Synergistic improvement of oxygen reduction reaction on gold/cerium-phosphate catalysts

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\textbf{ABSTRACT}

The main challenge in fuel cells lies in improving slow oxygen reduction reaction (ORR) kinetics causing low conversion efficiencies. Here, we introduce the Au/CePO\textsubscript{4}-binary nanocomposites as effective oxygen reduction catalysts in alkaline media. The ORR activity comparable with Pt is achieved through the serial 4-electron reduction pathway. The bifunctionality of CePO\textsubscript{4} is suggested to explain the remarkably enhanced activity on the Au/CePO\textsubscript{4} nanocomposites. Significantly, the own catalytic activity of CePO\textsubscript{4} for hydrogen peroxide is demonstrated, validating synergistic effects with Au for complete ORR.

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\textbf{Introduction}

Fuel cells converting chemical energy to electrical energy have attracted a lot of interests as one of future-power-generation technologies for green economy. However, a low conversion efficiency caused by slow kinetics of oxygen reduction reaction (ORR) has been a major problem hindering practical application [1–6]. Among several types, alkaline fuel cells (AFCs) are a promising route for realizing the application of fuel cells, because of the advantages such as low anode-fuel crossover, tolerance for CO poisoning, feasible activities for non-Pt metals (e.g., Au, Ag, etc.), and non-precious metal oxides (Fe-, Co-, Ni-based oxides) [7–14]. Though non-precious metal oxides generally cost much less than Pt, they have lower electronic conductivity, and the activity is relatively low. Furthermore, the understanding of the reaction mechanisms on the catalyst is still lacking.

Progress in the d-band model, which describes the relation between catalytic activity and electronic structure of transition metals, allows us to systematically design and predict a brand-new catalyst on the basis of transition metals [15–17].

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Of them, gold is known to be the most stable metal, which ensures long-term durability against dissolution. The use of pure Au still brings up cost concerns, which is the major challenge for the application. The cost effectiveness can be adequately overcome by the introduction of Au-based composites taking advantage of the controlled electronic structure of Au. The ORR on Au surface does not occur via complete 4-electron reduction like on Pt, which encourages much effort to be made for Au to achieve comparable activity to that of Pt by alloying Au with other metals, or by combination with various metal oxides or metal phosphates [18–21].

In alkaline media, the ORR proceeds predominantly in three different pathways [22,23], as seen below, and the equilibrium potentials for each reaction at pH 13 are denoted in terms of a reversible hydrogen electrode (RHE), considering the dependence of the equilibrium potential on pH [24]:

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- & E &= 1.23 \text{ V (vs. RHE)} \quad (1) \\
\text{O}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow \text{HO}_2^- + \text{OH}^- & E &= 0.72 \text{ V (vs. RHE)} \quad (2a) \\
\text{HO}_2^- + \text{H}_2\text{O} + 2e^- & \rightarrow 3\text{OH}^- & E &= 1.74 \text{ V (vs. RHE)} \quad (2b)
\end{align*}
\]

The direct 4-electron reaction (Eq. (1)) reduces oxygen to water or hydroxyl ion as a reaction product. However, 2-electron (Eq. (2a)) or series 4-electron (Eq. (2a) → Eq. (2b)) reaction generates hydrogen peroxides as bi-products or intermediates. The pathways are sensitive to the type and crystallographic orientation of transition metals. In the case of Au, (100) planes exhibit the highest activity through the series 4-electron reduction pathway, whereas partial oxygen reduction to hydrogen peroxide (Eq. (2a)) occurs on (111) and (110) planes [25,26].

In the previous publications [20,21], we showed that the Au/AlPO₄ nanocomposite catalysts enabled 4-electron reduction in alkaline media with (111) and (110) Au orientations. The AlPO₄ in the binary nanocomposite played a role in enhancing the catalytic activity of Au by electronic interactions with Au, and did not participate in ORR. Therefore, ideas on finding other metal phosphate compound that may have its own catalytic activity remained a future work to achieve better ORR efficiency.

In this paper, the Au/CePO₄-binary nanocomposites are introduced as an effective oxygen reduction catalyst in alkaline media. The ORR activity comparable with Pt is demonstrated through the serial 4-electron reduction pathway. The bi-functionality of the CePO₄ in Au/CePO₄ is suggested to explain the remarkably enhanced activity. Significantly, the own catalytic activity of CePO₄ for HO₂ intermediates is demonstrated, bringing synergistic effects with Au for more complete ORR.

**Experimental procedure**

The Au/CePO₄ nanocomposites were prepared by co-sputtering using Au and CePO₄ targets on ITO-coated glass at room temperature. In order to control the Au/CePO₄ ratio, Au-sputtering power was fixed to 10 W, and CePO₄-sputtering power was changed between 20 W and 60 W. The as-deposited samples were annealed at 200 °C for better adhesion to the ITO electrodes. In order to distinguish the effect of metal phosphates, the Au/AlPO₄ nanocomposites were prepared in the same manner [20]. For the comparison of ORR activity, the pure Au, Pt, CePO₄, and AlPO₄ films were also prepared.

