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Electrocatalytic oxidation of CO on supported gold nanoparticles and submicroparticles: Support and size effects in electrochemical systems

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Abstract

We investigated the catalytic activity of gold particles toward CO electrooxidation by cyclic voltammetry and found that the formation of oxidic gold species on the surface of gold nanoparticles (AuNPs) is a necessary condition for electrooxidation of CO. The maximum potential in the positive-going sweep has a great effect on the formation of gold oxides as well as on the activity of AuNPs. We report the support-dependent electrooxidation of CO in aqueous solution as the first example of the contribution of the support to the high catalytic activity of AuNPs in electrochemical systems. We also show that particle size, reported to be a dominant factor in the catalytic oxidation of CO on AuNPs in solid–gas reaction systems, is no longer a critical factor controlling the activity of AuNPs in electrochemical systems. We demonstrate that indium tin oxide-supported gold submicroparticles, which are believed to be catalytically inactive due to their "large" size, exhibit surprisingly high activity toward electrooxidation of CO.

Keywords: Gold; CO oxidation; Electrocatalysis; Indium tin oxide

1. Introduction

Although bulk gold is catalytically inert, small gold nanoparticles (AuNPs) dispersed on metal oxides exhibit surprisingly high catalytic reactivity toward low-temperature oxidation of CO in solid–gas reaction systems [1–3]. Significant efforts have been made to elucidate the origins of the unusually high activity of AuNPs/support systems [4–19]. Different mechanisms have been proposed, including quantum size effect [4], support contribution [5–11], effect of low-coordinated sites [12–15], and effects of charge states or electronic structure of the AuNPs [16–19]. Although the exact origins of the catalytic activity of supported AuNPs remain under debate, it has been documented that the size of AuNPs is a critical factor influencing the activity in solid–gas reaction systems. It has been shown that only AuNPs of diameter <10 nm exhibit extraordinary high activity toward CO oxidation [1–19], and that this activity decreases sharply as the particle size increases. For the larger AuNPs (diameter >10 nm), nearly no activity is observed [3,5,14]. On the other hand, the support on which AuNPs are dispersed is widely accepted as another crucial factor controlling the activity of AuNPs/support catalysts. It has been demonstrated that even with identical particle sizes, the activity of AuNPs differs greatly when using different metal oxide supports [5].

Electrocatalytic oxidation of CO in aqueous solution also has been observed on AuNPs supported by conductive substrates [20–22]. However, only small AuNPs (diameter <6 nm) were used to investigate the electrocatalytic properties for CO oxidation in aqueous solution [20–22]. This may be due to the fact that only small AuNPs show high catalytic activity in solid–gas systems. It is self-evident that the heterogeneous catalytic oxidation of CO at the interface of solution and AuNPs electrodes should be quite different from that at the solid–gas interface. In addition, the potential applied to electrode can greatly influence the surface states of both AuNPs and the underlying electrode and thus may change the reaction mechanism. As a result, the factors determining the activity of AuNPs in solid–

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gas systems, such as the size of the particles and the nature of the supports, still may not be the key factors in electrochemical systems, although other factors that do not exist in the solid–gas interface, such as the potential and the composition of the solution, may play key roles in the oxidation of CO. The purpose of this work is to clarify the activity-determining factors for the electrocatalytic oxidation of CO on AuNPs in solution.

2. Experimental

2.1. *Preparation of gold nanoparticle assemblies on ITO and Pt substrates*

The indium tin oxide (ITO) and the Pt substrates were first sonicated successively in acetone, water, and methanol. After cleaning, both the ITO and Pt substrates were immersed in the 1,12-dodecanediamine (DDA) solution (5.0×10^{-3} M) of absolute methanol for 48 h to form a DDA monolayer on their surfaces [23,24]. The resulting film-coated ITO and Pt substrates were rinsed with copious absolute methanol and then dried under a stream of high-purity N_2. The gold colloidal nanoparticles were prepared by adding aqueous sodium citrate (3.5 mL, 1 wt%) into boiling $HAuCl_4$ (100 mL, 2.4×10^{-4} M) solution under vigorous stirring [25]. The average particle size, determined by transmission electron microscopy using a JEM-200CX (JEOL, Japan), was 13 ± 1.0 nm. Before use, the pH of the colloid solution was adjusted to 4.0. The above-mentioned ITO and Pt substrates, which were modified with amino-terminated DDA monolayers, were immersed in the gold colloid for 12 h to form nanoparticle assemblies. Micrographs of AuNPs-modified ITO and Pt substrates were obtained using a Philips FEI XL30 SFEG scanning electron microscope with an accelerating potential of 10 kV.

