Size-dependent catalytic activity of copper nanoclusters for oxygen electroreduction in alkaline solution

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By using 2-mercapto-5-n-propylpyrimidine (MPP) as capping ligands, copper nanoclusters with different core sizes were prepared using a chemical reduction method. The as-prepared copper nanoclusters were loaded onto a glassy carbon electrode and their size effect on the electrocatalytic activity towards the oxygen reduction reaction (ORR) was investigated with electrochemical techniques in alkaline electrolyte. Cyclic voltammetric (CV) studies showed that the onset potential of ORR on smaller copper nanoclusters is more positive than that on larger copper nanoclusters. Compared to the larger clusters, higher current density of ORR was obtained using the smaller copper nanoclusters. These CV results indicate that the smaller Cu nanoclusters exhibit higher catalytic performance for ORR. In rotating-disk voltammetric studies, ORR on the synthesized MPP monolayer-protected copper nanoclusters is mainly dominated by a two-electron transfer pathway to produce H2O2.

Keywords: copper; nanocluster; oxygen reduction; electrocatalysis; voltammetry

1. Introduction

It is widely accepted that coin metals, such as gold, silver and copper, are catalytically inert for most reactions. With the extensive studies on nanomaterials in the last decades, it has been found that metal materials on the nanometer scale exhibit much higher catalytic activity compared to the corresponding bulk metals [1–8]. For instance, Herzing et al. [9] observed high catalytic activity in CO oxidation with gold clusters containing only \(\sim\)10 gold atoms (\(\sim\)0.5 nm in diameter). In comparison with bulk materials, the fraction of low-coordinated atoms at the surface increases remarkably in small nanoclusters. For oxygen reduction on the surfaces of catalysts, the adsorption of O2 molecules is one of the crucial steps. For small metal clusters with low-coordinated metal atoms, the narrow gap between the d-band and the Fermi level makes oxygen molecules adsorption on the cluster surface more easy than on the close-packed counterparts. It is well known that the surface area and the fraction of surface atoms of metal nanoparticles depend strongly on the core size of the nanoparticles. Therefore, much attention has been focused on studies of particle size effect on their catalytic activity. Recently, oxygen electrochemical reduction was studied with a series of gold nanoclusters with sizes smaller than 2 nm (0.8 to 1.7 nm) [3]. It was found that the Au nanoclusters exhibited much high electrocatalytic activity for oxygen reduction and higher catalytic performance.
was obtained at the smaller clusters. Tang et al. [10] studied the size-dependent activity of 3 and 7 nm gold nanoparticles for oxygen reduction and they found that the 3 nm particles exhibited 2.5 times higher kinetic current compared to the 7 nm particles. These studies indicated that the catalytic properties of coin metals can be manipulated by altering the particle size.

Electrocatalytic oxygen reduction reaction (ORR) is one of the extremely critical cathodic processes in fuel cells [11]. Pt and Pt-based metal alloys have been widely examined as cathode electrocatalysts for ORR with the most efficient four-electron reduction of adsorbed oxygen to water. In order to reduce the high cost of Pt loading on both anode and cathode, and realize fuel cell commercialization practically, extensive research efforts have been devoted to the non-Pt electrocatalysts both experimentally and theoretically, mainly including transition metal oxides [12,13], transition metal sulfides [14], transition metal macrocyclic complexes [15,16] and metal-containing porphyrin systems. With non-Pt electrocatalysts, the mechanism of ORR by the less efficient two-electron reduction of O_2 to hydrogen peroxide or efficient four-electron reaction is critically dependent on the electrode materials and the electrolytes.

Due to the significant electrocatalytic activity towards oxygen reduction, copper complexes have attracted much attention in recent years [17–19]. For instance, Brushett et al. [18] studied the catalytic activity of a carbon-supported copper complex of 3,5-diaminotriazine and found that the copper complex exhibits comparable oxygen reduction catalytic performance to that of Pt/C cathode and significantly greater mass activity than that of Pt/C- or Ag/C-based catalysts. Recently, we synthesized copper nanoclusters (Cu_n with n ≤ 8) by a one-pot wet chemical reduction method [20]. The synthesized Cu clusters also exhibit high catalytic activity for oxygen reduction. The properties of small nanoclusters, especially below 10 nm, could be dramatically different from larger ones due to quantum size effects. The ORR with Cu nanoclusters with sized smaller than 10 nm, however, is still scarce due to the difficulty in the synthesis of small Cu clusters.

