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Charge state-dependent catalytic activity of [Au\textsubscript{25}(SC\textsubscript{12}H\textsubscript{25})\textsubscript{18}] nanoclusters for the two-electron reduction of dioxygen to hydrogen peroxide

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The electrochemical production of H\textsubscript{2}O\textsubscript{2} from O\textsubscript{2} catalyzed by [Au\textsubscript{25}(SC\textsubscript{12}H\textsubscript{25})\textsubscript{18}] was studied as a function of the charge states (-1, 0 and +1). Maximum H\textsubscript{2}O\textsubscript{2} production (~ 90%) was obtained from the negatively charged clusters (Au\textsubscript{25}\textsuperscript{-1}) due to the efficient electron transfer from the anionic Au\textsubscript{25} cluster into the LUMO (π*) of O\textsubscript{2}.

As a promising sustainable energy carrier, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), have been one of the most important chemicals in the world and produced in large scale in industry. The oxygen reduction reaction (ORR) in aqueous solutions occurs mainly by two pathways: the direct 4-electron reduction pathway from O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}, and the 2-electron reduction pathway from O\textsubscript{2} to H\textsubscript{2}O. In polymer electrolyte membrane fuel cells (PEMFCs), the 4-electron direct pathway is highly preferred. In contrast, the 2-electron reduction pathway is then used in industry for H\textsubscript{2}O\textsubscript{2} production. These two pathways always compete with each other during the ORR process. Such situation in turn presents the hope of finding an active, selective, and stable electrocatalyst for the electrochemical production of H\textsubscript{2}O\textsubscript{2} in alkaline media.

Recently, gold nanoclusters, which consist of only several to tens of metal atoms, exhibited promising applications in catalysis. Of particular interest is Au\textsubscript{25}(SR)\textsubscript{18} cluster whose structure has been well characterized by theoretical calculations and single-crystal X-ray crystallography. Previous theoretical and experimental studies have revealed that anionic Au nanoclusters can activate the O\textsubscript{2} molecule and generate superoxo-or peroxo-like via electron transfer from the Au nanoclusters core to the LUMO (π*) of the O\textsubscript{2} molecule. Recently, extensive studies have demonstrated that the anionic charge of atomically precise Au\textsubscript{25} nanoclusters could facilitate the adsorption and activation of molecular species, such as O\textsubscript{2} and CO\textsubscript{2}, and thus improve the reactivity of the clusters. Inspired by these interesting findings, here, for the first time, we studied the electrocatalytic activity of [Au\textsubscript{25}(SC\textsubscript{12}H\textsubscript{25})\textsubscript{18}] nanoclusters for the synthesis of H\textsubscript{2}O\textsubscript{2} from two-electron reduction of dioxygen and investigated the influence of the cluster charge states on the electrochemical production of H\textsubscript{2}O\textsubscript{2} in alkaline media.

Atomically precise Au\textsubscript{25} nanoclusters with different charge states (-1, 0 and +1) were synthesized through an efficient one-phase method (see Electronic Supplementary Information).
bands centered at 677, 443, and 392 nm. For the Au$_{25}$ nanoclusters, which are the characteristic spectroscopic fingerprints of the thiol-capped Au$_{25}$ nanoclusters. Besides, apart from the three main absorption bands, there are additional fine spectral features, including a broad shoulder at ~800 nm, and another small shoulder at ~550 nm. To our surprise, the present revised synthesis can enhance the yield of Au$_{25}$ nanoclusters to ca. 60% by Au atom. Note that the reported highest yield of [Au$_{25}$(SR)$_{18}$] TOA$^-$ was 49%. From the UV-Vis spectra shown in Fig. S1, the UV-Vis absorption of the crude product is almost superimposable with that of the purified nanoclusters, indicating an extraordinarily high purity of the as-synthesized Au$_{25}$ nanoclusters. Both UV-Vis absorption and MS analysis unambiguously demonstrate the successful synthesis of Au$_{25}$ nanoclusters with high purity and yield.

