Controlling the Size of Au Nanoparticles on Reducible Oxides with the Electrochemical Potential

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1. INTRODUCTION

Supported Au nanoparticles (NPs) have been extensively studied as catalysts for important chemical reactions, such as CO oxidation,\textsuperscript{1} CO oxidation,\textsuperscript{2–6} H\textsubscript{2}O splitting,\textsuperscript{7,8} CO\textsubscript{2} reduction,\textsuperscript{9,10} and water-gas shift reaction.\textsuperscript{11} They are also widely used as photocatalysts for their plasmonic response to visible light.\textsuperscript{12–14} When Au NPs are dispersed on a reducible oxide support, such as Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{15–17} Co\textsubscript{3}O\textsubscript{4},\textsuperscript{16,17} TiO\textsubscript{2},\textsuperscript{17–24} or CeO\textsubscript{2},\textsuperscript{25–32} they exhibit improved sintering stability and catalytic activity. The enhanced stability is attributed to the strong chemical bonding between the Au NPs and surface oxygen vacancies in the support oxide.\textsuperscript{33–35} The improved catalytic activity originates from the Au/oxygen vacancy interface being highly catalytically active at the triple-phase boundary between the Au, oxide, and gas molecules.\textsuperscript{36} In addition, previous reports showed that charged Au species, Au\textsuperscript{+} or Au\textsuperscript{3+}, were formed at the interface between the reducible support oxides and Au NPs through electron transfer between them\textsuperscript{36–40} and acted as active sites for oxidation reactions, such as CO oxidation.\textsuperscript{36,40} It was proposed that these charged Au species induced the formation of reactive intermediate peroxide species or charge transfer from Au to O\textsubscript{2} and improved the CO oxidation rate. Even when the support oxide is irreducible, Au NPs show substantial increase in their catalytic activity at the size of less than 2 nm due to a high density of reactive defect sites (steps or kinks) and change in the electronic structure.\textsuperscript{35} Therefore, it is preferred to make small Au NPs in order to obtain a high density of the catalytically active Au/oxygen vacancy interface or to increase the particles’ intrinsic catalytic activity. Controlling the size of supported Au NPs is also important for their application to photoelectrochemical water splitting since their plasmonic response to light changes with their size.\textsuperscript{41} The preparation of such supported Au NPs is typically done by impregnating Au precursors into the surface of the support oxide, followed by calcination in air. During the calcination, the oxide surface forms oxygen vacancies at elevated temperatures as it equilibrates with the pO\textsubscript{2} of the ambient air (pO\textsubscript{2} = 0.21 atm).\textsuperscript{35} Meanwhile, the impregnated Au species forms stable bonding with the oxygen vacancies while being reduced to metallic NPs.

The role of oxygen vacancies in the activity and stability of supported Au NPs has been studied thoroughly; however, how they affect the size of the supported Au NPs has not been
studied. Oxygen vacancies are known to act as nucleation sites for Au NPs, but their effect on the size of the Au NPs has not been clearly revealed. Increasing the annealing temperature, which would lead to a higher concentration of oxygen vacancies, resulted in even larger Au NPs due to the increase in their growth rate. Most of the conventional methods for fabricating supported Au NPs rely on the pO\textsubscript{2} of the ambient air at 400–500 °C in forming oxygen vacancies at the oxide surface during calcination. Using different gas environments, such as H\textsubscript{2}, during this calcination step, can possibly be one way of changing the amount of the surface oxygen vacancies in the oxide. However, this also changes the Au/gas interfacial energy which can change the final size of the Au NPs in an unwanted way. Other than using different gases, different sizes and shapes of support oxides are also known to have different amounts of oxygen vacancies at the surface, for example, nanorods vs nanosphere. Incorporating divalent dopants into support oxides, such as TiO\textsubscript{2} and CeO\textsubscript{2}, can form additional surface oxygen vacancies. Although these approaches have shown that having more surface oxygen vacancies improved the activity and stability of the Au NPs, they are dependent on multiple parameters at the same time or do not enable a dynamic and quantitative way to control the NP density.

Given the clear relationship between the surface oxygen vacancies of the support oxide and the nucleation and stability of the Au NPs, it is intriguing to think whether one can also systematically control the size of Au NPs by controlling the surface oxygen vacancies. This question has not been addressed to date. If we can selectively tune the oxygen vacancy concentration of the oxide surface, we expect to enable a systematic size control of the Au NPs. For example, increase in the number of the oxygen vacancies would serve as additional nucleation sites of Au NPs and make smaller NPs. At the same time, the resulting Au NPs would be thermally stable due to the stabilizing effect of the oxygen vacancies.

