Control of Morphology of Silver Clusters Coated on Titanium Dioxide during Photocatalysis

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Supported metal catalysts have been used extensively in many current industrial processes. The morphology of coated metal on a support is usually an important factor affecting the efficiency of the catalyst. In this study, the investigation is focused on a photocatalytic process to coat silver clusters on titania (P-25 TiO_2) with an emphasis on the morphology control of coated silver clusters. For the first time, the particle size and the deployment intervals of silver clusters are controlled with an innovative method that involves the in-situ formation of water-insoluble transitory species such as AgBr, AgCl, or Ag_2O on the surface of titanium dioxide. Experimental results demonstrated that the transitory particles function as physical spacers, which temporarily occupy some of the active site on the titanium dioxide surface and act as reservoirs for Ag^+ ions to keep the local Ag^+ concentration on TiO_2 extremely low. The silver clusters coated on titania are found to be stable in the spherical *silver-3c syn* crystalline form indicated by TEM, XRD, and XPS measurements.

Introduction

Nanosize silver clusters have been extensively studied due to their unique catalytic properties,[1–10] despite the fact that nanosize silver particles or clusters are thermodynamically unstable in water.[11,12] The short lifetime of silver clusters in solution has greatly restricted the realization of their potentials, and this shortcoming has, in turn, attracted a great deal of interest in prolonging the lifetime of these clusters.[13,14] One of the most effective methods to stabilize these clusters is to immobilize the metal clusters onto a solid support. Solid supported metal catalysts also offer a much greater surface area per unit of metal without introducing difficulties in dispersion and postreaction separation.[15–17] It is anticipated that the size and morphology of the metal clusters immobilized on a solid support have a profound impact on the activity of the catalyst.[18–20]

Conventional methods for coating of metal onto a solid support include physical blending and chemical precipitation followed by surface adsorption. Both approaches have great difficulty in controlling the morphology of deposited metal clusters. Though photoinduced deposition of various noble metals onto semiconductor particles has been extensively reported,[21–32] there were limited studies that focus on the use of this technique to produce metal clusters having well-controlled particle size and deployment morphology.

In this study, a simple and straightforward photocatalytic method was employed to deposit silver clusters with a certain degree of control in coating morphology. In this paper, key influential factors, such as surfactant, pH, and concentration of Ag^+ ion will be reported. A strategy that involves the use of water-insoluble silver oxide/halides as physical blockers and silver ion reservoirs will be presented. The potential applications of this unique approach will be discussed.

Experimental Section

Preparation of Ag/TiO_2 Particles. A suspension of TiO_2 was first prepared by mixing 500 mg of TiO_2 (Degussa P-25 with

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Table 1. Experimental Conditions of the Corresponding TEM Photos Where SDS Refers to Sodium Dodecyl Sulfate[a]

silver precursor	initial pH or pH region	surfactant	conc of surfactant ($\times 10^{-4}$ M)	TEM result
none	none	none	none	Figure 1a
AgNO$_3$	natural			Figure 1b
AgNO$_3$	natural	SDS	2.0	Figure 1c
AgNO$_3$	3.0	SDS	2.0	Figure 1d
AgNO$_3$	4.0; 5.0; 6.0; 7.0	SDS	2.0	Figure 1e
AgNO$_3$	11−12			Figure 2a
AgNO$_3$	11.42			Figure 2b
AgNO$_3$, NaCl	10−12			Figure 3a
AgNO$_3$, NaBr	10−12			Figure 3b

[a] Other conditions: [AgNO$_3$] = 3.8×10^{-3} M; 8 mL of ethanol; 500 mg of TiO$_2$ in 120 mL of twice-distilled water.

an anatase/rutile crystalline ratio of 8:2 and surface area of 50 m^2/g and 78.0 mg of AgNO$_3$ with 120 mL of twice-distilled water in a round-bottom flask. The suspension was purged with a stream of nitrogen for 15 min and then irradiated for 6 h using a high-pressure mercury lamp (250 W with the major emission wavelength at ca. 365 nm). The suspension was then centrifuged, and the supernatant was removed for atomic absorption spectrometry (AAS) analysis. The particles were washed with distilled water and centrifuged (7000 rpm for 10 min) five times before TEM analysis without drying. Other analyses (see below) were conducted on samples that were dried in an N$_2$ flow at 473 K for 6 h.