In the present study, we synthesized 2-mercapto-5-n-propylpyrimidine-capped copper nanoclusters with different core sizes. The prepared Cu nanoclusters were subsequently assembled on a glassy carbon electrode surface to study their electrocatalytic properties for oxygen reduction in alkaline media. As will be shown, the synthesized Cu nanoclusters exhibit definite catalytic activity for ORR in cyclic and rotating-disk voltammetric measurements and their electrocatalytic performance depends obviously on the core size. The purpose of our work was to study the size effect and the mechanisms of the oxygen reduction on Cu nanoclusters, which will be helpful to develop novel non-platinum cathode electrocatalysts for fuel cells.

2. Experimental

2.1. Chemicals

Copper(II) nitrate trihydrate (99.5%, analytical reagent grade), and sodium borohydride (98%) were obtained from Acros Organic. Tetra-n-octylammonium bromide (98%) and 2-mercaptopro-5-n-propylpyrimidine (MPP, 98%) were obtained from Alfa Aesar. Water was supplied by a Water Purifier Nanopure water system (18.3 MΩ cm). All chemicals were used as received without any further purification. Ultrapure N_2 and O_2 were used for the deaeration and oxygen reduction reaction, respectively.
2.2. Synthesis of Cu nanoclusters

The MPP-protected Cu nanoclusters were synthesized according to the modified procedure reported previously [21]. In a typical synthesis, 0.025 g of copper(II) nitrate and 0.136 g of tetra-n-octylammonium bromide were co-dissolved in 25 mL of absolute alcohol, and this solution was stirred at 80°C for 30 min. This solution was then cooled in ice water. 0.0766 g of 2-mercapto-5-n-propylpyrimidine (MPP) was added to this solution with vigorous stirring under an argon stream for 6 h; 0.047 g of sodium borohydride in 5 mL of ethanol was then added into the reaction mixture. The solution was left to react for 7 h. A maize precipitate was isolated by centrifugation, washed repeatedly with ethanol and vacuum dried. Finally the products were re-dispersed in toluene for further use. The core size of the Cu nanoclusters can be controlled by changing the initial feed ratio of MPP and copper salt concentration. Here three samples of MPP-protected copper nanoclusters were prepared with the initial molar ratio of MPP to copper varying from 4 to 2 and 1. The synthesized Cu nanoclusters are denoted as Cu-MPP(4×), (2×), and (1×), respectively.

2.3. Electrochemistry

Prior to the assembly of the Cu nanoclusters onto an electrode surface for electrocatalytic assessment, a glassy carbon (GC) electrode (3.0 mm diameter) was polished with alumina slurries (5, 1 and 0.5 µm) and cleansed by sonication in 0.1M HNO₃, H₂SO₄ and Nanopure water for 10 min successively. 10 µL of the as-synthesized Cu nanoclusters in CHCl₃ (1 mg mL⁻¹) was then drop-cast onto the clean GC electrode surface by a microliter syringe and was dried by a gentle nitrogen flow for ca. 2 min. The electrode was then rinsed with Nanopure water and ethanol to remove the impurities. The resulting Cu nanocluster-modified electrodes are denoted as Cu-MPP(x×) (x = 4, 2 or 1)/GC.

The Cu-MPP/GC electrode prepared above was used as the working electrodes. A Ag/AgCl (in 3M NaCl, aq) and a Pt coil were used as the reference and counter electrodes, respectively. All electrode potentials in the present study were referred to this Ag/AgCl reference. Cyclic voltammetry and rotating-disk voltammetry were carried out using a CHI 750D electrochemical workstation. The rotating-disk voltammograms on all electrodes were measured at the potential scan rate of 20 mV s⁻¹. Oxygen reductions were examined by first bubbling the electrolyte solution with ultrahigh purity oxygen for at least 15 min and then blanketing the solution with an oxygen atmosphere during the entire experimental procedure. All electrochemical experiments were carried out at room temperature.

