

The mechanism change by switching the reactants from water to hydroxyl ion for electrocatalytic water oxidation: A case study of copper oxide microspheres

Xiaoqiang Du^{a*}, Jingwei Huang^b and Yong Ding^{b*}

^a Chemical Engineering and Environment Institute, North University of China, Taiyuan 030051, People's Republic of China. E-mail: duxq16@nuc.edu.cn

^b State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China. E-mail: dingyong1@lzu.edu.cn

Characterization technique

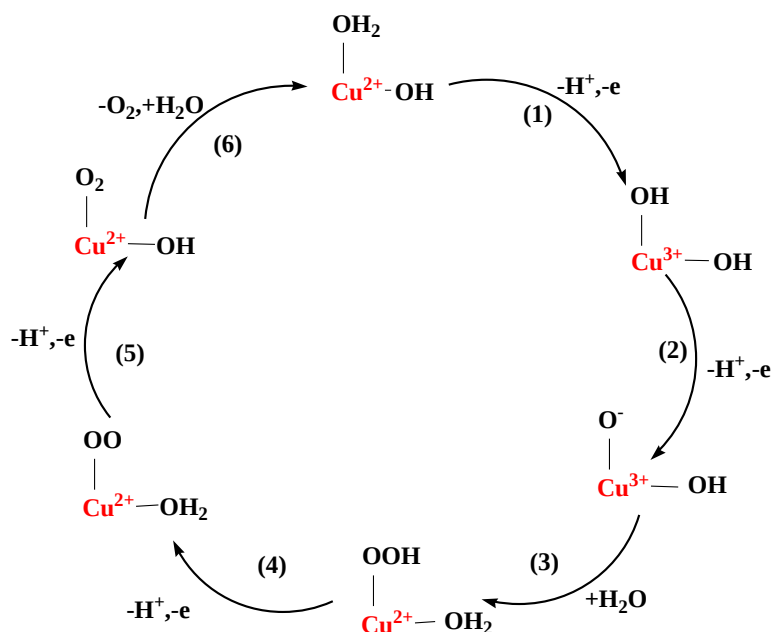
X-ray photoelectron spectra (XPS) were measured by ESCALAB250xi with X-Ray monochromatisation. PXRD data were collected with a PANalytical X'Pert Pro Diffractometer operated at 40 kV and 40 mA with Cu K α radiation (step size: 0.017°, step time: 10.34 s). SEM observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 5.0 kV. TEM images were obtained with a JEOL JEM-2010 instrument operated at 200 kV.

N₂ Adsorption for BET Surface Area Determination.

Nitrogen adsorption-desorption at 77 K was performed with a Micromeritics ASAP 2020M system. A sample mass of ~120 mg was used for adsorption analysis after pretreatment at 80 °C for ~8.0 h under vacuum conditions and kept in N₂ atmosphere until N₂-adsorption measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods.

Text of XPS analyses

The samples prepared for XPS analyses were processed according to the following procedure: first, catalyst powders were added on to an Al foil and pressed under high pressure to be a thin film and the thickness of the catalyst films was hundreds of nanometers. Then, the resulted samples were used for XPS tests.



Scheme S1. Proposed Reaction Mechanism for CuO microspheres for Water Oxidation.

Because CuO can undergo a conversion of the oxidation state in the oxygen evolution reaction (OER) that is similar to cobalt oxide.¹ Therefore, we suppose that the dominant reaction pathway for copper oxide catalyst may be the single Cu(II)OH site mechanism, as shown in Scheme 1. In the OER process, a Cu atom with an oxidation state of 2+ serves as the center connected by -OH and H_2O ligands. Because H_2O adsorption on the surface is favorable thermodynamically, the OER directly splits H_2O on a Cu^{2+} site to produce an adsorbed -OH . Then, it loses a proton to form an O^- anion, so a Cu-O^- group would form after two proton-coupled electron transfer (PCET) steps (steps 1 and 2 in Scheme 1). After the nucleophilic attack of a solvent of water molecule on the Cu-O^- group, a hydroperoxo CuOOH group as well as the O-O bond was yielded (step 3 in Scheme 1). Then a superoxo (step 4 in Scheme 1) and molecular O_2 (step 5 in Scheme 1) would form via two PCET steps. Finally, O_2 is evolved, and the catalyst is recovered when a H_2O molecule connects to the Cu site (step 6 in Scheme 1).