In this study, we demonstrate a novel electrochemical approach to control the size of oxide-supported Au NPs by modulating the amount of the surface oxygen vacancies in the support oxide. The applied electrochemical potential, U, allows us to control the concentration of surface oxygen vacancies without changing the gas environment. This approach alters the oxide-metal interface energy while keeping the Au/gas interfacial energy constant. In addition, this electrochemical approach allows us to control the effective pO\textsubscript{2} of the support oxide, hence the corresponding oxygen vacancy concentration, in orders of magnitude wider than that achievable using reducing gas mixtures. We use two different oxides, La\textsubscript{0.8}Ca\textsubscript{0.2}MnO\textsubscript{3−δ} (LCM) and Pr\textsubscript{0.9}Ce\textsubscript{0.1}O\textsubscript{2−δ} (PCO) thin films were deposited onto (100)-oriented single crystals of YSZ (yttria-stabilized zirconia, 8 mol % Y\textsubscript{2}O\textsubscript{3}, MTI Corp.) via pulsed laser deposition (PLD). The LCM thin film was deposited at a substrate temperature of 700 °C in 0.5 mTorr O\textsubscript{2} and cooled down to room temperature in 500 mTorr O\textsubscript{2}. The deposition of the PCO thin film was done at a substrate temperature of 500 °C in 10 mTorr O\textsubscript{2} and cooled down to room temperature in 400 mTorr O\textsubscript{2}. In order to remove the pre-existing surface CaO layers, which formed at the surface of the LCM during the PLD deposition, the as-deposited LCM thin films were immersed in high-purity deionized water for 1 min. The effect of this pre-treatment process was investigated by a previous study by Kubicek et al. The thickness of the thin films was measured using a Bruker DXT Stylus profilometer and was measured 80–100 nm. The out-of-plane X-ray diffraction (XRD, Rigaku Smartlab) measurement showed that the LCM thin films had a preferential texture along (110) and (111), and the PCO films were epilayer having the (200) orientation (Figure S1). Before the PLD deposition, the back side of the YSZ crystals was coated with porous Pt by applying Pt paint (SPI Corp.) and heating it at 700 °C in air for 30 min to form a solid layer. After the PLD deposition, a thin layer of gold (0.25, 0.5, or 1.5 nm) was deposited onto the LCM or PCO thin films by AC sputtering. The resulting Au/LCM and Au/PCO samples were electrochemically polarized under different potentials at 770 and 700 °C, respectively, in air. The surfaces of the films were imaged by high-resolution scanning electron microscopy (HRSEM) using a Zeiss Merlin HRSEM.

2.2. X-ray Photoelectronic Spectroscopy Measurement. The chemical composition of the Au/LCM and Au/PCO films’ near-surface region was characterized by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics VersaProbe II X-ray photoelectron spectrometer equipped with a monochromated Al Kα X-ray source. The angle between the analyzer and the surface plane was set to 45°. The integrated area of each element’s (or each chemical species) XPS spectrum was normalized by its sensitivity factor for quantification.

2.3. Lateral Polarization Method. Lateral polarization method enabled us to investigate a wide range of potentials with a small number of thin-film samples, thus minimizing experimental artifacts. Possible experimental artifacts include using samples from different
PLD batches or different experimental conditions such as variations in sputtering conditions or annealing temperatures. This method is based on the original design by Huber et al., and the utility of this method was previously demonstrated by our group. First, to make a cell for the lateral polarization method (please refer to Figure 2b), Pt paste (SPI Corp.) was applied at the back side and one edge of the YSZ crystal before the thin-film growth process to form a porous Pt counter electrode (CE). The deposited Pt electrode was kept at 700 °C in air for 1 h. After depositing a thin film onto the YSZ substrate, electrical contact points were created via sputter deposition of a Ti adhesion layer (10 nm), followed by an Au contact layer (100 nm). The regions for the sputtering were defined by a Kapton mask which covered the film surface, leaving a 2 mm gap at the side for depositing the upper side of the CE. The Au working electrode (WE) was deposited through a 3 × 7 mm² rectangular opening of the mask at a distance of 3 mm from the CE. With such a configuration, we could create the electrical connection between the WE and CE along the thin-film electrode. Upon application of the electrical potential to the WE, the thin film serves as an ohmic resistor for the electronic current, resulting in a linear voltage drop across the distance between the WE and CE. After the polarization experiments, the surface of the thin film was analyzed with a variety of characterization tools, such as XPS and SEM, while scanning the sample surface between the WE and CE. The corresponding local potential on each point was determined by the distance of the local analysis point from the WE and the full applied voltage at the WE contact (Figure 2b, bottom graph).