3. Results and discussion

3.1. Synthesis of Cu nanoclusters with different core size

In the present study, three samples of MPP-protected copper nanoclusters were prepared by changing the molar ratio between protecting ligands and copper precursor. It is well known that the growth dynamics of metal nanoparticles includes two competing processes, metal core growth form the nucleation of zero-valence metal atoms and the passivation of metal clusters by surface protecting ligands. Based on such mechanism, the metal particle size could be controlled by changing the ligand concentration during the reaction. In previous studies, size-controlled synthesis of silver and ruthenium nanoparticles has been achieved by controlling the initial dithiocarbamate ligand–metal feed ratios [22,23]. The
core diameters of the synthesized copper nanoclusters were evaluated with transmission electron microscopy (TEM). Figure 1a shows a high-resolution TEM micrograph of the Cu nanoclusters with the ligand–metal ratio of 4 (i.e. Cu-MPP(4×)). Due to the tiny size of the Cu-MPP(4×) clusters, the core diameter is difficult to obtain accurately from TEM measurements. In our previous studies, mass spectrometry of the Cu nanoclusters was carried out and Cu₈ clusters were found to be the dominant components. So the average core size of Cu-MPP(4×) is smaller than 1.0 nm. Figure 1b shows the TEM image of the Cu-MPP(2×) nanoclusters. The average core size of Cu-MPP(2×) was found to be 6.9 nm. With the ligand-to-metal ratio decreasing, the core size of the copper nanoclusters increases. From the TEM image shown in Figure 1c, it was determined that the average size of the Cu-MPP(1×) nanoclusters increases to 10.8 nm. The TEM characterization indicates that the size of the copper can be effectively controlled by changing the ratio of ligand-to-metal.
3.2. Electrochemical cyclic voltammetry

The electrocatalytic activity of the copper nanoclusters with different core sizes towards oxygen reduction reaction (ORR) was then examined by electrochemical cyclic voltammetry (CV). Figure 2 shows the cyclic voltammograms of the Cu-MPP(4×)/GC, Cu-MPP(2×)/GC and Cu-MPP(1×)/GC electrodes in 0.1M KOH solution saturated with nitrogen (black curves) and oxygen (grey curves) at a potential scan rate of 0.1 V s⁻¹. On all the electrodes, compared to the CVs in nitrogen-saturated electrolyte, obvious oxygen reduction current can be observed when the KOH solution was saturated with oxygen, suggesting the obvious electrocatalytic activity of the synthesized copper nanoclusters towards oxygen reduction. The electrocatalytic activities of the copper nanoclusters can be evaluated and compared with the onset potentials and current densities of ORR. It can be seen

![Cyclic voltammograms](image)

Figure 2. Cyclic voltammograms of the Cu-MPP(4×)/GC (a), Cu-MPP(2×)/GC (b) and Cu-MPP(1×)/GC (c) electrodes in 0.1M KOH solution saturated with nitrogen (black curves) and oxygen (gray curves). Potential scan rate 0.1 V s⁻¹.
by comparing the CVs shown in Figure 2 that these two important parameters are significantly different at the three electrodes. As for onset potential, −0.07, −0.11 and −0.19 V were obtained at Cu-MPP(4×)/GC, Cu-MPP(2×)/GC and Cu-MPP(1×)/GC electrodes, respectively. This means that the onset potential of ORR on the smallest copper nanoclusters (< 1 nm) is 120 mV more positive than that on 10.8 nm copper clusters. Obviously, the onset potential of ORR shows negative shift with increasing core size of the copper nanoclusters. At the Cu-MPP(4×)/GC electrode, the oxygen reduction current density at −0.30 V was measured to be approximately −0.31 mA cm⁻². However, the current density of ORR at the same potential decreases to −0.25 and −0.13 mA cm⁻² at Cu-MPP(2×)/GC and Cu-MPP(1×)/GC electrodes, respectively. The voltammetric studies show clearly that the electrocatalytic activity of Cu nanoclusters towards ORR is strongly dependent on the Cu cluster size, i.e. the smaller copper clusters exhibit the higher electrocatalytic activity for oxygen reduction. Such a result is in accordance with our previous finding with gold nanoclusters [3].