2.2. *Electrodeposition of gold submicroparticles (AuSMPs) on ITO substrates*

The electrochemical deposition of AuSMPs on ITO substrates was carried out in 10^{-4} M $HAuCl_4$ solution with 1 M KCl as the supporting electrolyte. A deposition potential (0 V vs SCE) was applied to the ITO substrate to prepare AuSMPs on its surface. The size of the AuSMPs was controlled by varying the electrodeposition time. After electrodeposition, the resulting electrodes were rinsed with copious water and then transferred immediately to the deoxygenated 0.5 M KOH solution.

2.3. *Electrochemical determination of the total surface area of AuNPs and AuSMPs*

To obtain the total surface areas of AuNPs and AuSMPs, cyclic voltammetric (CV) measurements were first performed on particle modified ITO or Pt electrodes in 0.5 M KOH solution that was purged of oxygen by saturating with high-purity N_2 for 25 min. The potential range of CV measurements was −0.4–0.7 V (vs SCE), and the scan rate was 100 mV s^{-1}. After correction for a double-layer charging current, the area under the reduction current peak was obtained from the CV curve. This area reflects the amount of charge needed to reduce the gold oxides formed on the particle surfaces in the positive scan [26,27]. Therefore, the total surface area of the gold particles can be represented by the amount of reduction charge, which is used to normalize the catalytic oxidation current.

2.4. *Electrocatalytic oxidation of CO*

The electrode kinetic measurements were carried out in a gas-sealed box with a gas inlet tube reaching to the bottom of the electrochemical cell to facilitate gas–liquid saturation. The electrocatalytic oxidation measurements were conducted by cyclic voltammetry with a potential range of −0.4–0.7 V (vs SCE) in 0.5 M KOH after the solution was saturated with CO for 45 min. During electrooxidation of CO, the KOH solution was continuously bubbled with CO. The electrocatalytic oxidation current was normalized by dividing by the gold oxide reduction charge obtained at the same electrode in 0.5 M KOH. All electrochemical measurements were performed on a CHI660A electrochemical workstation (CH Instruments) using a conventional three-electrode cell at room temperature. The cell has a circular window on the bottom to ensure that the area of electrode exposed to solution is 0.26 cm^2. A saturated calomel electrode (SCE) and a Pt foil were used as reference and counter electrodes, respectively. All potentials are reported with respect to SCE.

3. Results and discussion

3.1. *Effect of the applied potential on the activity of AuNPs toward CO electrooxidation*

To eliminate the size effect when studying the influence of the applied potential and the support on the catalytic activity of AuNPs, the colloidal gold particles with identical size and shape were used. These gold particles were prepared by the Frens method [25] and had an average diameter of 13 ± 1 nm. The DDA was used as a linking molecule to immobilize AuNPs on ITO [23] and Pt [24] substrates. The AuNPs are negatively charged due to the adsorption of anions at pH > 2 [28,29]. The amino-terminated monolayers are positively charged in aqueous solution of pH 3–6 due to the protonation of amino groups [30]. Therefore, amino groups are usually used to immobilize AuNPs by the strong electrostatic interactions [29,31]. Figs. 1a and 1b show the SEM images of AuNPs assembled on ITO and Pt substrates, respectively. The AuNPs are uniformly dispersed on both substrates, with particle density of ca. 3.8×10^{10} particles cm^{-2} on ITO and ca. 8.1×10^{10} particles cm^{-2} on Pt.

As shown in Fig. 2a, the unmodified ITO and Pt electrodes are electrochemically inert within the scanned potential range of −0.4–0.7 V in 0.5 M KOH. However, after modification with AuNPs, both electrodes exhibit CV features of gold electrodes [26] (Fig. 2b), suggesting that the AuNPs have good electrical contact with the ITO and Pt substrates. The current