3. RESULTS AND DISCUSSION

3.1. Electrochemical Size Control of Au NPs on a Mixed Conducting Support Oxide, La$_{0.8}$Ca$_{0.2}$MnO$_3$. In order to electrochemically control the surface oxygen vacancy concentration of the support oxide and hence the size of the Au NPs on it (Figure 1), the support oxide must be mixed ionic–electronic conducting (MIEC). Also, it is preferred that the oxide is MIEC in oxidizing conditions to be able to control the size of the Au NPs in air. To this end, we chose Ca-doped lanthanum manganite (La$_{0.8}$Ca$_{0.2}$MnO$_{3.95}$, LCM) as a support oxide because it is MIEC in oxidizing conditions and has high stability at elevated temperatures. We used LCM thin films deposited by PLD on a YSZ substrate. A porous Pt layer was painted at the back side of the YSZ substrate to be used as a counter electrode, and a thin layer of Au with a thickness of 0.25 nm was sputter-deposited on the LCM surface before polarization experiments (Figure S2).

We used the lateral polarization approach to tune the amount of oxygen vacancies at the LCM surface. The lateral polarization method allows us to investigate the effects of different electrochemical potentials on the same sample and thus avoid sample history-dependent artifacts, such as variations in the pre-treatment processes, temperatures, or pO$_2$. Figure 2a,b shows the comparison between the conventional polarization method and lateral polarization method. In the conventional method (Figure 2a), single polarization is applied to each sample in each experiment. Therefore, a number of samples should be consumed in separate experiments to test a wide range of potentials, which can accompany potential experimental artifacts. In contrast, in the lateral polarization approach (Figure 2b), we can exploit a gradient of electrical potential formed laterally along the sample surface under a bias. Such a gradient of electrical potential is formed due to the unique configuration of the WE and CE, which allows the electronic current to flow laterally along the thin-film sample, while the ionic current flows vertically. Therefore, depending on which local point we analyze at the sample surface, we get different local potentials and thus can investigate the effects of different potentials as long as they are in between the potential applied to WE and 0 V (ground) (Figure 2b, bottom graph).

To make Au NPs under electrical potentials, two LCM samples with a thin layer of Au (0.25 nm) were kept at 770 °C in 1 atm O$_2$ for 10 min under lateral polarization. −0.8 and +0.8 V were applied to the WE of each LCM sample. After the polarization experiments, we measured SEM on four different local points of each sample surface chosen along the WE-to-CE direction. The corresponding local potential on each point was determined by the distance of the local analysis point from the WE and the full applied voltage at the WE contact (±0.8 V) (Figure 2b, bottom graph); the local potentials were ±0.2, ±0.4, ±0.6, and ±0.7 V. The SEM results in Figure 3 show a clear trend in the size of the Au NPs on the LCM surface with respect to the applied local potentials. Under a higher negative potential applied (Figure 3a–d), the size of the Au NPs decreases and it goes down to less than 10 nm at −0.7 V. The bottom bar graphs show that the number density of the small Au NPs, <7 nm and between 7 and 13 nm, increases and that of the bigger NPs decreases as the potential becomes more negative. It is well known that applying negative potentials to MIEC oxides reduces them and forms additional oxygen vacancies in them. Therefore, the SEM results coincide well with our hypothesis that Au NPs would be finely dispersed on the oxide surface under a high concentration of surface oxygen vacancies that act as nucleation sites. On the other hand, when positive potentials are applied, bigger Au NPs having the average size of 20 nm are formed (Figure 3e–h). This result is interpreted as the opposite effect of the negative potential: applying positive potentials removed the surface oxygen vacancies by oxidizing the LCM film and hence resulted in a low concentration of nucleation sites. Also, the average size and size distribution of the Au NPs (the bottom bar graphs) almost do not change under different positive potentials. We think this is because the oxygen vacancy concentration of the LCM surface almost does not change under these highly oxidizing conditions induced by positive potentials. Detailed explanation is given in the later section.
is noteworthy that applying high negative potentials formed small Au NPs (<10 nm) even at 770 °C, which is well beyond the conventional calcination temperature (400–500 °C).<sup>21,35,44</sup> We think that the high concentration of the oxygen vacancies at the LCM surface formed strong bonding with the Au NPs and prevented the sintering of the Au NPs at such a high temperature. To further confirm the above results, we conducted the same experiments using the conventional polarization method (Figure 2a) and found that the electrochemical size control of Au NPs was still possible (Figure S3); applying high negative potentials again formed finely distributed Au NPs (<10 nm). We also confirmed that annealing an Au/LCM sample for 3 h 15 min under −0.6 V still formed small Au NPs (<10 nm), meaning that these Au NPs did not undergo sintering for quite a long time at such a high temperature (Figure S4a). Moreover, the electrochemical size control of Au NPs was also possible with a higher initial loading of Au (0.5 and 1.5 nm, sputter-deposited) (Figures S5 and S6) and with a different deposition technique (0.3 nm, e-beam evaporator) (Figure S7).

