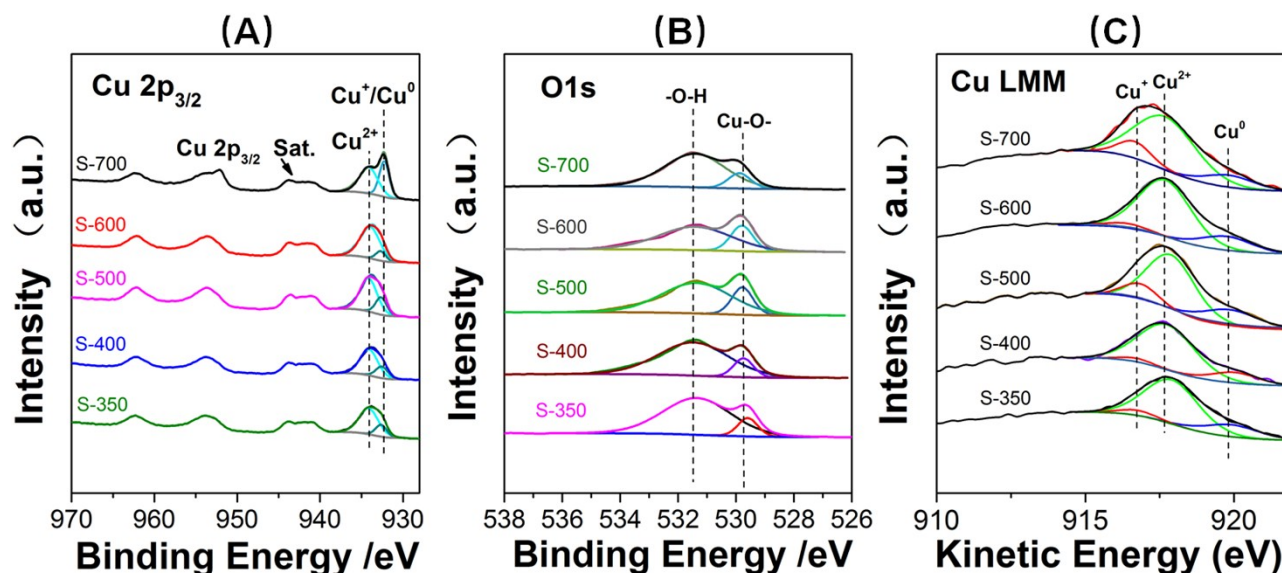


Fig. S8 X-ray photoelectron (A, B) and Auger spectra (C) of the samples annealed at different temperatures.

Table 2. Summary of the Cu LMM peak-fitting results

Sample	S-350		S-400		S-500		S-600		S-700	
	K.E.[eV]	At.%	K.E.[eV]	At.%	K.E.[eV]	At.%	K.E.[eV]	At.%	K.E.[eV]	At.%
Cu^0	919.93	19.34	920.13	15.35	919.87	19.45	919.74	19.76	919.85	13.15
Cu^+	916.75	3.29	916.78	3.55	916.85	14.07	916.39	9.6	916.66	12.65
Cu^{2+}	917.91	77.37	917.83	81.1	917.88	66.48	917.69	70.63	917.69	74.21