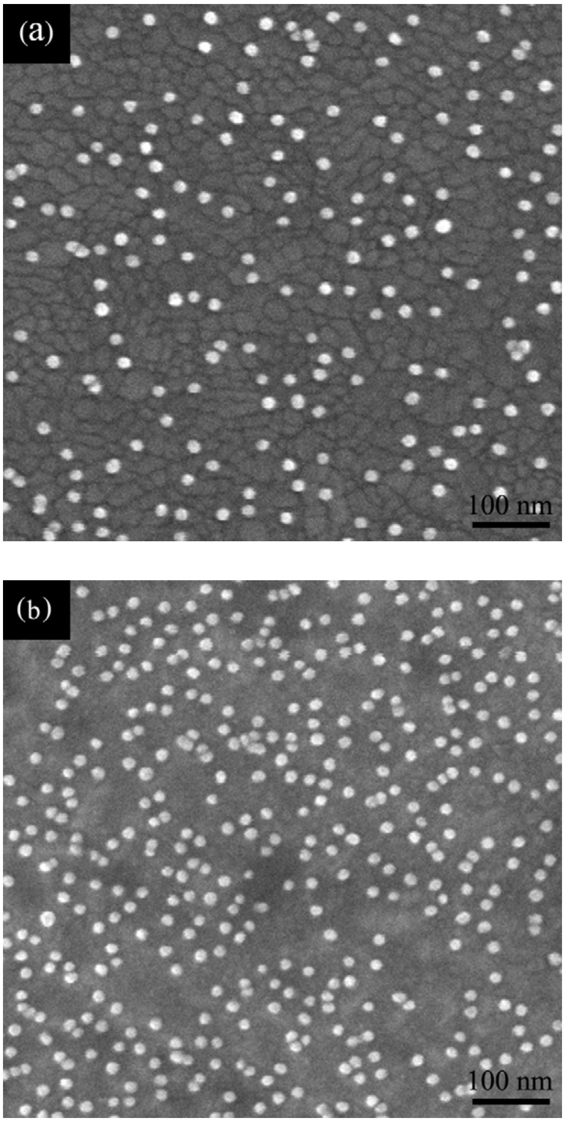

Fig. 1. SEM images of AuNPs dispersed on (a) ITO and (b) Pt substrates.

peak at 0.35 V in the positive scan in Fig. 2b indicates the formation of gold oxides on the surface of AuNPs, whereas the peak at −0.02 V in the negative scan reflects the reduction of gold oxides formed in the preceding positive scan [26].

After the alkali solution was saturated with CO, both the bare ITO and Pt electrodes exhibited CV features similar to those obtained in the solution without CO (data not shown), indicating that these electrodes have no activity for CO electrooxidation. However, after modification with AuNPs, both electrodes demonstrated reactivity toward CO. Fig. 3a shows the typical CV behavior of AuNPs-modified ITO electrodes (AuNPs/ITO) in 0.5 M KOH saturated with CO. Bulk gold exhibited a reduction peak of gold oxides at about 0 V in the negative scan (Fig. 3b) in CO-containing solution, whereas the AuNPs/ITO exhibited an oxidation peak at nearly the same potential. Such CV behavior of AuNPs modified electrode has been reported previously, and the oxidation peak in the negative-going sweep was ascribed to the electrocatalytic oxidation of CO on AuNPs [20–22].

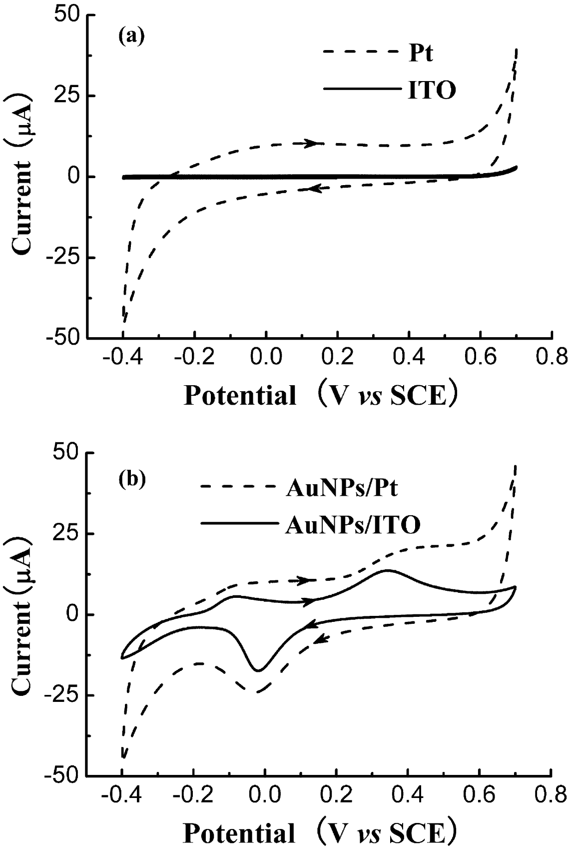

Fig. 2. Cyclic voltammograms of (a) bare Pt and bare ITO electrodes in 0.5 M KOH, (b) AuNPs/Pt and AuNPs/ITO electrodes in 0.5 M KOH. Scan rate: 100 mV s^{-1}.