Under the fixed feed amount of Au (0.25 nm, sputter-deposited), the size of the Au NPs and their number density should be in a trade-off relationship. To confirm this, we plotted the number density of the Au NPs shown in Figure 3 with respect to their average size. As can be seen in Figure 4a, the result clearly shows that these two parameters (light blue circles) well follow the predicted trade-off relationship (dashed line). The predicted trade-off curve is drawn by considering the initial amount of Au (0.25 nm, sputter-deposited) and assuming that the contact angle between the Au NPs and LCM is 45°. However, it should be noted that this contact angle was used just for quantification and does not have physical meaning. We also assumed that there was no loss of Au during polarization at high temperature because Au is hardly incorporated into the perovskite phase. Similarly, the number density and size of the Au NPs prepared with higher initial Au loadings, 0.5 and 1.5 nm, were plotted in the same graph as triangles and a square, respectively (Figures S5 and S6). It can be seen that the samples with the higher Au loadings formed Au NPs having higher contact angles with the LCM support: 50° when the initial Au loading is 0.5 nm and 55° when 1.5 nm. Also, the Au NPs formed under the same high negative potential (−0.6 V) but under different initial Au loadings (the data points with a black borderline and square data point) showed a similar number density of around 2 × 10<sup>15</sup>/m<sup>2</sup>. Only the size and contact angle of the Au NPs changed as the initial Au loading varied. This implies that 2 × 10<sup>15</sup>/m<sup>2</sup> is the upper-bound number density of the Au NPs under the given density of the nucleation sites, that is, oxygen vacancies or their clusters, formed by the applied potential (−0.6 V). Further chemical and quantitative analysis on the Au/LCM samples was done with XPS. Figure 4b shows the Au 4f spectra of the samples in Figure 3 normalized by the amount of all the metal elements present at the sample surface (La + Ca + Mn + Au). Each spectrum is shifted by referring to the peak location of the La 4d spectrum due to its chemical inertness. It can be seen that the Au 4f<sub>7/2</sub> peak of all samples is located at the binding energy of 84 eV, meaning that all the Au NPs are present as a form of Au<sup>0</sup>. Due to its surface sensitiveness, XPS quantification of Au also gives us a rough estimation of the interfacial area between the Au NPs and LCM. Indeed, the amount of Au/(La + Ca + Mn + Au) quantified by XPS increases (×1.86) as much as the expected increase in the interfacial area between the Au NPs and LCM (×1.69) as the size of the Au NPs decreases (Figure S8a). Also, we confirmed that the size of the Au NPs did not change because of the Ca segregation on the LCM surface. CaO<sub>x</sub> phases can form on the LCM surface under negative potentials as can be seen from our previous studies,<sup>57,63</sup> and it is possible that this new surface phase changes the Au/oxide interfacial.
energy. However, XPS analysis showed that the amount of CaO$x$ was very little or irregular with respect to the applied potential (Figures S3d and S8b), presumably due to the short annealing time (10 min). We further confirmed that the bright particles in Figure 3 were not CaO$x$ particles by annealing a bare LCM sample in the same conditions and measuring SEM on it (Figure S9); no bright particles were observed at the surface.

