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Boosting the catalysis of AuCuMo for oxygen reduction: Important roles of an optimized electronic structure and surface electrochemical stability

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Abstract: The slow kinetics of the oxygen reduction reaction (ORR) remains a great challenge in many energy storage and conversion devices, such as alkaline fuel cells and metal-air batteries. Herein, a self-supported Au-based alloy (AuCuMo) was successfully synthesized by a one-pot hydrothermal method. By combining Cu and Mo, the electronic structure of Au was finely tuned. Furthermore, the electrochemical stability of surface Cu was enhanced by the incorporation of Mo. Benefitting from these advantages, the reaction of oxygen and oxygenated intermediates on AuCuMo was optimized, and the intrinsic activity was improved. AuCuMo thereby exhibited superior ORR activity and stability compared to commercial Pt/C catalysts.

Keywords: oxygen reduction reaction; gold-based alloy; surface electrochemical stability; intrinsic activity.

Introduction

As an important reaction in metal-air batteries and alkaline fuel cells, the oxygen reduction reaction (ORR) in alkaline media has received much attention recently.[1-3] However, the sluggish kinetics of the ORR have hindered the development of these energy storage and conversion devices. Extensive efforts have been made to address this challenge. The Pt/C catalyst is well known to exhibit excellent activity. However, the limited natural resources and low stability of Pt restrict its wide applications.[4, 5] Therefore, various electrocatalysts, including transition metal oxides[6] and heteroatom-doped carbon[7, 8], have been exploited. However, the low electronic conductivity of transition metal oxides and the poor stability of heteroatom-doped carbon during operation (for example, start-up and shut-down during fuel cell operation) remain great challenges.[9] As potential candidates for Pt-based electrocatalysts, Au-based catalysts have the advantages of high conductivity, high stability and relatively high storage but suffer from low activity due to their weak oxygen-binding ability. Hence, continuous work has focused on the activity optimization of Au-based electrocatalysts. In earlier research, alloying precious metals with inexpensive metals has been proposed to reduce the cost and improve the catalytic activity of precious metal catalysts. [10-14] As a feasible and effective strategy, it also works for Au-based catalysts. Hence, Au-based bi-/trimetallic nanomaterials were developed, and the addition of a second/third metal could tailor the electronic structure of Au and generate a synergistic effect. [15-18] For example, several studies have focused on Au-Cu-based catalysts, where the addition of Cu,

which has a strong oxygen-binding ability, could enhance the absorption of oxygen and thereby the activity of the catalyst. However, the stability of the Au-Cu-based catalyst needs to be improved.[15, 16] Herein, a trimetallic AuCuMo nanobranched alloy was developed. The addition of Mo as a third element enhanced the electrochemical stability of Au-Cu. Furthermore, the addition of Cu and Mo effectively optimized the electronic structure of Au; hence, the activity and stability of AuCuMo towards ORR electrocatalysis was significantly improved.



Scheme 1. Schematic of AuCuMo synthesis.

Experimental

Chemicals

Nafion (5% w/w) and commercial Pt/C (20 wt. %) were obtained from Alfa Aesar. Octadecylamine (95 wt. %), HAuCl₄·4H₂O (99 wt. %), CuCl₂·2H₂O (99 wt. %), (NH₄)₆Mo₇O₂₄·4H₂O (99 wt. %), DMSO (99 wt. %), n-hexane (95 wt. %), ethanol (99 wt. %) and KOH (95 wt. %) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. All reagents were used without further purification.

Sample synthetic methods

Scheme 1 shows the synthetic route of the AuCuMo catalyst. The precursor solution containing the three metal salts and octadecylamine was thoroughly and homogeneously mixed by magnetic stirring. The hydrothermal process was performed in a drying oven. Octadecylamine was used as the surfactant and reducing agent and removed by repeated centrifugation.

In a typical procedure, octadecylamine (7 mmol), CuCl₂·2H₂O (0.2 mmol), and $(NH_4)_6Mo_7O_{24}·4H_2O$ (0.05 mmol) were dispersed in a mixed solution (DMSO: H₂O = 20 mL: 42.48 mL). Next, a HAuCl₄·4H₂O solution (0.2 mmol of HAuCl₄·4H₂O in 8.32 mL aqueous solution) was added, followed by magnetic stirring for 24 hr. Then, the solution was transferred to an autoclave, and a hydrothermal process at 120 °C was carried out for 48 hr. Afterwards, the sample was filtered and washed with ethanol and n-hexane three times.

The synthesis of AuCu was the same as the synthesis of AuCuMo but without the addition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

Material characterization

To obtain structure and morphology information, X-ray diffraction (XRD, D8 Advance), scanning electron microscopy (SEM, Hitachi SU8010) and transmission electron microscopy (TEM; FEI Talos F200s and Tecnai G2 F20) were applied. To obtain electronic structure environment information, X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII) was applied. ICP (Vista MPX) was applied to obtain bulk component information.