Fig. 4a shows the effect of applied potential on the activity of AuNPs/ITO for the electrocatalytic oxidation of CO. From Fig. 4a, two features are immediately apparent: (1) the catalytic oxidation peak current increases as the scan range is extended positively, and (2) the oxidation peak cannot be observed in the negative scan unless the potential exceeds 0.4 V in the preceding positive scan. The positive extension of the scan range results in the increase of surface gold oxides, as can be seen from the increasing of the reduction peak of gold oxides in 0.5 M KOH without CO (Fig. 4b). Moreover, Fig. 4b also demonstrates that gold oxides cannot be formed on the surface of AuNPs unless the maximum potential in the positive-going sweep exceeds 0.4 V. From Figs. 4a and 4b, it can be safely concluded that the presence of gold oxide on the surface of AuNPs is a necessary condition for the catalytic oxidation of CO, and that the more the amount of gold oxides, the higher the activity of AuNPs. This is in good agreement with recently obtained results in solid–gas systems [18,19]. To explain the action of gold oxides in the catalytic reaction, van Bokhoven et al. [19] proposed a mechanism in which oxidic gold species act as reaction intermediates: $Au^0 + O_2 \rightarrow Au_yO_x$; $Au_yO_x + CO \rightarrow Au^0 + CO_2$. In the electrochemical system studied here, the gold oxides on the AuNPs surface are formed not by activation of oxygen, but rather by electrooxidation of gold in alkali medium: $Au^0 + OH^- - e^- \rightarrow Au_yO_x + H_2O$.

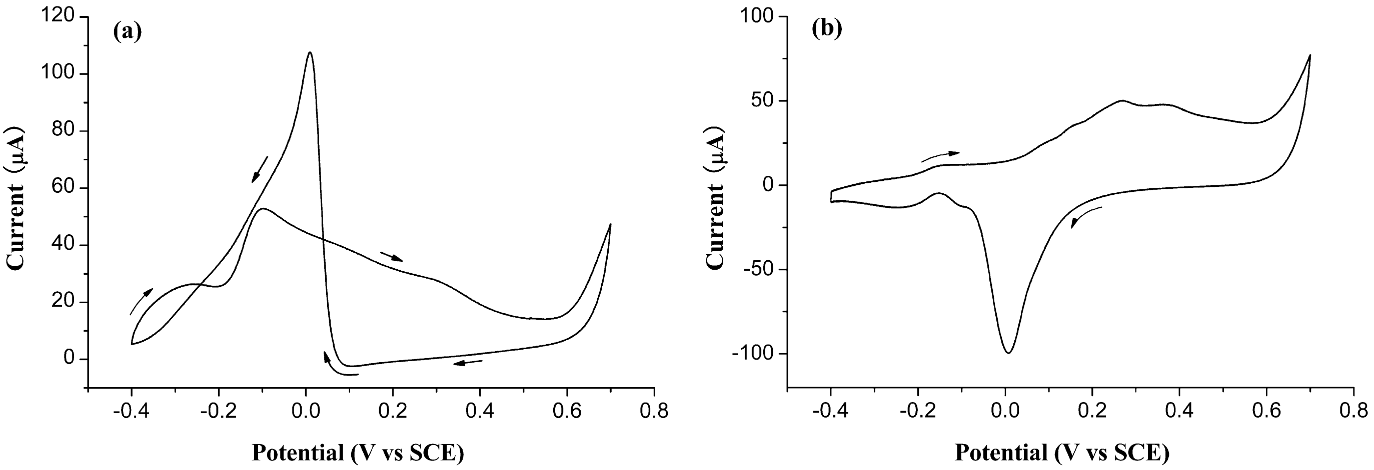

Fig. 3. Cyclic voltammograms of AuNPs/ITO (a) and bulk Au (b) electrodes in 0.5 M KOH saturated with CO. Scan rate: 100 mV s^{-1}.