1. Kwapien, K.; Piccinin, S.; Fabris, S. J. Phys. Chem. Lett. 2013, 4, 4223.

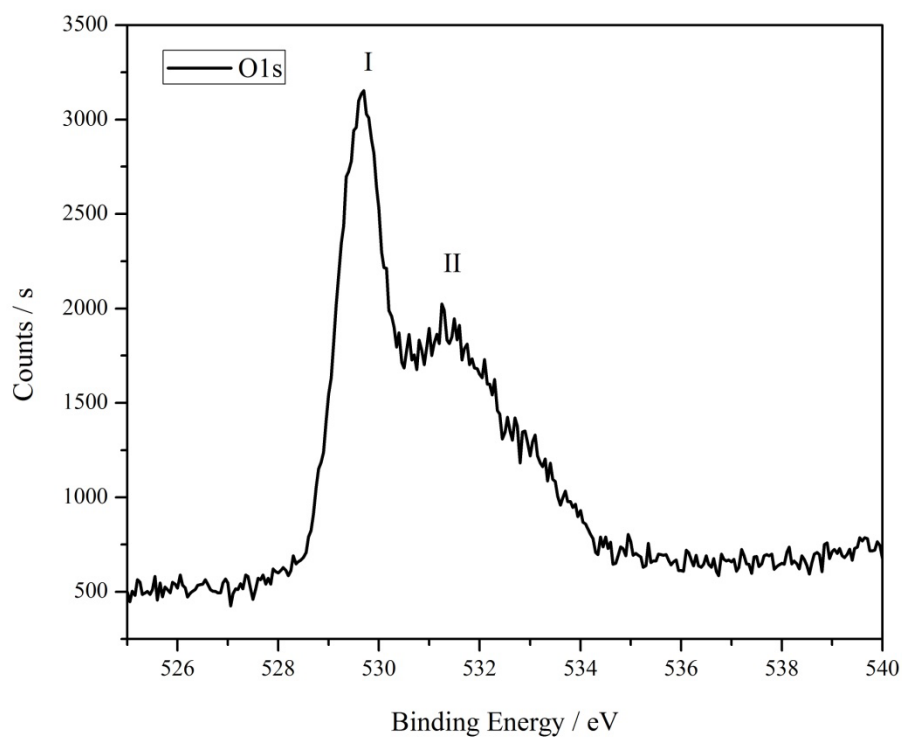


Fig. S1. Typical XPS spectrum of CuO microspheres: O 1s.