Electrochemical measurements

A CHI760E electrochemical workstation and RRDE-3A apparatus were employed to perform the electrochemical measurements at 25 °C. For the electrode preparation, 1 mg catalyst (AuCuMo, AuCu and commercial Pt/C) was dispersed in a solution of 1.6 mL ethanol and 0.4 mL Nafion (0.2 % w/w in a mixture of ethanol), and the solution was ultrasonically mixed for 30 minutes. Next, for RDE (3 mm in diameter), 13 µL solution was dip-coated on the surface; for RRDE (4 mm in diameter), 25 µL solution was dip-coated on the surface. After drying under ambient conditions, RDE or RRDE was used as the working electrode in the three-electrode system, and Ag/AgCl (saturated KCl solution) and Pt foil were used as reference and counter electrodes, respectively. Here, in 0.1 M KOH, all potentials were referenced to the standard reversible hydrogen electrode (RHE) according to E (RHE) = E (Ag/AgCl, saturated KCl solution) + 0.965 V. For the electrochemical test, the details were as follows: First, cyclic voltammetry (CV) was conducted from 0.05 to 1.1 V at 50 mV s⁻¹ in argon without rotation for catalyst activation. Then, for ORR background correction, CV was performed from 0.2 to 1.1 V at 10 mV s⁻¹ in argon with a rotating speed of 1600 rpm. Next, the CV was measured between 0.05 and 1.1 V at 50 mV s⁻¹ in O₂ without rotation for the ORR. Finally, linear sweep voltammetry (LSV) was performed from 1.1 to 0.2 V at 1600 rpm to evaluate the ORR performance. For the RRDE test, the ring potential was set at 1.2 V. For the chronoamperometric (CA) test, the i-t curve was obtained under a constant potential of 0.765 V for 15000 s. To

determine the electron transfer number (n), the rotating speeds ranged from 900 to 2025 rpm, and n was calculated according to Koutecky–Levich (K-L) equations (1) and (2):

$$1/j = 1/j_k + 1/j_d = 1/j_k + 1/(B\omega^{1/2})$$
(1)

$$B = 0.62nFD_{o_2}^{2/3} v^{-1/6} C_{o_2}$$
⁽²⁾

where j is the measured current density, j_k is the kinetic-limiting current density, j_d is the diffusion-limiting current density, and ω is the electrode rotation rate. D_{O_2} is the diffusion coefficient of O₂ ($D_{O_2} = 1.86 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), F is the Faraday constant (96485 C mol⁻¹), C_{O_2} is the concentration of O₂ dissolved in the electrolyte ($C_{O_2} = 1.21 \times 10^{-6} \text{ mol cm}^{-3}$), and υ is the kinetic viscosity of the solution ($\upsilon = 0.01 \text{ cm}^2 \text{ s}^{-1}$).

The RRDE test was further applied to measure the hydrogen peroxide yield (% HO_2^{-}) and the electron transfer number (n) during the ORR.

$$n = 4 \times \frac{abs(j_D)}{abs(j_D) + j_R / N}$$
(3)

$$\% HO_2^{-} = 100 \times \frac{2j_R / N}{\operatorname{abs}(j_D) + j_R / N}$$
 (4)

where j_D and j_R could be determined from polarization curves directly and the collection efficiency (N) was 0.424.

Results and discussion



Figure 1. (A) SEM image, (B) TEM image of AuCuMo. (C, D) Enlarged HRTEM images of AuCuMo. (E, F, G, H, I, J) HAADF-STEM image and elemental mappings of AuCuMo.

The hydrothermal method was used to synthesize AuCuMo branched nanostructures, where a soft template was adopted. [19] In our previous work, it was found that the coexistence of gold and copper precursors has great significance in the synthesis of nanobranches. [18, 20, 21] In this work, a molybdenum precursor was added to form AuCuMo nanostructures. As shown in the SEM image (Figure 1A) and TEM image (Figure 1B, C), the as-synthesized AuCuMo shows a branched nanostructure, similar to that of AuCu (Figure S1). The typical interplanar distance of 0.217 nm (Figure 1D) corresponds well to the d-spacing of the (111) crystal plane of Au-based alloys as a result of the addition of smaller Cu and Mo atoms to the (111) planes of Au (0.235 nm). Moreover, different growth directions and dislocations are

observed in the distorted part of the AuCuMo branch in Figure 1D, and twin crystals are observed for AuCu in Figure S1. These defects can act as active sites in electrocatalysis.[22] Elemental mapping shows a homogeneous distribution of Au, Cu and Mo in the nanobranch (Figure 1G, H, I, J). Similar morphology and features are observed for AuCu (Figure S1). The XRD patterns of AuCuMo and AuCu are shown in Figure S2. AuCuMo and AuCu show similar XRD diffraction patterns, and diffraction peaks of gold, copper and molybdenum monocomponents are not observed; hence, the synthesis of a single-phase alloy is further verified.