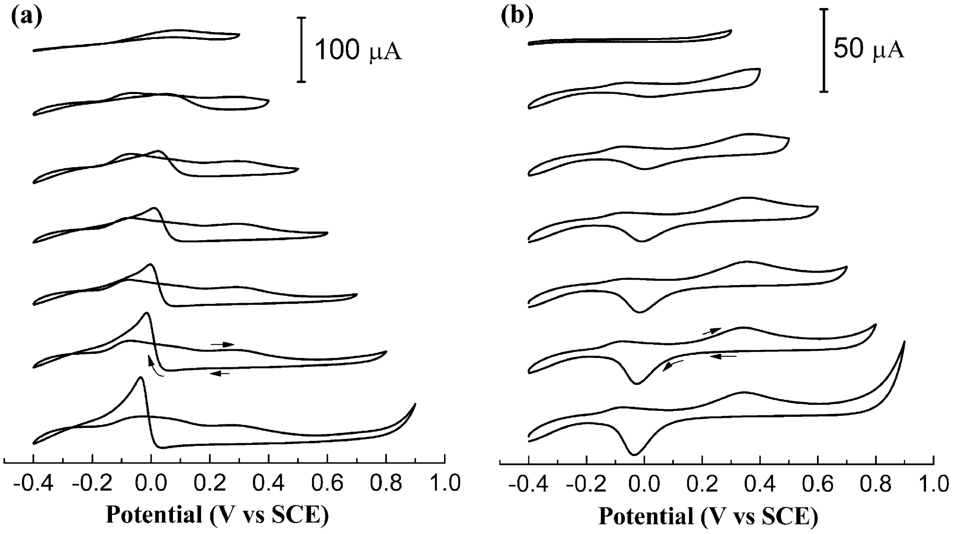

Fig. 4. Cyclic voltammograms of AuNPs/ITO electrode in 0.5 M KOH saturated with CO (a) and with no CO (b).

The catalytic action of gold oxides in electrooxidation of CO can be clearly seen by comparing the charges for gold oxides reduction and CO oxidation in the same AuNPs/ITO electrode. As shown in the CV curve in Fig. 2b (solid line), which was obtained in KOH solution without CO, the area under the reduction peak represents the charge needed for gold oxide reduction. The total charge for CO oxidation in the same AuNPs/ITO electrode can be obtained by measuring the area under the oxidation peak in Fig. 3a. The calculated charges for gold oxides reduction and for CO oxidation are ca. 2.4×10^{-5} and 2.0×10^{-4} C, respectively. The latter is more than eight times greater than the former, suggesting that gold oxides on the surface of AuNPs act not only as oxidants, but also as promoters for CO electrooxidation. In other words, the gold oxides must take part in the electrooxidation of CO and facilitate the electron transfer from CO to ITO electrodes. But the exact mechanism of this process is not quite clear and is under further study. Herein, we should point out that the existence of oxidic gold species do not necessarily result in high activity toward CO electrooxidation, as can be seen from the CV behavior on bare gold, on which large amount of gold oxides were formed but no catalytic oxidation current could be observed (Fig. 3b).

The foregoing discussion demonstrates that both the electrochemical measurements conducted in this work and the kinetic studies carried out in solid–gas systems [18,19] point out to the same thing, that is, the formation of gold oxides (in solid–gas reaction systems, usually described as the activation of oxygen) on the surface of AuNPs is the prerequisite to CO oxidation.

3.2. Effect of the substrate on the activity of AuNPs toward CO electrooxidation

The support effect on the catalytic activity of AuNPs was investigated by comparing the oxidation current at AuNPs/ITO and AuNPs/Pt electrodes. Although the AuNPs are identical in size and shape, the particle density on the ITO and the Pt substrates differs. Thus, the influence of particle density must be excluded when we study the support effect. As shown in

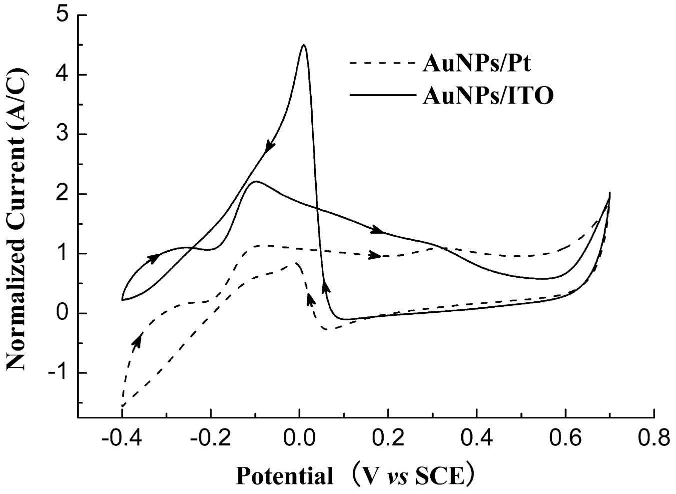

Fig. 5. Normalized cyclic voltammograms of AuNPs/Pt and AuNPs/ITO in 0.5 M KOH saturated with CO. The AuNPs/Pt and the AuNPs/ITO electrodes are the same as those used in Fig. 2b, respectively. The currents are normalized by dividing by the corresponding charges under the reduction peaks in Fig. 2b after corrected for double-layer charging current. Scan rate 100 mV s^{-1}.