3.2. Electrochemical Size Control of Au NPs on a Support Oxide with Low Reducibility and Electronic Conductivity (Pr$_{0.1}$Ce$_{0.9}$O$_2$). Next, we tested another oxide, Pr$_{0.1}$Ce$_{0.9}$O$_{2−δ}$ (PCO), as a support of Au NPs. Though its non-doped form is more widely used as a support oxide, we incorporated Pr into CeO$_2$ as an aliovalent dopant to increase the amount of oxygen vacancies via charge neutralization ([Pr$_{0.1}$Ce$_{0.9}$]$^{+}$ = 2[V$_{O}^-$]). Due to the low electronic conductivity of PCO, the lateral polarization approach was not applicable, and hence, the conventional polarization method was used. The same thickness of the Au layer (0.25 nm) was sputter-deposited onto the PCO thin films before polarization experiments. The Au/PCO samples were kept at 700 °C in 1 atm O$_2$ for 10 min under different potentials, −1.8, −1.5, −1.2, −0.6, 0, and +0.6 V, and the SEM image of each sample was taken afterward (Figure 5). It was confirmed that most of the applied voltage translated to the overpotential on the dense PCO films (the detailed explanation is available in the Supporting Information). First of all, we found that much higher negative potentials, $\geq$ −1.5 V, are required to make Au NPs having comparable size (<10 nm) with those on the LCM. Under the potentials above −1.2 V, the resulting Au NPs had very similar average size and size distribution (the bottom bar graphs) between each other just as the Au/LCM samples polarized under positive potentials. Such a difference between the LCM and PCO could be either because of their different electrical properties or because the chemical species that acted as the nucleation sites of the Au NPs were different. The detailed discussion on this is given in the next section. We also confirmed that annealing an Au/PCO sample for 1 h under −1.5 V still formed small Au NPs (<10 nm), meaning that these Au NPs did not undergo sintering for quite a long time at such a high temperature (Figure S4b). These results further evidence the relationship between the amount of surface oxygen vacancies and the size of Au NPs and also demonstrate that this electrochemical method can be generally applied to different support materials.

Just as on the LCM, we plotted the number density of the Au NPs on the PCO with respect to their average size. As can be seen in Figure 6a, the number density and size of the Au NPs on the PCO were very similar to those on the LCM (Figure 3).
NPs well followed the expected trade-off relationship when the contact angle between the Au NPs and PCO is assumed to be 45°. A possible reason for the small deviation of the two data points having 10 nm on the x-axis from the 45° curve is discussed in the Supporting Information. Further chemical and quantitative analysis on the Au/PCO samples was done with XPS. Figure 6b shows the Au 4f spectra of the Au/PCO samples normalized by the total amount of the metals (Pr + Ce + Au). Different from the Au NPs on the LCM, those on the PCO have different shapes of Au 4f spectra depending on the applied potential, meaning that they have different oxidation states. It can be seen that as the potential becomes negative, the portion of the Au⁺ species at 84 eV decreases and that of the charged Au species, Au⁺ and Au⁻ at 85 and 82 eV, respectively, starts to increase. Also, the peak location of the Au⁺ and Au⁻ species shifts to a lower binding energy as the higher negative potential is applied.

The changes in the Au 4f spectra of the Au NPs on the PCO are summarized in Figure 7a. Under a low negative or positive potential (> −1.2 V), only Au⁺ and Au⁰ components are observed. Au⁺ on CeO₂ is known to form due to the charge transfer between Au and Ce in the support CeO₂,⁴⁴,⁶⁸ the standard reduction potential of Au⁺ to Au⁰ (+1.69 V) is lower than that of Ce⁶⁺ to Ce⁴⁺ (+1.72 V).⁴⁶ Interestingly, as the potential becomes negative, the Au⁺ starts to form at −1.2 V and its amount increases significantly at the potential under which the size of the Au NPs changed (−1.5 V). This implies that the formation of the Au⁺ species and the decrease in the size of the Au NPs occurred at the same time. We think both can be explained by the formation of additional oxygen vacancies at potentials lower than −1.5 V. Previous studies showed that the Au⁺ species and Ce³⁺ or Ti³⁺ were formed on the Au/CeO₂ or Au/TiO₂ via charge neutralization with positively charged oxygen vacancies (VO⁺) under reducing conditions. Also, as explained above, additional oxygen vacancies can act as additional nucleation sites for Au NPs and reduce their size under reducing conditions (U ≤ −1.5 V).

Interestingly, Figure 7a shows that the portion of the Au⁺ species also increases under the negative potential. We think that Au⁻ was the predominant species when the sample was under < −1.5 V at 700 °C, but a majority of the Au NPs were oxidized, while the sample was being cooled down to room temperature. Figure 7b shows that the peak location of the Au⁺ and Au⁻ components in the Au 4f spectra move to the lower binding energy as a higher negative potential is applied. This result coincides with the fact that the higher negative potential reduces PCO more strongly and thus the resulting Au NPs as well. Figure 7c schematically shows the resulting distribution of the different Au species at different potentials.