To obtain the kinetic parameters of ORR on copper nanoclusters, the reaction kinetics of oxygen reduction at the copper nanoclusters were also studied with rotating-disk voltammetry. Figure 3 shows a series of rotating-disk voltammograms (RDVs) of ORR recorded at Cu-MPP(4×)/GC, Cu-MPP(2×)/GC and Cu-MPP(1×)/GC in an oxygen-saturated 0.1M KOH solution at different rotation rates (from 225 to 3600 rpm). It can be seen that on all the electrodes, the limiting current density increases with increasing rotation rate. Again, the reduction current displayed in Figure 3 suggests the apparent activity of the synthesized copper nanoclusters towards ORR.

The kinetic parameters of ORR on the copper nanoclusters can be analyzed with the Koutecky–Levich equations:

\[ \frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B \omega^{1/2}}, \]  

\[ B = 0.62nFC_OD_O^{2/3}v^{-1/6}, \]

\[ J_K = nFkC_O, \]

where \( J \) is the measured current density, \( J_K \) and \( J_L \) are the kinetic and diffusion limiting current densities, respectively, \( \omega \) is the electrode rotation rate, \( n \) is the overall number of electrons transferred, \( F \) is the Faraday constant, \( C_O \) is the bulk concentration of \( O_2 \) dissolved in the electrolyte, \( D_O \) is the diffusion coefficient for \( O_2 \), \( v \) is the kinematic viscosity of the electrolyte and \( k \) is the electron transfer rate constant. According to Equations (1) and (2), the number of electrons transferred and \( J_K \) can be obtained from the slope and intercept of the Koutecky–Levich plots, respectively. Based on the Koutecky–Levich equations, the corresponding Koutecky–Levich plots on the three electrodes are shown in Figure 4. It can be seen that the slopes remain approximately constant over the potential range from −0.86 to −0.98 V, indicating consistent numbers of electron transfer for ORR at different electrode potentials. By using the reported values [24,25] of \( C_O = 1.2 \times 10^{-3} \) mol L⁻¹, \( D_O = 1.9 \times 10^{-5} \) cm² s⁻¹ and \( v = 0.01 \) cm² s⁻¹, the kinetic limiting current density \( J_K \) at −0.86 V was calculated to be −5.62, −0.70 and −1.08 mA cm⁻² at Cu-MPP(4×)/GC, Cu-MPP(2×)/GC and Cu-MPP(1×)/GC electrodes, respectively. From the slopes of the plots in Figure 4, the numbers of electrons transferred were determined to be 2.2, 2.5 and
Figure 3. Rotating-disk voltammograms obtained on the Cu-MPP(4×)/GC (a), Cu-MPP(2×)/GC (b) and Cu-MPP(1×)/GC (c) electrodes in 0. M KOH solution saturated with oxygen at different rotation rates (shown as figure legends).

1.7, respectively, for ORR on Cu-MPP(4×)/GC, Cu-MPP(2×)/GC and Cu-MPP(1×)/GC electrodes.