Fig. 2b, the area under the reduction peak (after correction for the double-layer charging current) reflects the amount of charge needed to reduce the surface gold oxides. In other words, the reduction peak area (or reduction charge) reflects the true surface amount of oxidic gold species. For each AuNPs modified electrode used in this work, the CV response in 0.5 M KOH was first recorded to obtain the amount of gold oxides (represented by the reduction charge) on the AuNP surface. To eliminate the influence of particle density, the CV curves obtained in CO-saturated solution were normalized by dividing by the corresponding charge under the reduction peaks in 0.5 M KOH. Moreover, for all samples, the potential window was fixed in the range −0.4–0.7 V to rule out the influence of the potential on the amount of gold oxides. The normalized CV curves on AuNPs/Pt and AuNPs/ITO, shown in Fig. 5, demonstrate that the catalytic oxidation current is more than 4 times greater in AuNPs/ITO than in AuNPs/Pt.

Before ascribing this activity difference to the support effect, we need to know the average amount of gold oxides per particle on the ITO and Pt substrates. The total charge for the reduction of gold oxides on particle-modified electrodes is ca. 4.2×10^{-5} C for AuNPs/Pt and 2.4×10^{-5} C for AuNPs/ITO (see Fig. 2b). Therefore, on the basis of particle density on the two substrates, the average reduction charge per particle is ca. 5.2×10^{-16} C on the Pt substrate and 6.3×10^{-16} C on the ITO substrate. These two values closely agree, suggesting that the amount of gold oxides on each gold particle is similar no matter which substrate is used. Then it can be concluded that the great difference in reactivity toward CO oxidation between AuNPs/ITO and AuNPs/Pt arises not from the amount of gold oxides, but rather from the different nature of the substrate. This means that even in electrochemical systems, the substrate has a great effect on the catalytic activity of AuNPs. We believe that the difference in activity arises from the different routes through which gold oxides react with CO on ITO and Pt electrodes. The high activity of AuNPs/ITO suggests that the ITO substrate participates in the reaction and plays a key role either in stabilizing the gold oxides [21] or in lowering the activation energy of CO electrooxidation. Therefore, it is likely that the oxidation of CO occurs preferentially at the Au–ITO interface rather than at sites far from the ITO substrate. This also can explain the fact that no electrocatalytic activity is observed on bare gold electrode, because there is no Au–ITO interface.

3.3. Effect of particle size on the activity of gold/support system toward CO electrooxidation

It should be pointed out that, in this work, the high activity of ITO-supported AuNPs toward CO electrooxidation has been obtained on relatively large (13 nm) particles, which are believed to be far less active in solid–gas reaction systems [3,5,14]. As we know that in solid–gas systems, the adsorption and activation of oxygen on AuNPs/support system is a crucial factor in the low-temperature oxidation of CO [18,19]. It has been proposed that, compared with the large AuNPs, the small AuNPs (<10 nm) more readily activate oxygen (form oxidic gold species) at their surfaces [12,14,18,19] or at the AuNPs–support interfaces [7–11], and thus are more active toward CO oxidation. In an electrochemical system, gold oxides can be easily formed by applying a positive potential to the electrode; for example, a positive scan over 0.4 V in 0.5 M KOH can generate a layer of gold oxides on the surface of AuNPs regardless of the support and the particle size (see Figs. 2b and 4b). Thus, particle size has little effect on the formation of gold oxides in electrochemical system. In other words, unlike in the solid–gas reaction systems, the size of the gold particles is no longer the dominant factor for CO oxidation in electrochemical systems, due to the ease of formation of gold oxide on various-sized AuNPs. This is why such large AuNPs exhibit high catalytic activity for CO electrooxidation. To provide further support for this point, we prepared gold submicroparticles (AuSMPs) on ITO electrodes and investigated their electrocatalytic activity toward CO oxidation.

Fig. 6 shows SEM images of AuSMPs prepared on ITO substrates by electrochemical reduction of $HAuCl_4$ at 0 V for different durations. The particle size distributions for each deposition time, shown in Fig. 7, demonstrate that the average particle size increased from ca. 150 to 525 nm as the deposition time was increased from 15 to 1800 s. These ITO-supported AuSMPs are too large to be catalytically active for CO oxidation in solid–gas reaction systems; however, they exhibit high activity toward CO electrooxidation in the alkali solution, as can be seen in Fig. 8. Similar to the CV curves obtained at AuNPs-modified electrodes (Fig. 5), the currents in Fig. 8 are also normalized by dividing by the corresponding gold oxide reduction charge obtained at the same electrode in 0.5 M KOH without CO. The current peaks for catalytic oxidation of CO can be seen in the negative scan given in Fig. 8, providing solid evidence that high catalytic activity is not confined to small (<10 nm) AuNPs in the electrochemical system. Fig. 8 also shows that the catalytic oxidation current decreases when the