Figure 2. (A) 1-50 cycle CV curves of AuCuMo and AuCu. (B) CV curves of AuCuMo after the activation process. (C) CV curves of AuCu after the activation process.

In a surface-sensitive reaction such as the ORR, the surface condition is important for electrocatalysis.[23] Here, the CV patterns in Ar-saturated 0.1 M KOH are useful for analysing the surface conditions of AuCuMo and AuCu. Initially, a 50-cycle CV (sweep rate: 50 mV s⁻¹) served as an activation process, and the potential window ranged from 0.05 to 1.665 V (Figure 2A). After activation, as shown in Figure 2B, a stable curve was obtained at a scan rate of 10 mV s⁻¹ on negative scanning, and the characteristic reduction of Au and Cu oxide was observed. The peaks located at 0.85 V and 1.08 V correspond to Au oxide, and the peaks located at 0.31 V and 0.62 V correspond to Cu oxide, respectively.

For AuCu, the same procedure was performed, and the surface conditions are shown in Figure 2C. It is worth noting that the surface electrochemical stability is important for ORR electrocatalysis. [24] Here, the electrochemical stability of surface Cu in AuCuMo and AuCu is obviously different. Taking the peak corresponding to Cu(II)-to-Cu(I) reduction as an example, during the activation process shown in Figure 2A, the Cu(II)-to-Cu(I) reduction peak area undergoes a decrease of 59.7 % for AuCuMo, while for AuCu, the peak undergoes a decrease of 97.4 %. This sharp contrast illustrates that the electrochemical stability of surface Cu was distinctly enhanced as a result of the addition of Mo into the Au-Cu system. In addition, as shown in Figure 2C, the ratio of the Cu reduction peak to the Au reduction peak for AuCu is much lower than that for AuCuMo in Figure 2B, and the electroactive and electrostable Au and Cu in AuCuMo could be favourable for catalytic activity.

The ORR on AuCuMo, AuCu and commercial Pt/C was studied via linear sweep voltammetry (LSV) in 0.1 M KOH saturated with O₂. The onset potential (E_{onset}) and the half-wave potential ($E_{1/2}$) are important descriptors for the assessment of ORR performance.[25] Here, for AuCuMo, the E_{onset} is 1.03 V, which is 30 mV and 50 mV more positive than those of Pt/C (1.00 V) and AuCu (0.98 V), respectively (Figure 3A). Furthermore, the $E_{1/2}$ of AuCuMo is 0.875 V, which is positively shifted by 16 mV and 50 mV compared to Pt/C (0.859 V) and AuCu (0.825 V), respectively (Figure

3A). To further understand the reaction kinetics for the ORR, mass transport-corrected Tafel plots were obtained. Figure 3B shows that AuCuMo, AuCu and Pt/C possess Tafel slopes of 47.7, 44.7 and 68 mV dec⁻¹, respectively. The smaller Tafel slopes of AuCuMo and AuCu indicate faster kinetic behaviour. [26] To obtain the electron transfer number (n), LSV measurements were recorded at different rotation rates (Figure 3C). The corresponding Koutecky-Levich (K-L) plots are shown in Figure 3D. Based on the K-L equation, the electron transfer number n is calculated to be approximately 4, which is further confirmed by rotating ring disk electrode (RRDE) tests (Figure 3E, F). The results indicate a quasi-four-electron ORR pathway and a low amount of H_2O_2 (< 3 %) for AuCuMo.



Figure 3. (A) RDE polarization curves of AuCuMo, AuCu and commercial Pt/C. (B) Tafel plots of AuCuMo, AuCu and commercial Pt/C. (C) RDE polarization curves of AuCuMo at different rotation rates. (D) K-L plots of the ORR on AuCuMo. (E) Disk and ring currents for AuCuMo. (F) Electron transfer number (n; top) and H₂O₂ yield

(bottom) for AuCuMo.

The durability of AuCuMo, AuCu and commercial Pt/C was assessed by a CA method. Strikingly, there is no obvious decay (< 0.5 %) of AuCuMo after the whole testing time (15000 s) (Figure 4A), demonstrating that the AuCuMo catalyst exhibits better durability than AuCu and Pt/C. To account for electrocatalytic stability, the CV was performed before and after the CA test and compared. As shown in Figure 4B, no obvious change in the CV curve was observed, especially for the reduction peaks of Au and Cu; hence, the surface electrochemical stability of Au and Cu was achieved on the AuCuMo surface, and the durability was distinctly enhanced.



