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A sea anemone-like CuO/Co₃O₄ composite: an effective catalyst for electrochemical water splitting

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A facile unipolar pulse electro-deposition combined with thermal oxidation method was applied for fabrication of CuO/Co₃O₄ composite on carbon electrode for water electrolysis, and found that the sea anemone-like one with 3D hierarchical structure formed at -0.8 V exhibited excellent performance for water electrolysis at low overpotential with high stability.

Hydrogen is an ideal candidate for the replacement of fossil fuel energy in the future due to its zero emission of carbonaceous species during its utilization. Hydrogen production via electrochemical splitting of water using natural energy such as solar and wind energy has attracted increasing interest. In the course of seeking highly efficient catalysts for water electrolysis, the biggest challenge is to reduce the amount of noble metals¹ in the electrode or replace them with those inexpensive materials². However, these non-precious materials always have lower activity than noble metals. To solve this problem, increasing the number of active sites of these materials by fabrication of three-dimensional (3D) nanostructure is an efficient approach³. In particular, direct fabrication of these materials with 3D branched core/shell heterostructures on conductive substrate are of great interest because it could result in the larger surface area for efficient transport of electron, ions and generated gases in the electrode which is beneficial to maximize the utilization of these water electrolysis materials^{3,4}. Moreover, nanostructured hybrid materials with two or more components could show synergetic properties through the reinforcement or modification of each other⁵. To date, various electrodes with 3D heterostructures have been developed and showed amazing enhanced properties for water electrolysis. For instances, Chen et al.³ and Liu et al.⁶ respectively synthesized NiCo₂O₄ and α -Fe₂O₃ nanorod arrays

on carbon cloth as anode for oxygen evolution reaction(OER), and found that a current density of 10 mA/cm² in alkaline electrolyte can be achieved at overpotentials of 320 and 420 mV, respectively. Shi et al.⁷ prepared tungsten nitride nanorods array on carbon cloth as cathode for hydrogen evolution with high catalytic activity at all pH values. Cheng et al.⁴ in-situ grew core/shell nanorod array consisting of Cu(OH)₂-CuO nanosheets as the shell and Cu as the core on Cu foil, and found that a current density of 10 mA/cm² can be obtained at an overpotential of 410 mV with a long-term stability (at least 22 h) of catalytic activity. Nevertheless, numerous efforts are still required for the facile and controllable synthesis of hybrid heterostructures with well defined morphology at low growth temperature for large scale water electrolysis.

Recently, the earth-abundant Fe, Co, Ni and Mn oxides have been investigated as potential electrocatalysts for water splitting^{6, 8-10}. Among them, cobalt oxides are promising bifunctional catalysts for water electrolysis under the same conditions^{2,9}. The abundant and diversiform d-orbitals endow cobalt oxides with the highly active sites for electrocatalytic water splitting^{11, 12}. Fabrication of CuO/Co₃O₄ nanowire heterostructures by thermal oxidation method has been recently reported⁵, which show high performance for lithium ion batteries application, such a kind of materials could be also applied for water electrolysis. In this study, a facile unipolar pulse electro-deposition (UPED) combined with thermal oxidation method is applied for the fabrication of CuO/Co₃O₄ composite on carbon electrode. It is expected that hierarchical CuO pillar@Co₃O₄ nanosheet core/shell array on the electrode with high catalytic activity for water electrolysis can be obtained.

Cu/Co(OH)₂ precursor of CuO/Co₃O₄ composites is prepared by UPED on carbon rod (CR) electrode, and the procedure follows the method described in details elsewhere¹³. Herein, the potentials applied during the on-time operation ranged from -0.2 to -1.2 V. Other parameters, i.e., pulse duration, pulse cycle times and concentration of preparation solution are optimized. It is found that the electrode with the highest catalytic performance is obtained when the pulse duration, pulse cycle times are 1 s and

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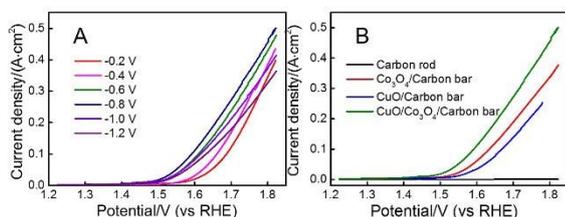


Fig. 1. (A) Polarization curves of CuO/Co₃O₄ composite catalyst prepared at different potential; (B) Polarization curves of carbon rod substrate, Co₃O₄, CuO and CuO/Co₃O₄ composite catalyst prepared at -0.8V in 1 M KOH solution, scan rate: 2 mV/s.

500 in the solution of 0.1 M Co(NO₃)₂ and 0.05 M Cu(NO₃)₂ (for details of experiment and optimization, see ESI†).