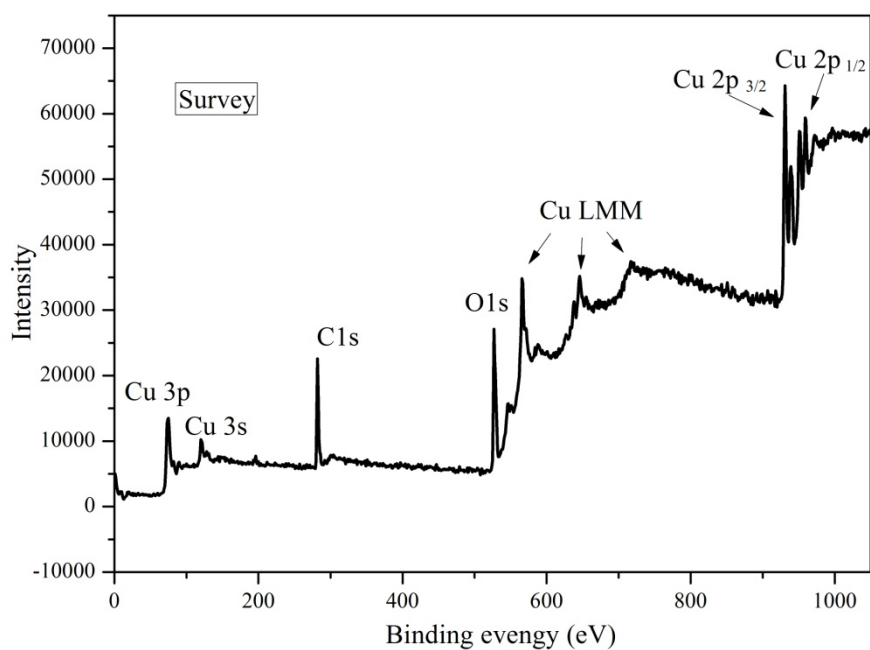


Fig.S2.X-ray photoelectron spectroscopy (XPS) survey data of the CuO microspheres.

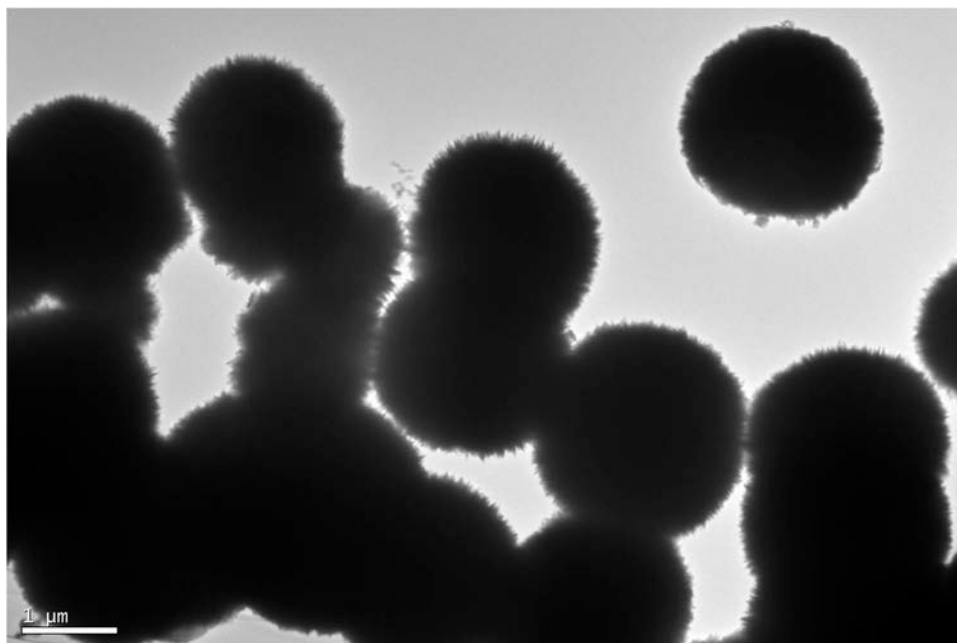


Fig. S3. TEM image of CuO microspheres.