The RDE results indicate that the oxygen reduction on the synthesized copper clusters is mainly dominated by a two-electron transfer pathway to produce H₂O₂. The capping ligands will surely reduce the active sites on the copper cluster surface. It should be noted that the present study highlights the core size effect of copper nanoclusters on their catalytic activity toward ORR. To prevent the agglomeration of the Cu nanoclusters during the investigation, the protecting ligands were not removed for all the studied samples in the electrochemical measurements. The low interfacial charge transfer obtained in RDVs may be ascribed to the passivated surfaces of the copper nanoclusters. However, the obvious voltammetric currents from ORR indicate that the copper nanoclusters show considerable
catalytic activities even if their surfaces are capped with organic ligands. It should be pointed out that the relative amount of capping agents is different on the three samples with different core sizes. According to the previous studies reported by Murray and co-workers [26], the surface coverage of ligands increases with decreasing core size of metal...
nanoclusters. For instance, the alkanethiolate surface coverage increases from 51% to 63% when the metal core radius decreases from 0.98 nm to 0.65 nm. In the present work, the different amount of capping agents on the samples should not be the main reason for the difference in catalytic properties, since the smaller copper clusters with larger ligand coverage, however, exhibit higher catalytic activity.

4. Conclusion
Copper nanoclusters with different core sizes were synthesized successfully with 2-mercapto-5-n-propylpyrimidine (MPP) as protecting ligands. The size effect of the synthesized copper nanoclusters on the electrocatalytic activity for ORR was investigated with CV and RDV in alkaline electrolyte. The CV studies indicate that the core size of copper clusters exhibits a strong effect on their electrocatalytic activity towards oxygen reduction. By comparing the onset potential and current densities of ORR, the catalytic performance decreases with the core size increasing and the smallest clusters exhibit the best electrocatalytic activity. Two-electron reduction process of adsorbed oxygen was derived from the kinetic results of rotating disk voltammograms, and the low efficient pathway shown in this study may be ascribed to the capping ligand-passivated surfaces of the copper nanoclusters.

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References
[1] M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, Gold catalysts prepared by co-precipitation for low-temperature oxidation of hydrogen and of carbon monoxide, J. Catal. 115 (1989), pp. 301–309.
[2] M. Valden, X. Lai, and D. W. Goodman, Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties, Science 281 (1998), pp. 1647–1650.
[3] W. Chen and S. W. Chen, Oxygen electroreduction catalyzed by gold nanoclusters: Strong core size effect, Angew. Chem. Int. Ed. 48 (2009), pp. 4386–4389.
[4] B. E. Hayden, D. Pletcher, and J. P. Suchsland, Enhanced activity for electrocatalytic oxidation of carbon monoxide on titania-supported gold nanoparticles, Angew. Chem. Int. Ed. 46 (2007), pp. 3530–3532.
[5] F. Boccuzzi, G. Cerrato, F. Pinna, and G. Strukul, FTIR, UV-Vis, and HRTEM study of Au/ZrO2 catalyst: Reduced reactivity in the CO–O2 reaction of electron-deficient gold sites present on the used samples, J. Phys. Chem. B 102 (1998), pp. 5733–5736.
[6] J. Solla-Gullon, J. Hernandez, E. Herrero, A. Aldaz, and J. M. Feliu, Electrochemistry of shape-controlled catalysts: Oxygen reduction reaction on cubic gold nanoparticles, J. Phys. Chem. C 111 (2007), pp. 14078–14083.
[7] W. Chen, D. Ny, and S. W. Chen, SnO2–Au hybrid nanoparticles as effective catalysts for oxygen electroreduction in alkaline media, J. Power Sourc. 195 (2010), pp. 412–418.
[8] Y. Z. Lu, Y. C. Wang, and W. Chen, Silver nanorods for oxygen reduction: Strong effects of protecting ligand on the electrocatalytic activity, J. Power Sourc. 196 (2011), pp. 3033–3038.
[9] A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon, and G. J. Hutchings, Identification of active gold nanoclusters on iron oxide supports for CO oxidation, Science 321 (2008), pp. 1331–1335.
[10] W. Tang, H. F. Lin, A. Kleiman-Shwarsctein, G. D. Stucky, and E. W. McFarland, Size-dependent activity of gold nanoparticles for oxygen electroreduction in alkaline electrolyte, J. Phys. Chem. C 112 (2008), pp. 10515–10519.
[11] W. Chen, J. M. Kim, S. H. Sun, and S. W. Chen, *Electrocatalytic reduction of oxygen by FePt alloy nanoparticles*, J. Phys. Chem. C 112 (2008), pp. 3891–3898.