As shown in Fig.1, the electrolysis performance tests of CuO/Co₃O₄ composite, pure CuO and Co₃O₄ electrodes are carried out using the linear sweep voltammetry (LSV). Obviously, the catalytic activity of composite electrode highly depends on the deposition potential. CuO/Co₃O₄ composite prepared at -0.8 V shows the best catalytic performance for OER with a lower overpotential to afford the same current density. For comparison, catalytic properties of pure CuO and Co₃O₄ were tested. As shown in Fig. 1B, CuO and Co₃O₄ both show electrochemically active toward the OER, the overpotentials of 312 mV and 284 mV respectively are needed to afford a current density of 10 mA/cm². In contrast, the CuO/Co₃O₄ composite electrode exhibits greatly enhanced catalytic activity with only an overpotential of 227 mV to drive the same current density. This overpotential is much lower than those behaviors of previously reported OER catalysts in alkaline conditions, including CCHH/MWCNT (285 mV)¹⁴, NiCo₂O₄ (320 mV)³, Co₃O₄ (320 mV)⁹, Cu/(Cu(OH)₂-CuO) (417 mV)⁴, Mn₃O₄/CoSe₂ (450 mV)¹⁰, α-Fe₂O₃ NA/CC (420 mV)⁶, α-MnO₂-SF (490 mV)¹⁵, and comparable to the those best values reported, such as NiFe-LDHs(235 mV)¹⁶, NiFe-GO-LDHs(206 mV)¹⁷ and NiFe-CNT-LDHs (223 mV)⁸. O₂ productivity of CuO/Co₃O₄ composite electrodes is also measured (Fig. S4, ESI†), and the composite exhibits a high Faraday efficiency of 95%.

This excellent catalytic performance should be attributed to the microstructure and morphology of Co₃O₄ and CuO materials. Fig. 2 shows SEM images of pure CuO, Co₃O₄ and CuO/Co₃O₄ composite prepared by UPED under different applied potentials. Pure CuO material (Fig.2A) shows a large-size particle structure which should be accumulated by irregular lumps, due to the fast reaction rate of Cu²⁺ reduction. While pure Co₃O₄ material (Fig.2 B) obtained at the same condition shows a uniform meshy nanosheet structure which could provide more active sites for water electrolysis. Interestingly, the morphology and structures of CuO/Co₃O₄ composite materials are completely dependent on the pulse potential. At the applied potential of -0.2 V (Fig.2 C),

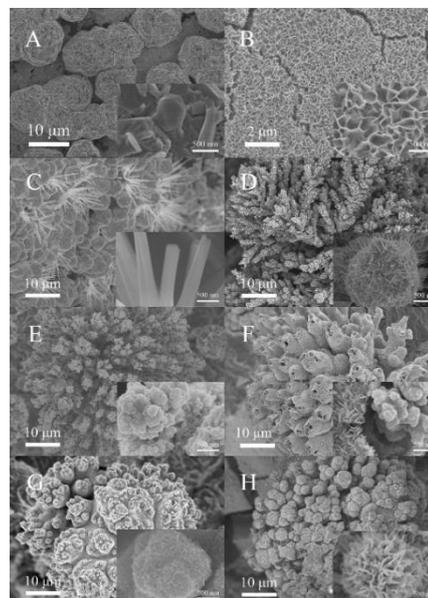


Fig. 2 SEM images of pure CuO (A), Co₃O₄ (B) and CuO/Co₃O₄ composite catalysts (C-H) obtained at different preparation potentials (C: -0.2V, D: -0.4V, E: -0.6V, F: -0.8V, G: -1.0V, H: -1.2V). Insets show enlarged images

smooth CuO nanorods with a diameter of about 200 nm and some pandan leaf-like arrays with several micrometers in length are formed on the electrode, where the arrays grow dispersedly and randomly. At the applied potential of -0.4V (Fig.2 D), a pin needle-like morphology is obtained, in which the sphere is covered by slender thorns. At the applied potential of -0.6 V (Fig.2 E), a dispersive branch structure with a stamen-like array appears, in which the composite is composed with nanoparticle and nanosheet, and the particle size is much smaller than the one obtained at -0.4V. Similar particles with more loose combination with a 3D structure are formed on the electrode at -0.8V. As shown in Fig. 2F and Fig. 3A-B, a sea anemone-like core-shell structure formed by nanosheets grow around the inside particles uniformly is obtained, which showed a hierarchical core/shell array consisting of nanosheets as the shell and nanoparticles as the core. Further changing the potentials to -1.0V and -1.2V, the dispersive branch structure disappears and a large-size accumulative morphology is obtained (Fig. 2 G and H, Fig. S5, ESI†), which should be not benefit for electrons and electrolyte circulation.

Stimulated by this novel 3D hierarchical core/shell array architectures (Fig.3 A-B), CuO/Co₃O₄ composite obtained at -0.8V are characterized by BET, XRD, EDS, TEM and SEM with higher magnification. Revealed by BET results (Fig. S6, ESI†), the CuO/Co₃O₄ composite shows higher surface area (168.5m²/g) than pure CuO (114.4 m²/g) and Co₃O₄ (153.6 m²/g) materials, and the pore sizes of composite range in 3–16 nm. Fig.