For those experiments in which a chloride or bromide effect was examined, a predetermined amount of NaCl or NaBr (equal molar to AgNO$_3$) was added into the suspension to convert AgNO$_3$ into the corresponding AgCl or AgBr. A solution of NaOH (0.1 M) or HNO$_3$ (0.1 M) was used to adjust the solution's pH value to the desired value. For those surfactant experiments, a predetermined amount of sodium dodecyl sulfate (SDS) (2×10^{-4} M) was added at last during the sample preparation.

Characterization of Resulting Particles. Transmission electron micrographs were obtained on a Philips EM-120 TEM with an accelerating voltage of 100 keV. The particles obtained after the irradiation and workup were dropped onto the surface of carbon membrane and dried at ambient conditions before analysis. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5300 ESCA instrument (Mg Kα radiation; 1253.6 eV; 10^{-7} Pa). The C 1s photoelectron peak (binding energy at 284.6 eV) was used as energy reference. X-ray diffraction (XRD) patterns were collected on a D/max-2500 commercial instrument (Cu Kα, $\lambda = 1.541\,78$ Å) with a scan speed of $2\theta = 8.0$ deg/min. Atomic absorption spectrometry (AAS) was done on the resulting solutions immediately to avoid the photolysis of AgNO$_3$.
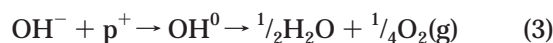
Results and Discussion

To control the morphology of silver clusters with desired size and distribution pattern on a given surface area of titania, such influencing factors as surfactant, pH, local concentration of Ag$^+$ ion, and the source of silver ion were examined. As shown in Table 1 and Figures 1−3, the degree of impact of these factors on the deposition morphology and particle sizes varies. The discussion of each individual factor in this section will be followed by an overall review of the inter-relationship among these factors. It is a prerequisite, however, that the starting suspension must be stable and well dispersed. In all cases, the photoreduction of silver ions is nearly 100% to the completion.

Effect of Surfactant and pH. When a simple dispersion of TiO$_2$ particles containing silver nitrate, without any pH adjustment and other chemical additives, was exposed to ultraviolet irradiation, the surface-adsorbed silver ions were reduced to metal and subsequently accumulated to islands on TiO$_2$ particles via a photocatalytic process. The size of these metal islands was

typically large and polydispersed. The metal islands could grow rapidly and sometimes overshadowed the original TiO$_2$ particles. While Figure 1a shows a representative TEM micrograph of native TiO$_2$ particles, Figure 1b captured the randomness and the overgrown metal islands on TiO$_2$ for samples obtained without any pH adjustment (ca. 5−6) and the presence of other chemical additives.

One strategy to reduce such a rapid overgrowth on the TiO$_2$ surface is to limit the local concentration of the silver ions. One method of accomplishing such an objective is to use a surfactant. More specifically, at the pH where the experiments are usually conducted, the surface of TiO$_2$ particles tends to be positively charged after the adsorption of silver ions. An anionic surfactant could adsorb onto the surface to limit the available sites for reduction and the number of nucleation sites for metal islands to grow. As a result, the average metal particle size becomes smaller and the size distribution becomes relatively narrower, as shown in Figure 1c. Although the morphology of the deposition is still far from even and reproducible, it is a vast improvement over the result shown in Figure 1b.

In addition to surfactant, it is known that the surface charge and the adsorptivity of silver ions are highly influenced by the pH of the suspension. This phenomenon can also be used to control the local concentration of silver ions on the surface and the nucleation kinetics for the deposition of metal clusters.[33] Therefore, an integrated use of pH adjustment and surfactant adsorption may be more effective in controlling the deposition morphology of deposited metal islands on the surface of TiO$_2$. An obvious direct impact of pH on the system is also its dispersion quality. To obtain a well-dispersed TiO$_2$ system, the initial pH of the suspension should be away from the isoelectric point (IEP) of P-25 TiO$_2$ particles (6−7).[31] The pH employed should also ensure the stability of Ag$^+$ ions. If the desired chemical and photochemical events are for Ag$^+$ to be adsorbed onto the surface of TiO$_2$ and receive electrons from the reduction sites, the pH should be in the range that allows such effective surface adsorption and prevents silver ions from precipitation. For example, at extremely low pH, the TiO$_2$ surface can be so positively charged that surface adsorption of silver cation becomes inefficient.[33] Oppositely, if the pH is too high, silver ions may precipitate out of solution as silver hydroxide or oxide particles. An additional fact that should be taken into account is that the pH of the solution and the concentration of Ag$^+$ ion will decrease during the course of photochemical reactions mediated on the surface of TiO$_2$, as shown in the following equations:[21]