[12] Y. Liu, A. Ishihara, S. Mitsushima, N. Kamiya, and K. Ota, *Transition metal oxides as DMFC cathodes without platinum*, J. Electrochem. Soc. 154 (2007), pp. B664–B669.

[13] S. V. Mentus, *Oxygen reduction on anodically formed titanium dioxide*, Electrochim. Acta 50 (2004), pp. 27–32.

[14] R. W. Reeve, P. A. Christensen, A. Hamnett, S. A. Haydock, and S. C. Roy, *Methanol tolerant oxygen reduction catalysts based on transition metal sulfides*, J. Electrochem. Soc. 145 (1998), pp. 3463–3471.

[15] H. S. Liu, C. J. Song, Y. H. Tang, J. L. Zhang, and H. J. Zhang, *High-surface-area CoTMPP/C synthesized by ultrasonic spray pyrolysis for PEM fuel cell electrocatalysts*, Electrochim. Acta 52 (2007), pp. 4532–4538.

[16] L. Zhang, J. J. Zhang, D. P. Wilkinson, and H. J. Wang, *Progress in preparation of non-noble electrocatalysts for PEM fuel cell reactions*, J. Power Sourc. 156 (2006), pp. 171–182.

[17] M. S. Thorum, J. Yadav, and A. A. Gewirth, *Oxygen reduction activity of a copper complex of 3,5-diamino-1,2,4-triazole supported on carbon black*, Angew. Chem. Int. Ed. 48 (2009), pp. 165–167.

[18] F. R. Brushett, M. S. Thorum, N. S. Lioutas, M. S. Naughton, C. Tornow, H. R. Jhong, A. A. Gewirth, and P. J. A. Kenis, *A carbon-supported copper complex of 3,5-diamino-1,2,4-triazole as a cathode catalyst for alkaline fuel cell applications*, J. Am. Chem. Soc. 132 (2010), pp. 12185–12187.

[19] S. Fukuzumi, H. Kotani, H. R. Lucas, K. Doi, T. Suenobu, R. L. Peterson, and K. D. Karlin, *Mononuclear copper complex-catalyzed four-electron reduction of oxygen*, J. Am. Chem. Soc. 132 (2010), pp. 6874–6875.

[20] W. T. Wei, Y. Z. Lu, W. Chen, and S. W. Chen, *One-pot synthesis, photoluminescence, and electrocatalytic properties of subnanometer-sized copper clusters*, J. Am. Chem. Soc. 133 (2011), pp. 2060–2063.

[21] P. J. G. Goulet and R. B. Lennox, *New insights into Brust–Schiffrin metal nanoparticle synthesis*, J. Am. Chem. Soc. 132 (2010), pp. 9582–9584.

[22] M. C. Tong, W. Chen, J. Sun, D. Ghosh, and S. W. Chen, *Dithiocarbamate-capped silver nanoparticles*, J. Phys. Chem. B 110 (2006), pp. 19238–19242.

[23] W. Chen, D. Ghosh, J. Sun, M. C. Tong, F. J. Deng, and S. W. Chen, *Dithiocarbamate-protected ruthenium nanoparticles: Synthesis, spectroscopy, electrochemistry and STM studies*, Electrochim. Acta 53 (2007), pp. 1150–1156.

[24] A. Sarapuu, M. Nurmik, H. Mandal, A. Rosental, T. Laaksonen, K. Kontturi, D. J. Schiffrin, and K. Tammeveski, *Electrochemical reduction of oxygen on nanostructured gold electrodes*, J. Electroanal. Chem. 612 (2008), pp. 78–86.

[25] R. E. Davis, G. L. Horvath, and C. W. Tobias, *Solubility and diffusion coefficient of oxygen in potassium hydroxide solutions*, Electrochim. Acta 12 (1967), pp. 287–297.

[26] M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, and R. W. Murray, *Alkanethiolate gold cluster molecules with core diameters from 1.5 to 5.2 nm: Core and monolayer properties as a function of core size*, Langmuir 14 (1998), pp. 17–30.