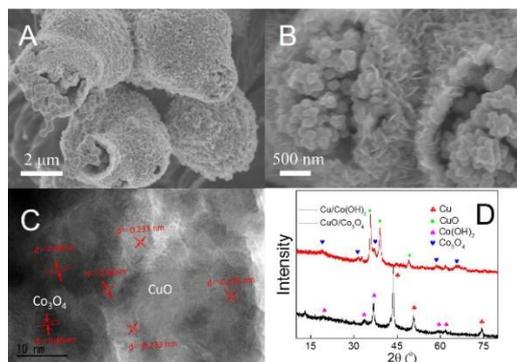


Fig. 3. Different magnification SEM images (A,B) and TEM image (C) of CuO/Co₃O₄ composite catalysts with a sea anemone-like morphology. (D) XRD patterns of CuO/Co₃O₄ composite catalyst before and after calcination

3(C) shows the high resolution TEM image of composite. The well-resolved lattice fringes with the interplanar spacing of 0.233 nm and 0.46 nm correspond to the (111) plane of CuO⁴ and the (111) plane of Co₃O₄⁵, respectively, strongly supporting the formation of CuO-Co₃O₄ composite phase. XRD patterns of the composite before and after calcination are shown in Fig. 3D. One can see that the composite is composed of all peaks of Cu⁴ and Co(OH)₂¹⁸ crystals before the calcination, but changed to CuO⁴ and Co₃O₄¹¹ crystals after the calcination. Revealed by EDS spectra (Fig. S7, ESI[†]), which is obtained by detecting the pillar core and nanosheet shell respectively, the core pillar are mainly consisted of Cu and O elements while the nanosheet shell is consisted of Co, O and trace amount of Cu elements. Combined with XRD data, one can confirm that the hierarchical core/shell array obtained at -0.8V is consisted of Co₃O₄ nanosheets as the shell and CuO pillar as the core. This kind of structure provides a series of advantages for water electrolysis. Firstly, both CuO and Co₃O₄ catalysts show good catalytic performance for OER. Compared with pure CuO and Co₃O₄ catalysts, the composite with smaller size of CuO nanoparticles and Co₃O₄ nanosheets are obtained, which should be benefit to expose more active sites⁵. Secondly, the direct growth of Cu/Co(OH)₂ precursor on CR by one-step electrodeposition ensures good interface connection between them, facilitating electrons flowing from the catalyst array to the current collector during anodic polarization. Thirdly, the porous core/shell array configuration largely increases the amount of contact areas between electrolyte and active sites, and the large surface area greatly facilitates ion and electron diffusions. Meanwhile, the inside CuO pillars not only serve as a physical support of this kind of nanoarrays but also provide the channels for electron transport, and simultaneously, the highly porous Co₃O₄ nanosheets are well wrapped around the CuO pillars, which favor the exposure of more active sites and thus enhance catalytic activity per geometric area. Fourthly, the open spaces between neighboring composite branches facilitate the diffusion of electrolyte and generation of oxygen. Finally the binder-free nature avoids the increase of various transfer resistances and the blockage of active sites and the inhibition of diffusion

Electrochemical impedance spectroscopy (EIS) of CuO/Co₃O₄ composite and pure CuO, Co₃O₄ electrodes (Fig. S8, ESI[†]). As expected, the CuO/Co₃O₄ electrode exhibits the lowest

charge transfer resistance (R_{ct}) of 0.29 Ω , while the R_{ct} of CuO and Co₃O₄ are 1.57 and 0.35 Ω respectively, implying that CuO/Co₃O₄ has lower charge transfer resistance through mutual reinforcement and/or modification of CuO and Co₃O₄. The time-dependent current density curve of CuO/Co₃O₄/CR electrode is collected at 1.8 V (Fig. S8, ESI[†]) where the cell shows a high hydrogen evolution rate. Only a slight fluctuation of the current is observed during 16 h, indicating that such a composite electrode is capable of maintaining its catalytic activity for a long time.

In summary, CuO/Co₃O₄ composite catalysts with various novel morphologies are synthesized by a facile unipolar pulse electro-deposition combined with thermal oxidation method. The morphology and microstructure of composite materials are highly dependent on the preparation potential. It is found that the sea anemone-like one with 3D hierarchical structure is formed at -0.8V. Benefit from its smart hybridization of CuO pillar@Co₃O₄ nanosheet core/shell array, the remarkably enhanced catalytic performances for OER is obtained. In addition, this electrode reveals low charge transfer resistance and excellent long-term durability. In view of the facile and efficient fabrication process and the low-cost nature of Cu and Co oxide, this material has great potential to be an inexpensive catalyst toward electrochemical water splitting.

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