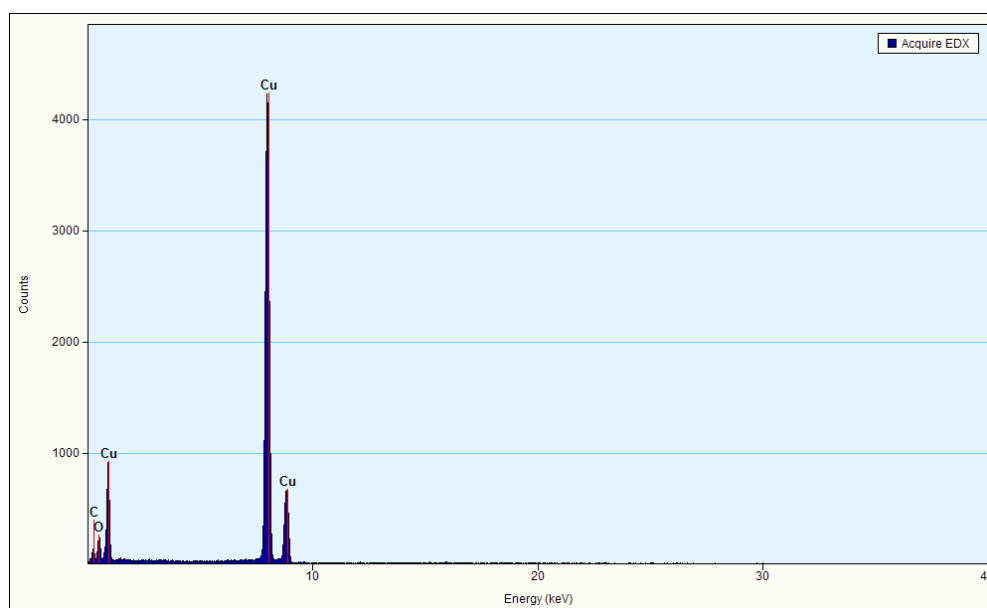


Fig. S4. EDS of the CuO microspheres.

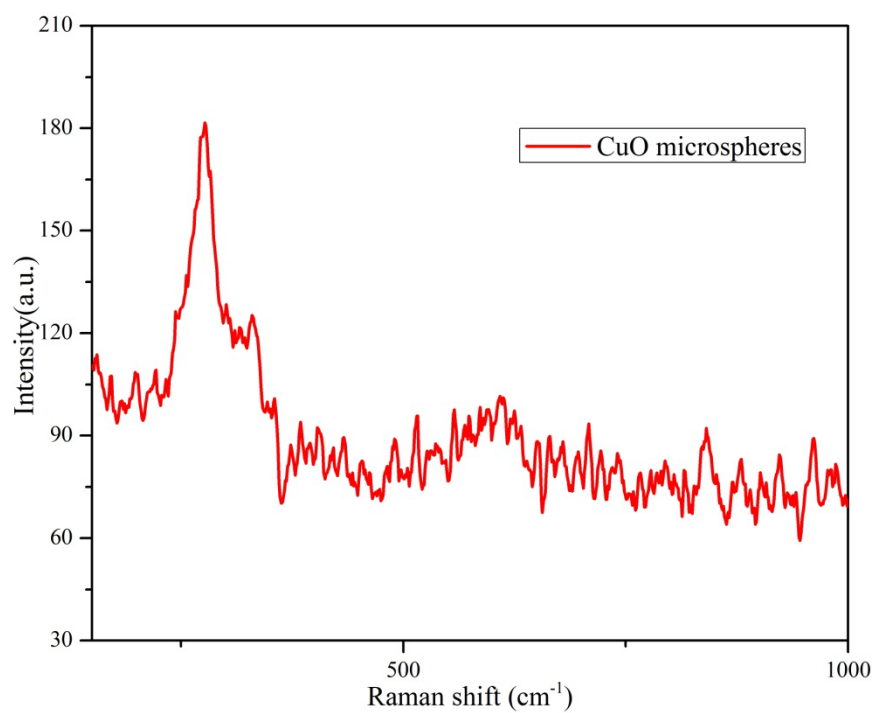


Fig. S5. Raman spectrum of CuO microspheres excited by 514.5 nm laser.