Due to their highly sensitive to the local environment, anionic Au$_{25}$ nanoclusters could be easily converted to charge neutral Au$_{25}^0$ nanoclusters by bubbling the CH$_2$Cl$_2$ solution with O$_2$. Earlier studies have shown that the charge state of the Au$_{25}$ nanoclusters could be conveniently identified from their optical spectroscopic features, that is, the relative intensities of the 400 and 450 nm peaks as well as the presence or absence of the 800 nm shoulder peak. One could clearly see from Fig. 1B that, for the neutral charge Au$_{25}^0$ nanoclusters, the absorption peak at 400 nm becomes more prominent while the 450 nm peak becomes less so compared to that of the Au$_{25}$ clusters. Concurrently, the 800 nm shoulder that is characteristic of Au$_{25}^0$ nanoclusters disappears and a new, small shoulder at 630 nm emerges. These results indicate the successful conversion of charge negative Au$_{25}^{-}$ nanoclusters to charge neutral Au$_{25}^0$, which is similar to the earlier reports. Meanwhile, according to the previous reports, the cationic Au$_{25}$ nanoclusters can be produced by using strong oxidizing agent, such as Ce(SO$_4$)$_2$. It can be seen from Fig. 1B that the spectroscopic fingerprints of Au$_{25}^0$ and Au$_{25}^+$ are different from the original Au$_{25}^-$ clusters. In addition, XPS are also used to distinguish the Au$_{25}$ nanoclusters with different charge states. As shown in Fig. 1C, the Au 4f$_{7/2}$ binding energy (BE) of the gold clusters shows a positive shift with the charge states changing from -1 (83.74 eV), 0 (83.89 eV), to +1 (84.02 eV), further suggesting the successful synthesis of Au$_{25}$ nanoclusters with different charge states.

The reduction of dioxygen to hydrogen peroxide was investigated in 0.1 M KOH solution using a GC RRDE with the same loading of the three kinds of gold clusters (20 µg/cm$^2$). The H$_2$O$_2$ production could be easily evaluated from the RRDE currents at a fixed potential (0.5 V vs. SCE), where the oxygen reduction current is negligible and H$_2$O$_2$ oxidation is diffusion-limited. Compared to the CV in N$_2$-saturated electrolyte, obvious reduction current can be observed from the oxygen reduction catalyzed by the gold clusters (Fig. 2A). However, based on the current density and onset potential, the charge state of the Au$_{25}$ shows significant effect on their catalytic activity. The most positive onset potential and the largest current density of ORR were obtained from the negatively charged clusters, indicating the highest catalytic activity of Au$_{25}^-$ clusters for ORR. Compared to the large Au nanoparticles (Au NPs, ~11 nm, TEM and UV-Vis spectrum are shown in Fig. S2 and S3), the Au$_{25}$ nanoclusters exhibited enhanced ORR catalytic activity. Fig. 2B shows the RRDE voltammograms recorded at GC blank electrode and the Au$_{25}$ nanoclusters. Similar to the CV results, the Au$_{25}^-$ (-0.115) shows more positive onset potential than Au$_{25}^0$ (-0.15 V) and Au$_{25}^+$ (-0.18 V) nanoclusters. Moreover, the half-wave potential on Au$_{25}^-$ nanoclusters is -0.3 V, about 20 and 50 mV more positive than those at the Au$_{25}^0$ and Au$_{25}^-$. These results indicate that within the present experimental context, the electrocatalytic activity of Au$_{25}$ nanoclusters for O$_2$ reduction to H$_2$O$_2$ increases with the decrease of the charge states, with Au$_{25}$ nanoclusters showing the highest activity.

The electron transfer number (n) and the percentage of hydrogen peroxide produced at the different Au$_{25}$ clusters can be evaluated from the RRDE measurements based on the following equations:

\[
\text{H}_2\text{O}_2 \% = 200 \times \frac{i_{RD}}{i_{RD} + i_{DIS}} \tag{1}
\]

\[
n = 4 \times \frac{i_{DIS}}{i_{DIS} + i_{RD}} \tag{2}
\]

where $i_{DIS}$ is the disk current, $i_{RD}$ is the ring current, and N is the current collection efficiency of the Pt ring (0.37).