The amount of the Au NPs on the PCO film is quantified by XPS and plotted with respect to the size of the Au NPs (Figure S10). Different from the Au/LCM samples, the amount of the increase in Au/(Pr + Ce + Au) with the decrease in the size of the Au NPs is far lower (×1.28) than the expected increase in the interfacial area between the Au NPs and PCO (×1.67). It is possible that the Au NPs are partially encapsulated by the support oxide, PCO, under high negative potentials, and this weakens the XPS signal from the Au NPs. Such an encapsulation of supported metal nanoparticles by the support oxide is known as strong metal–support interaction (SMSI). The SMSI is known to occur when supported metal nanoparticles are annealed under reducing conditions, for example, in H₂. For supported Au NPs, they are known to undergo the SMSI on TiO₂.⁷⁰–⁷² Given the high negative potential (−1.8 V) applied to the PCO, it is possible that our Au/PCO samples would have undergone the SMSI (additional explanation is given in the Supporting Information).

### 3.3. Oxygen Non-stoichiometry of Support Oxide Determines the Onset Potential Needed to Change the Size of Au NPs

The average size and number density of the Au NPs on the LCM and PCO are plotted with respect to the effective pO₂ applied to both oxides via polarization. The
effective $pO_2$ was calculated by using the Nernst equation and applied potentials. Figure 8a,b clearly shows that both the average size and number density of the Au NPs on the LCM start to change at a much higher effective $pO_2$ (the onset at $\log(pO_2) = 4$), that is, higher potentials, than those on the PCO (the onset at $\log(pO_2) = -25$). This implies that these oxides exhibit different oxygen non-stoichiometries at the surface in response to different potentials or $pO_2$.

Figure 8c shows the oxygen non-stoichiometry of the La$_{0.8}$Sr$_{0.2}$MnO$_3$-±δ (LSM) bulk ($\delta$, triangles and a solid line), or the amount of oxygen vacancies in it, with respect to the effective $pO_2$. We assumed here that the LSM and LCM would have similar oxygen non-stoichiometry at the same temperature and $pO_2$. Two steeply descending regions can be seen with the decrease in the $pO_2$. The first descending region at high $pO_2$ (the onset at $\log(pO_2) = 0$) is due to the oxygen release from the LSM lattice, while the cation vacancies are removed during the reduction. The second descending region at low $pO_2$ (the onset at $\log(pO_2) = -15$) is due to the formation of oxygen vacancies occurring with the reduction of $\text{Mn}^{3+}$. The average sizes of the Au NPs on the LCM at different effective $pO_2$ (blue circles) are plotted together with the non-stoichiometry curve of the LSM for comparison. It can be seen that the onset $pO_2$ where the LCM starts to change the size of Au NPs ($\log(pO_2) = 4$) matches roughly with the onset $pO_2$ where its oxygen deficiency starts to appear in the high-$pO_2$ region ($\log(pO_2) = 0$). This coincides well with our hypothesis that having more oxygen vacancies at the surface of the support oxide would form smaller Au NPs. Although a negligible amount of oxygen vacancies is expected to form in the LCM bulk in this $pO_2$ regime ($\delta > 0$), it is likely that the surface of the LCM still has some amount of oxygen vacancies that can interact with the Au NPs (please note that the oxygen non-stoichiometry curve in Figure 8c is obtained from the LSM bulk). A previous computational work showed that the surface of doped lanthanium manganite had $10^6$-times more oxygen vacancies than in the bulk at 1 atm $pO_2$ ($\log(pO_2) = 0$). In addition, X-ray absorption spectroscopy (XAS) measurements (total electron yield mode) on the LCM samples pre-treated at different effective $pO_2$ showed that the oxidation state of the LCM surface changed even under the $pO_2$ regime where its bulk oxygen non-stoichiometry is not supposed to change. This indicates that the changes of the “surface” oxygen vacancy concentration at high $pO_2$ are not...
negligible unlike in the bulk. As for the Au NPs formed under positive potentials (log(pO$_2$) > 0), their average size and number density are very similar between each other (Figure 8a,b). As briefly mentioned earlier, this is presumably because the oxygen non-stoichiometry of the LCM barely changes under a high pO$_2$ regime, and this is supported by the saturation of the oxygen non-stoichiometry curve of the LSM (flat black line starting from log(pO$_2$) = 0 in Figure 8c). It is known that the oxidation of lanthanum manganite is limited by the significant repulsive forces between the cation vacancies, V$_{La}^{m}$ and V$_{Mn}^{m}$, which prevent the formation of additional cation vacancies during oxidation. Therefore, the oxygen vacancy concentration of the LCM surface almost does not change under different positive potentials and so does the resulting size distribution of the Au NPs.