Electrochemical characterization, cyclic voltammetry (CV) and chronoamperometry were performed by using a potentiostat (CHI 604A: CH Instrumental Inc.). Hg/HgO and Pt wires were used as reference and counter electrodes, respectively. Oxygen reduction was measured in an O₂-saturated 0.1 M NaOH solution under the oxygen flow of 30 sccm at a scan rate of 50 mV/s. H₂O₂-reduction measurements were carried out in a N₂-purged 0.1 M NaOH solution, by adding 1.2 mM hydrogen peroxide. The surface orientation of Au in the Au/CePO₄ nanocomposites was estimated by underpotential deposition (UPD) using 1 mM lead nitrate (Pb(NO₃)₂·3H₂O) dissolved in 0.1 M NaOH at a scan rate of 50 mV/s.

X-ray photoelectron spectroscopy (XPS, AXIS-HSI: KRATOS) was used to analyze the electronic states of the Au (with monochromatic Mg Kα radiation), and the binding energy was calibrated by using the peak position of C 1s. The nanocomposite phase was identified by X-ray diffraction (XRD, D8 Advance: Bruker), and the grain size of Au was estimated using the Scherrer equation. The atomic ratios of Ce/Au in the Au/CePO₄ nanocomposites were confirmed to be 0.042, 0.053, and 0.086 with the CePO₄-sputtering powers of 20, 40, and 60 W, respectively, as measured by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima-4300 DV: Perkin–Elmer).

**Results and discussion**

X-ray diffraction for the nanocomposites (Fig. 1) confirms polycrystalline Au phase with amorphous cerium phosphate.

![Fig. 1 - X-ray diffraction of the Au thin film and Au/CePO₄ nanocomposites. The ideal peak positions and intensities for Au (JCPDS 04-0784) are marked at the bottom.](image-url)
The grain sizes of Au were estimated to 43 nm (pure Au), 29 nm (Ce/Au = 0.042), 9 nm (Ce/Au = 0.053), and 7 nm (Ce/Au = 0.086), respectively, by the Scherrer equation of $k \pi / \lambda \sin \theta$. The gradual decrease of Au-grain size with the increasing Ce/Au ratio is explained by the suppression of Au coarsening with CePO$_4$.

The pathway for ORR on gold surface largely depends on the crystallographic surface orientation. Therefore, as shown in Fig. 2, UPD of Pb was conducted to characterize the Au surface in Au/cePO$_4$. Since the ideal peak potentials for Pb desorption on Au (111), (100), and (110) are $\sim 0.44$, $\sim 0.48$, and $\sim 0.56$ V, respectively [27], the main desorption peaks are assigned to (111) and (110). In other words, Au (100) facets rarely exist in the nanocomposite, and this means that the Au/cePO$_4$ nanocomposite mainly has the pathway via partial oxygen reduction (Eq. (2a)) generating HO$_2$. The electrochemical surface areas were estimated to approximately 1.91, 1.78, 2.29, and 1.61 cm$^2$ per cm$^2$ sample, respectively, for pure Au, Ce/Au = 0.042, 0.053, 0.086. The nanocomposite with Ce/Au = 0.053 exhibits the largest area, due to the optimization between Au coarsening (grain growth) and electronic percolation among the Au nanocrystals [28–30].

To compare the ORR activities of Au and Au/cePO$_4$ composites, cyclic voltammograms were obtained in an O$_2$-saturated solution (pH 13). By the incorporation of CePO$_4$ to Au, two distinctive features are shown compared to the pure Au, as shown in Fig. 3. First, reduction current is remarkably promoted within the potential region of approximately 0.6–0.9 V, with a positive shift of the onset potential. Second, the oxidation peak at $\sim 0.9$ V (assigned to oxidation of residual HO$_2$ [31,32]) are hardly observed on the reverse sweep, which implies that HO$_2$ were almost consumed during the prior cathodic sweep. In particular, the Au/cePO$_4$ nanocomposite with Ce/Au = 0.053 exhibits the most enhanced catalytic properties for oxygen reduction with a most-positive shift of the onset potential, up to over $\sim 50$ mV compared to pure Au. The reduction current density is comparable to that of pure Pt, which is nearly twofold of pure Au, and the oxidative current peak on the reverse sweep (at $\sim 0.9$ V) is not observed.

The limiting current densities ($i_L$) for two- and four-electron processes were estimated to $-0.32$ and $-0.63$ mA/cm$^2$, respectively, from $i_L = -DnF$/$\delta$ [33], where $D$ is the O$_2$-diffusion coefficient ($\sim 2.6 \times 10^{-5}$ cm$^2$/s) [34], $F$ is the Faraday constant (96,485 C/mol), $\delta$ is the O$_2$-bulk concentration ($\sim 1.26$ mM) [35], $n$ is the number of involved electrons, and $\delta$ is the diffusion-layer thickness ($\sim 200$ $\mu$m), assuming no convection [36]. From the simple calculation, four-electron process is confirmed to be achieved in the Au/cePO$_4$ nanocomposite, which is further supported by the disappearance of the oxidative current for residual HO$_2$.