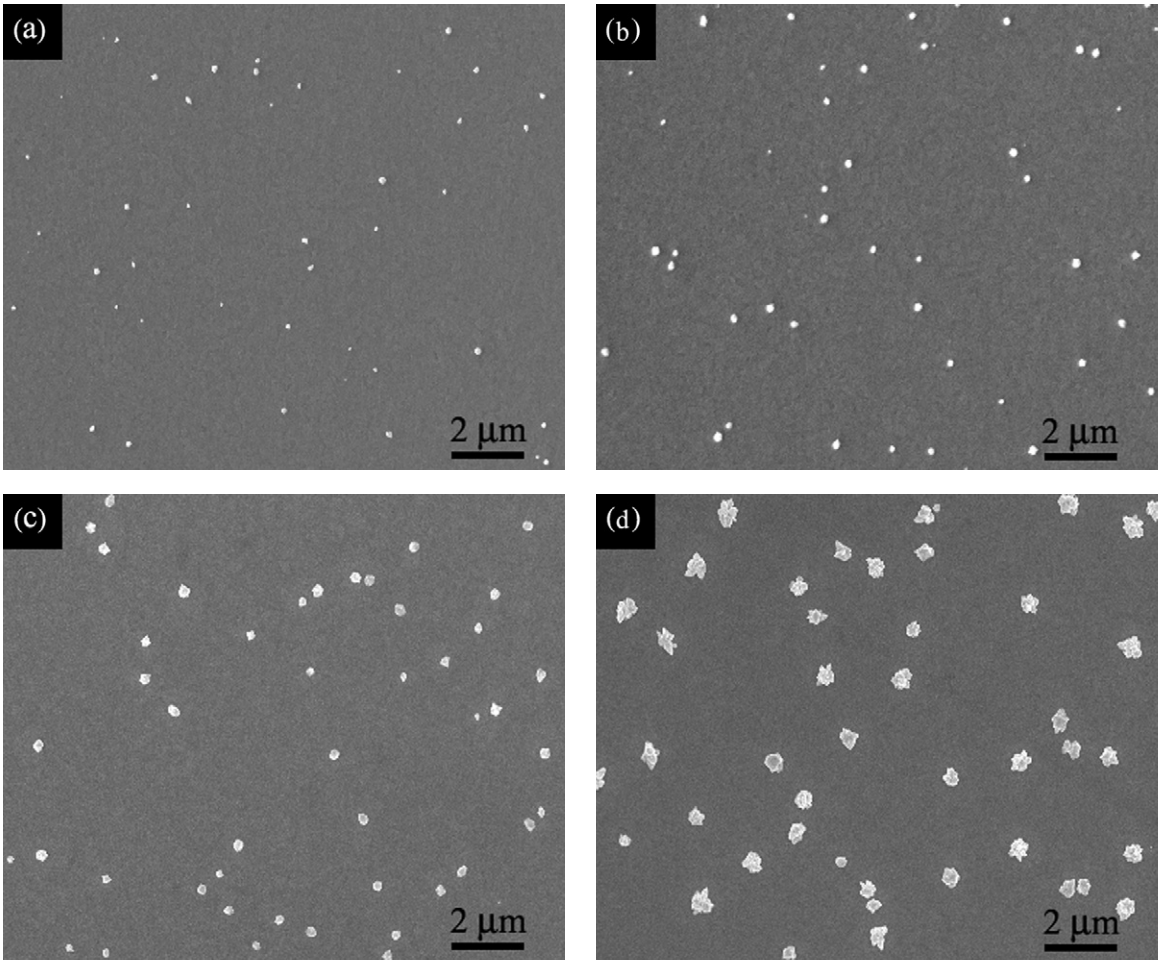

Fig. 6. SEM images of AuSMPs prepared on ITO substrates by electrodeposition at 0 V (vs SCE) in 10^{-4} M $HAuCl_4$ solution with 1 M KCl as supporting electrolyte. The deposition times are (a) 15, (b) 60, (c) 300, (d) 1800 s.

deposition time for AuSMPs is increased. This indicates that the activity of AuSMPs/ITO decreases with increasing particle size, because longer electrochemical deposition time results in larger AuSMPs. The size-dependent activity observed on these large AuSMPs is in line with the fact that the ratio of the Au–ITO interface area to the whole particle surface area decreases with increasing particle size. This provides further evidence that the Au–ITO interface is the active location for CO electrooxidation. Comparing Figs. 5 and 8 shows that for the samples with deposition time $\leqslant$300 s, the catalytic oxidation currents are at least 5 times greater on the large AuSMPs than on the small AuNPs. This finding suggests that the Au–ITO interface produced by electrodeposition of AuSMPs on ITO is catalytically more efficient than that produced by the assembly of AuNPs on ITO. We believe that the relatively lower activity of AuNPs/ITO may be due to the DDA monolayer, which acts as a linking layer to immobilize AuNPs on ITO substrates. The DDA molecules coat the ITO surface, attenuating the contribution of the support to CO electrooxidation. As for AuSMPs-modified ITO electrodes, AuSMPs are generated on ITO substrates by electrodeposition, with no DDA molecules introduced onto the ITO surface. As a result, the effect of the support contributes more to CO electrooxidation in AuSMPs/ITO systems compared with AuNPs/ITO systems.