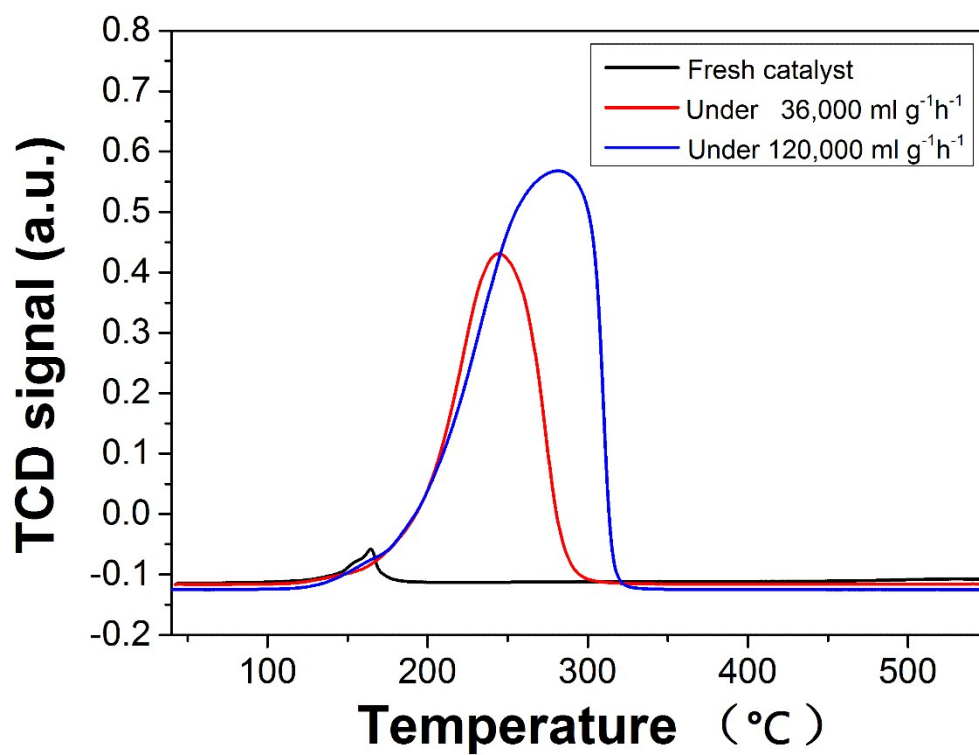


Fig. S9 TPR profiles of fresh S-500 and used at different space velocities

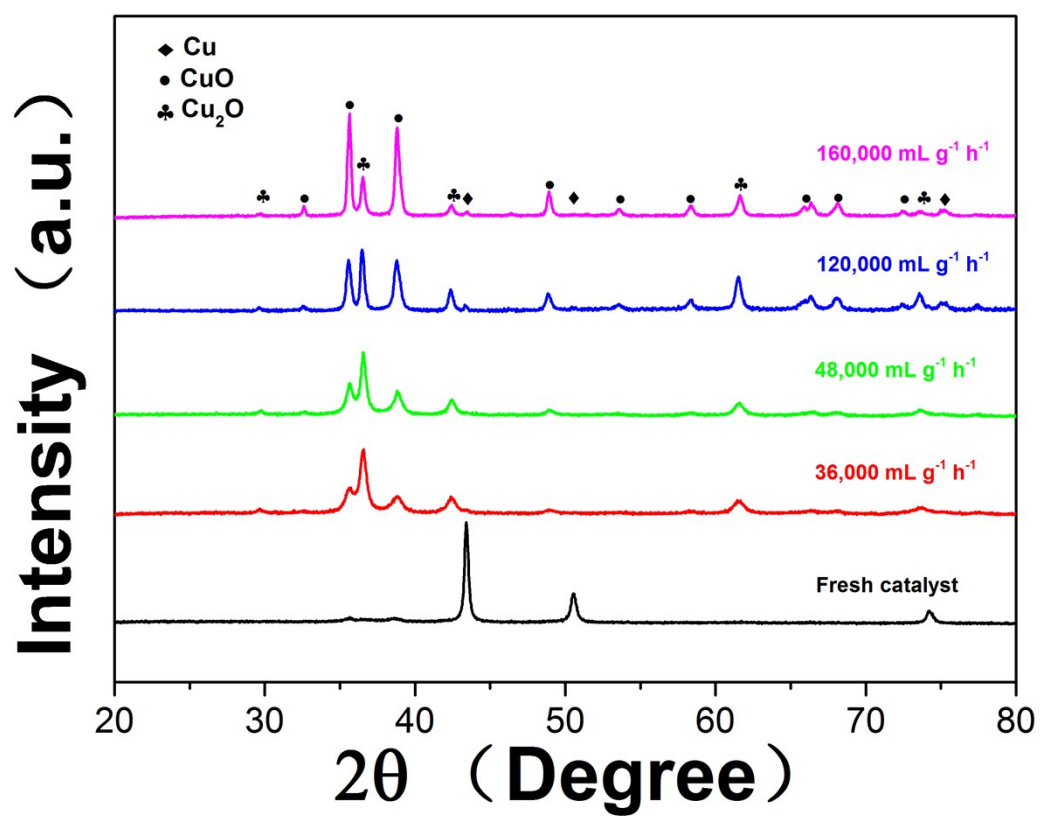


Fig. S10 XRD patterns of fresh catalyst and spent catalysts at the three space velocities

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