To better understand why the Au composite with CePO$_4$ induces the remarkable enhancement of catalytic activity, the electronic modification of Au is observed by XPS (Fig. 4). While pure Au is identified by 4$f_{7/2}$ and 4$f_{5/2}$ of 87.7 and 84.0 eV, respectively [37,38], the binding energy shifts lower in the Au/cePO$_4$ nanocomposites, and this changed electronic structure is due to the electron transfer between CePO$_4$ and Au by the Fermi level difference [39]. Many researchers have shown that
the shift direction of core level ($f$ band) is in accordance with that of valence level ($d$ band) determining the reactivity of transition metal surface [40–45]. Based on the results of $Au-4f$ shift toward lower binding energy, the position of the $d$-band center is estimated to be shifted up toward Fermi level. According to the $d$-band model, higher position of $d$-band centers (i.e., closer to the Fermi level) implies stronger bonds between adsorbates and metal surface, leading to further reduction of reactant molecules [46–49].

The XPS analyses reveal that combining $Au$ with $CePO_4$ induces favorable shift of $Au$-electronic level, facilitating reduction kinetics for the chemisorbed reactants on the $Au$ surface. Therefore, complete ORR can be achieved for the $Au$ nanocrystals that are effectively interacted with $CePO_4$.

The chronoamperometry with hydrogen peroxide can be a tool for identifying only the activity for the reduction of $HO_2^-$ (Eq. (2b)) on the way to the whole serial 4-electron reduction path, since hydrogen peroxide mainly exists as a radical form ($HO_2^-$) at pH 13 [24]. At the applied potential of 0.709 V (Fig. 5(a)), the pure $CePO_4$ shows negligible current. As the applied potential becomes negative down to 0.509 V (Fig. 5(b)), however, the reduction current for the pure $CePO_4$ appears, which implies that $CePO_4$ has its own catalytic activity on $HO_2^-$. Recently, our group reported the enhancement of ORR activity in $Au/AlPO_4$ with the same thin film composite geometry [20,21]. In order to compare the effect of metal phosphates on $Au$-catalytic properties, chronoamperometry and ORR experiments were performed again for the pure $AlPO_4$ and the $Au/AlPO_4$ nanocomposite (optimized by the composition, $Au/Al = 0.087$), respectively. The chronoamperometry results of Fig. 5(c) reveal that the pure $AlPO_4$ has no activity for $HO_2^-$, unlike the case of $CePO_4$ (Fig. 5(b) vs. Fig. 5(c)). Therefore, it is evident that the initial oxygen reduction on the $Au$ surface (Eq. (3)) leads to the formation of $HO_2^-$, and is extended to the reduction of $HO_2^-$ in which the $CePO_4$ itself can participate. This remarkable difference of the $HO_2^-$ reduction between $CePO_4$ and $AlPO_4$ is directly reflected on the ORR curves, as shown in Fig. 5(d).

In the cathodic region below ~0.7 V, the reduction current of $Au/ CePO_4$ is much higher than that of the $Au/AlPO_4$, and this is well explained by the reduction activity difference of $HO_2^-$ between $CePO_4$ and $AlPO_4$ in the similar voltage range. Furthermore, in the case of the $Au/ CePO_4$, the anodic current peak at ~0.9 V is hardly observed, unlike the $Au/AlPO_4$. This suggests that most of $HO_2^-$ is reduced on the $Au/ CePO_4$ surface through the functionality of the $CePO_4$. The enhancement mechanisms by $CePO_4$ are schemed in Fig. 5(e) and (f).

Although $CePO_4$ itself did not have reactivity for oxygen, it exhibited considerable activity for the reaction intermediate. Therefore, $CePO_4$ can actively participate in the catalytic reaction by reducing the residual $HO_2^-$ produced from the uncompleted ORR on $Au$. Because unaltered pure $Au$ has poor activity for $HO_2^-$, the catalytic characteristic of $CePO_4$ is effectively complementary to $Au$. The bi-functionality of $CePO_4$, both the modification of $Au$-electronic structure and the catalytic activity for $HO_2^-$, brings synergy for more complete ORR in the $Au/CePO_4$ nanocomposites.

Conclusions

Oxygen reduction activity for the $Au/CePO_4$ nanocomposites was investigated in alkaline media. Compared to the pure $Au$ showing partial 2-electron reduction, the binary composites exhibited nearly complete ORR through the serial 4-electron reduction pathway, fully reducing reaction intermediates.
Two enhancement mechanisms were demonstrated to explain the role of CePO4 in the composite catalyst. First, electronic interactions between the Au and CePO4, as revealed by XPS, enhanced the ORR kinetics for Au by the shift of Au energy levels determining adsorption properties of reactant molecules on Au surface. Second, its own catalytic activity for hydrogen peroxide reduction, observed by chronoamperometry, was effectively complementary to Au having poor activity for hydrogen peroxide. The bi-functionality of both the electronic modification of Au and the catalytic activity for HO2 conveys synergistic effect for efficient oxygen reduction. As a future work, performance with a full-cell configuration will be necessary to verify the potential for future applications as a fuel cell cathode. Also, the proposed strategy combining the two catalyst materials, each of which plays a different role, furnishes an advanced insight into the design of a new catalyst.

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