Figure 4. (A) Comparison of ORR stability on AuCuMo, AuCu and commercial Pt/C.(B) CV curves of AuCuMo before and after the stability test.

The enhanced ORR performance of the AuCuMo catalyst can be rationalized as follows. Initially, Mo is considered to be important for the surface stability of crystals.[27, 28] By adding Mo, Au and Cu become electrochemically stable on the surface of AuCuMo after CV activation, while for AuCu, the Cu content at the surface is very low after CV activation. For ORR electrocatalysis, Cu exhibits stronger oxygen adsorption than Au, and the existence of stable Cu at the surface could thereby enhance the adsorption of oxygen.[15]

Next, to investigate the variations in the desorption of oxygenated intermediates from the catalyst surface, XPS was performed (Figure 5A, S3). As shown in Figure 5A, the Au4f high-resolution XPS spectrum of AuCuMo displays two peaks corresponding to $Au^{0}(4f_{7/2})$ and $Au^{0}(4f_{5/2})$ at 84.22 and 87.92 eV, respectively. Compared to those of pure Au (83.42 and 87.12 eV) and AuCu (83.62 and 87.32 eV), the binding energies of Au4f for AuCuMo shift to higher values as a result of the addition of Cu/Mo (Figure 5B), leading to the electronic structure optimization of Au and rendering the desorption of oxygenated intermediates from the surface easier.[29] Furthermore, the metal valence-band structure, usually described quantitatively in terms of the d-band centre energy, can be significantly affected by the addition of the second/third metal, and to determine the d-band centre position of Au, the surface electronic structure of our bi-/trimetallic catalysts was studied using valence band XPS evaluations (Figure 5C, Figure S4)[30, 31]. After subtraction of the Shirley backgrounds, the intensity signals of the valence-band spectra are proportional to the density of states. Upon addition of Cu/Mo, the valence d-band centre changed , from -3.88 eV for Au, to -4.09 eV for AuCu, and -4.68 eV for AuCuMo. Such a change in the d-band centres is crucial in the precise regulation/reduction of binding strength between the catalysts and adsorbates. This will remove strongly adsorbed species from the Au-based catalyst surface and boost the intrinsic activity.



Figure 5. (A) XPS spectra of Au4f in AuCuMo, AuCu and Au. (B) Binding energies of $Au^0(4f_{7/2})$ in AuCuMo, AuCu and Au. (C) d-band centre energies of AuCuMo, AuCu and Au. (D) ICP quantitative analysis and XPS semi-quantitative analysis of the element content in AuCuMo. (E) ICP quantitative analysis and XPS semi-quantitative analysis of the element content in AuCu.

In addition, as shown in Figure 5D and 5E, for AuCuMo, from the ICP quantitative analysis, the Au: Cu: Mo ratio was 4.173: 10.088: 1 for the bulk catalyst; from the XPS semiquantitative analysis, the Au: Cu: Mo ratio was 8.296: 11.028: 1 for the catalyst surface, the Au content was 27.34 % for the bulk and 40.82 % for the surface, and more Au existed at the surface. For AuCu, the Au: Cu ratio was 1: 1 for the bulk catalyst and 0.454: 1 for the catalyst surface. The Au content was 50 % for the bulk catalyst and 31.21 % for the surface, and more Au existed inside the catalyst. The obvious difference in the number of surface active sites explains the increasing

ORR activity of AuCuMo. It is worth noting that, as shown in Table S1, compared to our previous research on Au-Cu-M (M= Co, Ni) trimetallic electrocatalysts[18, 29], AuCuMo exhibits the best ORR activity, which confirms the importance of the addition of Mo, and the continuous optimization of Au-Cu-M-based electrocatalysts will be carried out in future work.

Conclusion

In this work, a promising AuCuMo catalyst for the ORR in alkaline media was synthesized via a facile method. The enhanced properties originate from the improved intrinsic activity of Au boosted by the optimized electronic structure of Au by adding Cu and Mo and the enhanced electrochemically stable surface promoted by Mo. This work opens a new avenue to the preparation of active and stable Au-based electrocatalysts in the field of alkaline fuel cells and metal-air batteries.

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Appendix A. Supplementary materials

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2020.xxxxxx.

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OUTRO

Highlights

- Self-supported AuCuMo alloy exhibits high activity and stability for ORR.
- By incorporating Cu and Mo, the electronic structure of Au is finely tuned.
- Electro-chemical stability of surface Cu is enhanced by incorporation of Mo
- Electronic structure and surface electrochemical stability are crucial for ORR. •

stability

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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