As shown in Fig. 2C, the H$_2$O$_2$ production percentages on Au$_{25}^0$ and Au$_{25}^+$ clusters are 72% and 82%, respectively, which increases up to 86% on Au$_{25}^-$ clusters. The corresponding electron transfer number was calculated to be 2.28, 2.35, and 2.56, respectively, on Au$_{25}^-$, Au$_{25}^0$, and Au$_{25}^+$. The above results indicate that dominant two-electron ORR process occurs on Au$_{25}$ nanoclusters and Au$_{25}^-$ could be used as a promising electrocatalyst for the electrochemical synthesis of H$_2$O$_2$ in alkaline media. It should be noted that compared to the previous results [Au$_{25}$(SC$_2$H$_2$)$_{18}$]$_2$, the Au$_{25}$ nanoclusters passivated by short-chain ligands, phenylethylthiol, are favourable for the oxygen reduction to H$_2$O$_2$. Therefore, the protecting ligands covered on the cluster surface can also affect the catalytic properties. As can be seen from Fig. S4A, the diffusion-limiting currents at -0.5 V on Pt/C (1.12 mA) is nearly 2 times that of the Au$_{25}^-$ (0.55 mA), further indicating the dominant 2e ORR process on Au$_{25}^-$. Moreover, from Fig. S4B, only 2.1% H$_2$O$_2$ production...
percentages was obtained on Pt/C over the potential range of -0.65 to -0.45 V, and the calculated electron transfer number is 3.96. The above electrochemical results show that Pt/C is a kind of good catalyst for 4-electron reduction of dioxygen to water, and Au25 nanoclusters, however, are excellent catalysts for production of peroxide from 2 electron reduction of dioxygen.

Further investigations on the electrocatalytic synthesis of H2O2 at the different charged gold clusters have also been performed by RDE measurements. Fig. S5 shows the ORR polarization curves at different rotation speeds with current normalized by the 10 \text{RDE} measurements. Fig. S5 shows the ORR polarization curves at the different charged gold clusters have also been performed by RDE measurements. According to the Levich equation, the slopes of the plots for Au25+, Au250, and Au25− are -0.077, -0.054, -0.071 m\text{A/cm}^2 \text{rpm} respectively (Fig. S6), which agrees well with the theoretical value for the two-electron transfer process (-0.0714 m\text{A/cm}^2 \text{rpm}).

Mechanistically, oxygen adsorption and subsequently activation on the catalyst surface is the first step in the electroreduction of dioxygen. Generally, activation of O2 molecules on the bulk gold surface is thermodynamically unfavorable for the formation of chemisorbed intermediate. While for Au25 nanoclusters, the much lower coordination number of the surface atoms and the unique electronic structure (electron-rich icosahedral Au13 core surrounded by electron-deficient 12 Au atoms) render them more active for electrocatalytic oxygen reduction. In addition, DFT calculations have suggested that charging a cluster can increase its chemical activity with respect to oxygen. On the basis of earlier experimental and theoretical calculations, we propose that the strong effect of charge states on the electrocatalytic production of H2O2 could be attributed to the electron transfer from the anionic Au25− cores into the LUMO (π*).

In summary, we present a study of electrocatalytic synthesis of H2O2 in alkaline media by Au25 clusters and the effect of cluster charge states on their catalytic activity. The electrochemical studies showed that the maximum H2O2 production and the most efficient 2e− dioxygen reduction were obtained from the charge negative Au25− nanoclusters, followed by the neutral and cationic ones, indicating the significant effect of charge states of Au25− cluster on its catalytic properties. The present study has provided an insight into the highly selective two-electron reduction of dioxygen to hydrogen peroxide by controlling the charge states of gold nanoclusters.

This work was supported by the National Natural Science Foundation of China (No. 21275136).

Notes and references
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