4. Conclusion

We have shown that the formation of oxidic gold species on the surface of AuNPs is a necessary condition for the electrooxidation of CO. Our experimental results have identified a crucial catalytic role of supporting electrodes in Au particle/electrode systems. We have shown that the ITO electrode is not only a conducting support to provide electrical contact and a means of dispersing the gold particles on the surface, but also a promoter of the electrooxidation of CO. We have demonstrated that particle size is no longer a critical factor controlling the activity of AuNPs in electrochemical systems. These findings may shed new light on the origins of the high catalytic activity of gold particles toward CO oxidation.

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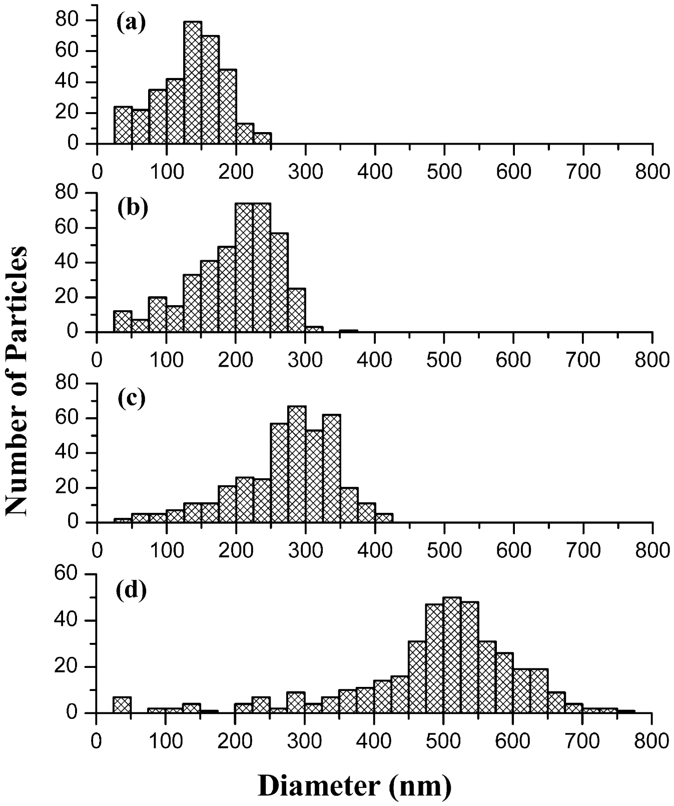

Fig. 7. Size distribution histograms of AuSMPs prepared on ITO substrates by electrodeposition at 0 V (vs SCE) in 10^{-4} M $HAuCl_4$ solution with 1 M KCl as supporting electrolyte. The deposition times are (a) 15, (b) 60, (c) 300, (d) 1800 s.

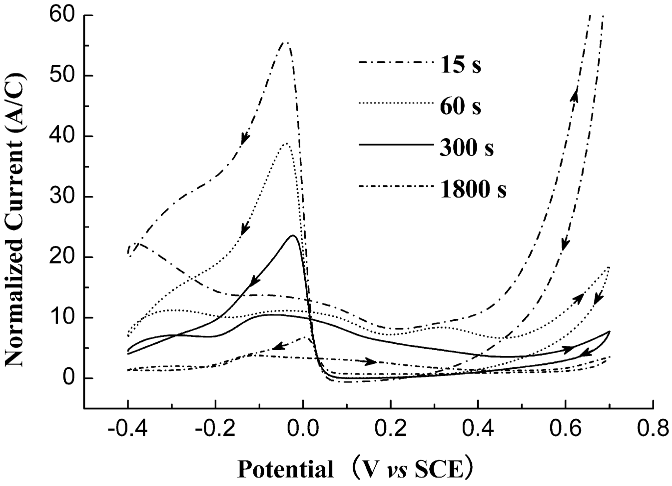

Fig. 8. Normalized cyclic voltammograms of AuSMPs/ITO in CO saturated 0.5 M KOH with different electrodeposition time for AuSMPs. Scan rate 100 mV s^{-1}.

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