Figure 6. (a) Trade-off relationship between the number density of the Au NPs vs the size of the Au NPs on the PCO (black dashed and solid curves). The curves are drawn by considering the initial amount of the Au layer (0.25 nm) sputter-deposited onto the PCO film and the contact angle between the Au NPs and PCO (30, 45, and 90°). The number density and size of the Au NPs on the PCO film (orange triangles) well follow the expected trade-off relationship when the contact angle is 45° (black solid curve). (b) Au 4f XPS spectra of the Au/PCO samples annealed under different potentials. The Au NPs on the PCO exhibit different oxidation states depending on the applied potential.

Figure 7. Different oxidation states of the Au NPs on PCO formed under different potentials. (a) Ratio of each Au$^+$ species (Au$^+$, Au$^0$, or Au$^-$) to the total Au (Au$_{tot}$). (b) Binding energy of the 4f$_{7/2}$ peak of the Au$^+$ and Au$^-$ species. (c) Schematics showing the distribution of the defects at the PCO surface and different Au species depending on the applied potential or corresponding effective pO$_2$ (pO$_2$,eff).
PCO also shows a similar shape of oxygen non-stoichiometry curve having two descending regions with decrease in the $pO_2$ (triangles in Figure 8d). The first descending region at high $pO_2$ (the onset at $\log(pO_2) > 0$) is explained by the formation of oxygen vacancies accompanied by the reduction of Pr$^{4+}$ to Pr$^{3+}$. The next descending region at low $pO_2$ (the onset at $\log(pO_2) = -20$) is due to the formation of the oxygen vacancies accompanied by the reduction of Ce$^{4+}$ to Ce$^{3+}$. The reason that the onset of the second descending region appears at the lower $pO_2$ in PCO ($\log(pO_2) = -20$) than in LCM ($\log(pO_2) = -15$) is because of the low reducibility of Ce$^{4+}$ compared to that of Mn$^{3+}$. The circles in Figure 8d show the average size of the Au NPs on PCO at different effective $pO_2$. The onset $pO_2$ where the PCO starts to change the size of Au NPs is around $\log(pO_2) = -25$, and this is close to the onset $pO_2$ where the oxygen vacancies start to form in the PCO in the low-$pO_2$ region ($\log(pO_2) = -20$). This again supports the relationship between the surface oxygen vacancies in support oxide and the size of the Au NPs. It is noteworthy that the average size of the Au NPs on the PCO almost does not change in the high-$pO_2$ regime ($\log(pO_2) < 0$) despite the huge changes in the amount of oxygen vacancies in this $pO_2$ regime. This can either be because PCO is not electronically conducting at high $pO_2$ or because the chemical species responsible for the nucleation of the Au NPs on the PCO were not the surface oxygen vacancies. Under low negative potentials, PCO has a low electronic conductivity, so the in-plane conduction from the line contact between the Au mesh (current collector) and the PCO surface to the open PCO surface would not occur efficiently. Therefore, most of the open PCO surface would equilibrate with the environmental $pO_2$ ($\log(pO_2) = 0$), and the resulting size distributions of the Au NPs under these potentials would hence be similar. Only under a high negative potential or low $pO_2$ around the second descending region ($\log(pO_2) < -20$ in Figure 8d), PCO would start to have an enough high electronic conductivity for its surface to uniformly equilibrate with the applied potential. Different from the PCO, the LCM has p-type conductivity at high $pO_2$, and hence, its defect chemistry can be tuned even at high effective $pO_2$. Such a high electronic conductivity of the LCM is because Ca$^{2+}$ in LCM (Ca$_6$O$_7$) is charge balanced by the conducting holes on Mn (Mn$_{Me}$). On the other hand, it is also possible that the PCO had different chemical species for the nucleation of the Au NPs instead of oxygen vacancies. Figure 7a and Figure 8d show that the size of the Au NPs on
the PCO starts to decrease when Ce$^{3+}$, oxygen vacancies, and Au$^{-}$ species form. If the nucleation site of the Au NPs on the PCO was Ce$^{3+}$, instead of the oxygen vacancies, their size would not change even with the change in the amount of oxygen vacancies at moderate pO$_2$, which is in line with the result in Figure 8d. However, the Au NPs formed under a high negative potential had the Au$^{-}$ species, and these Au species are not expected to nucleate on the negatively charged Ce$^{3+}$ (Ce$_{ox}^{-}$). Therefore, we think that the oxygen vacancies are still more likely to act as the nucleation sites of the Au NPs on the PCO.