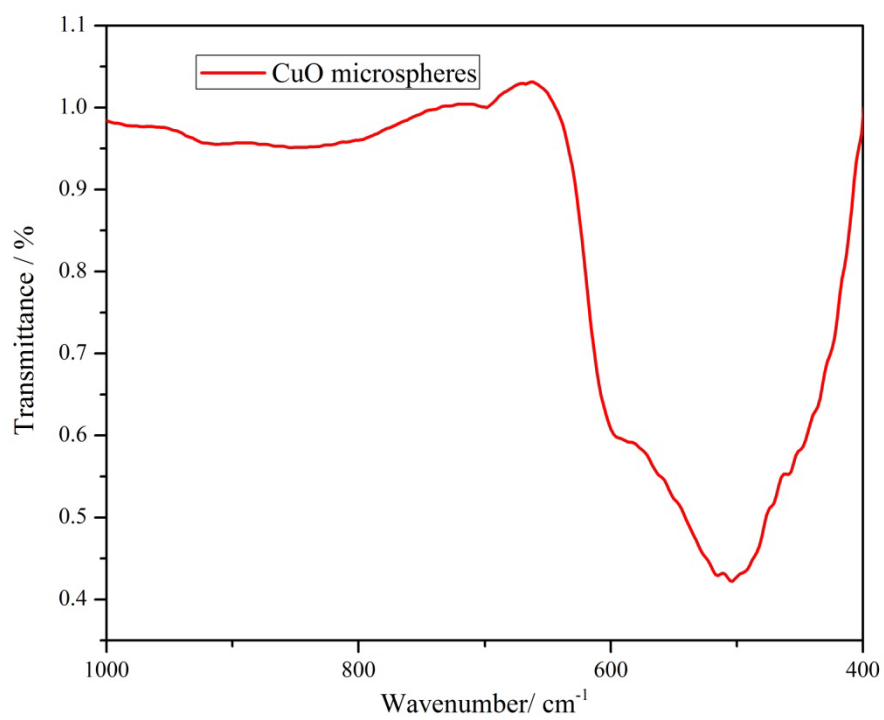


Fig. S6. FT-IR spectrum of the CuO microspheres.

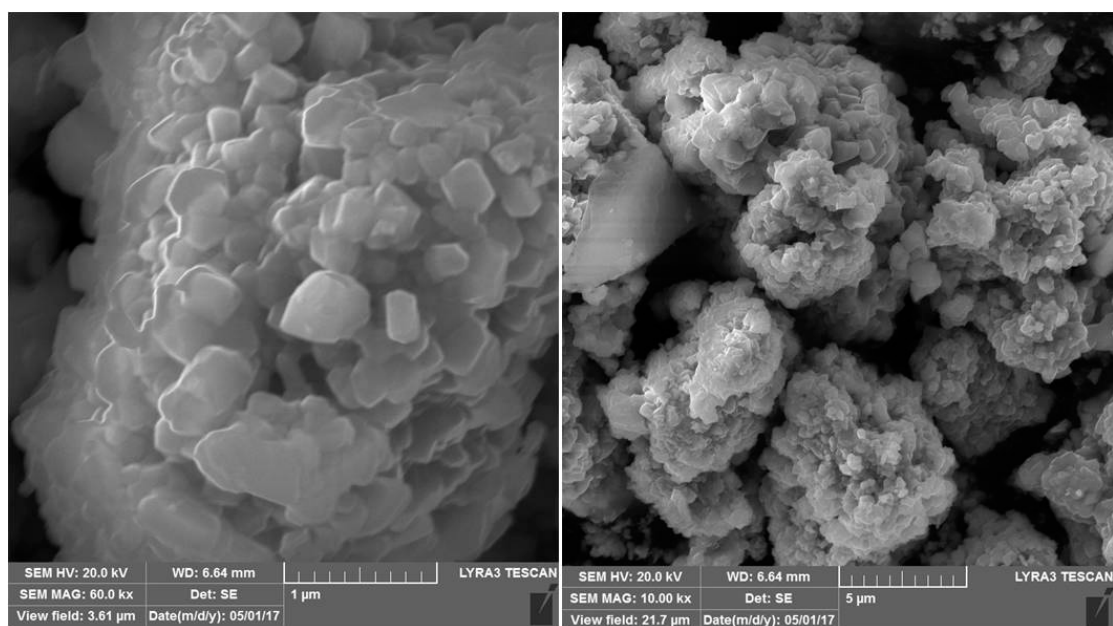


Fig. S7. SEM of images commercial CuO.