3.4. Thermal Stability of the Au NPs on Support Oxides. As shown earlier (Figure S4), the Au NPs on both support oxides, PCO and LCM, were thermally stable at 700 and 770 °C, respectively, under high negative potentials. In addition, we tested their thermal stability under gas conditions relevant to the catalytic applications of supported Au NPs. Two different Au/PCO samples were first prepared by annealing them at 700 °C under −1.5 and +0.6 V to form small and large Au NPs (Figure 9a,d). These samples were then kept in 5% H$_2$/N$_2$ at 450 °C for 18 h to test their thermal stability under the reducing condition (Figure 9b,e), and also, in 2% CO and 8% O$_2$ at 450 °C for 18 h to test their thermal stability under the oxidizing condition (Figure 9c,f). These gas conditions reflect different catalytic applications of supported Au NPs, such as hydrogenation reactions or CO oxidation. As can be seen in Figure 9b,e, the Au NPs formed under −1.5 V did not undergo noticeable sintering both under reducing and oxidizing conditions even after annealing at 450 °C for 18 h. The Au NPs formed under +0.6 V showed a good thermal stability under the reducing environment (Figure 9e), but they underwent some extent of sintering under the oxidizing condition (Figure 9f). This result indicates that the Au NPs formed under a high negative potential are not only small in size due to the high density of the nucleation sites (oxygen vacancies) but also stable against sintering due to the anchoring effect of the oxygen vacancies. We think that the oxygen vacancies in contact with the Au NPs were not fully oxidized during the CO oxidation reaction because CO continuously took the oxygen at the catalytically active Au/ CeO$_2$ interface during the reaction, and also, the oxygen vacancies were stabilized by forming a chemical bonding with the Au NPs. Likewise, the thermal stability of the Au NPs on the LCM formed under −0.6 V was examined in 5% H$_2$/N$_2$ at 450 °C for 17 h. As shown in Figure S11a,b, the Au NPs retained their size without undergoing noticeable sintering, thus showing its high thermal stability. Interestingly, when the as-deposited Au/LCM sample, that is, no pre-treatment step under the electrochemical potential, was annealed in the same conditions, significant agglomeration of Au was observed, as shown in Figure S11e,f. This clearly shows that the oxygen vacancies at the LCM surface formed under a high negative potential not only make finely distributed Au NPs but also prevent them from sintering under catalytically relevant conditions.

4. CONCLUSIONS

In this study, we demonstrated a novel electrochemical method to control the size of oxide-supported Au NPs. Support oxides with different reducibilities, LCM and PCO, were used as model oxides. We showed that the size of Au NPs depends strongly on the magnitude and sign of the electrochemical potential applied to the support oxides. Small Au NPs (<10 nm) were formed under a high cathodic potential, while bigger Au NPs (~20 nm) are formed under an anodic potential. Arguably, a high concentration of oxygen vacancies in the oxide surface induced by the cathodic potential acted as nucleation sites of the Au NPs and thus formed small Au NPs. The onset cathodic potential required to create small Au NPs depends strongly on the reducibility or oxygen non-stoichiometry of the support oxide. Interestingly, the Au NPs formed under the high cathodic potential exhibited high thermal and chemical stability. They did not undergo sintering even at 700 or 770 °C under the cathodic potential and also were highly stable in catalytically relevant conditions without potential. The effectiveness of this electrochemical method resides in the fact that the electrochemical potential can induce very low effective pO$_2$, that is, high concentration of oxygen vacancies, to the support oxide while keeping the Au/air interfacial energy constant. Selective control of the oxygen vacancy concentration, and thus the size of the Au NPs, without changing the Au/air interfacial energy is hard to achieve using other non-electrochemical ways, such as annealing in reducing gases.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c08422.

Additional characterization data (SEM, XRD, and XPS), detailed explanations on the mechanisms briefly introduced in the main text, and further discussion on the practicality of the electrochemical method introduced in this paper (PDF)

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Notes
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