$$TiO_2 + h\nu \rightarrow e^- + p^+ \quad (h\nu > E_{bg}) \tag{1}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{2}$$

$$OH^- + p^+ \rightarrow OH^0 \rightarrow {}^1\!/_2 H_2O + {}^1\!/_4 O_2(g) \tag{3}$$

$$Ag^+ + e^- \rightarrow Ag^0 \tag{4}$$

$$mAg^0 \rightarrow Ag_m \tag{5}$$

The reaction steps proposed include the creation of electron (e$^-$)−hole (p$^+$) pairs, the reaction of holes with OH$^-$ surface species, and the reaction of electron with adsorbed Ag$^+$ ions.

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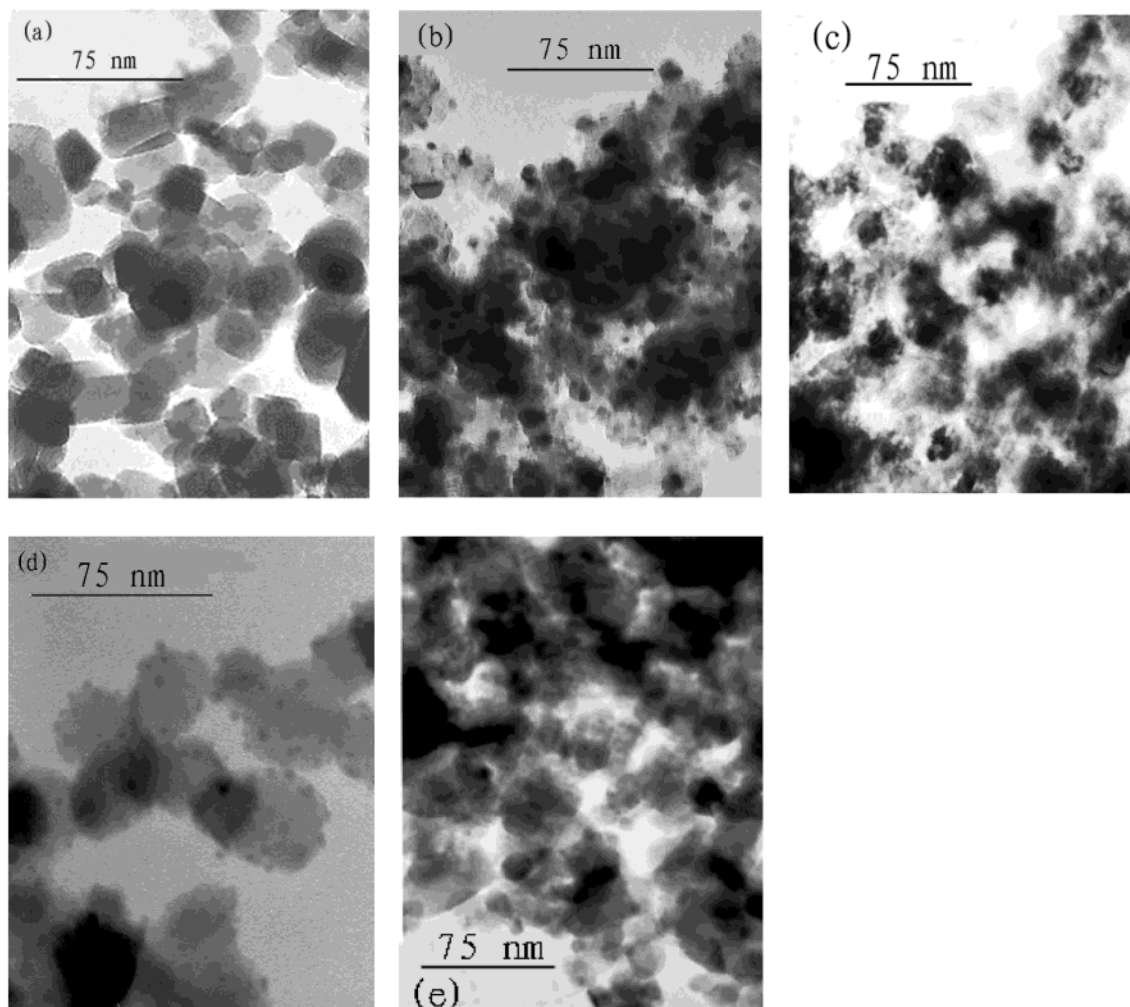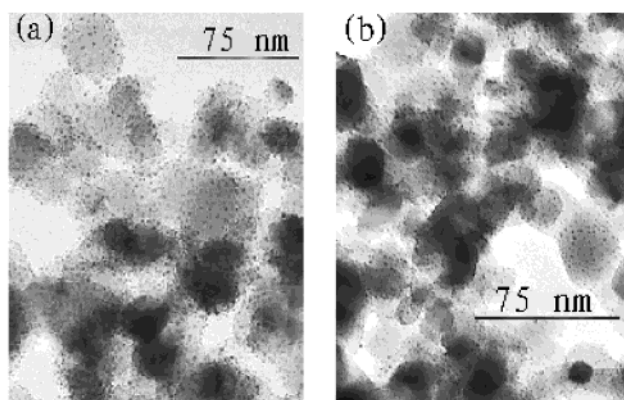
Figure 1. TEM images of TiO$_2$ raw material (a) and Ag/TiO$_2$ particles prepared under various conditions: (b) without the addition of surfactant and pH adjustment; (c) with the addition of SDS (sodium dodecyl sulfate) but without pH adjustment; (d) in the presence of 2.0×10^{-4} M SDS with the initial pH value adjusted to ~3.0; (e) in the presence of 2.0×10^{-4} M SDS with the initial pH value adjusted to 4−7.
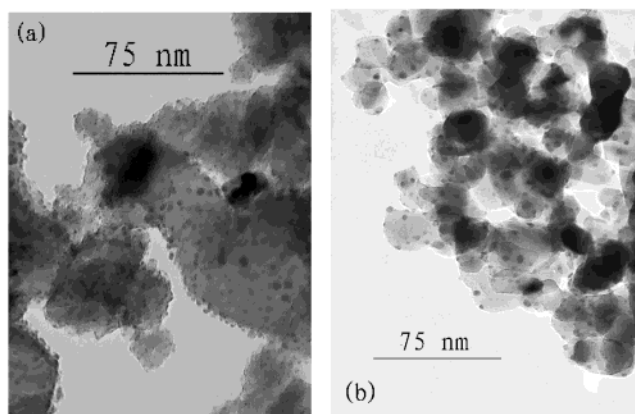
Figure 2. TEM images of Ag/TiO$_2$ particles: (a) prepared at the pH region 11−12 with irradiation; (b) prepared by treating the sample at pH = 11.42 without irradiation.

Figure 3. TEM images of Ag/TiO$_2$ particles: (a) prepared using AgCl as the source of Ag$^+$ ions at pH = 10−12; (b) prepared using AgBr as the source of Ag$^+$ ions at pH = 10−12.

A set of deposition experiments was carried out at different initial pH values and SDS concentrations. On the basis of the morphology of the deposited silver metal islands, an optimal condition was found at pH = ~3 and SDS concentration = ~0.2 mM. A representative result of such deposition is shown in Figure 1d. In comparison, the cluster size and size distribution of the deposits are much larger for the experiments carried out at a higher

initial pH (4−7). As shown in Figure 1e, even with the use of SDS the morphologies of the deposits are fairly heterogeneous. One explanation for the poor deposition morphology at higher pH is the fact that the solution pH is closer to the IEP value of the particles (ca. 6.25) and the TiO$_2$ particles tend to have a greater degree of aggregation. As the growth of the deposits may be significantly faster than the dissociation of these particles, the aggregation

may create large gaps among the silver clusters where the native particles were in contact.

Control of Ag$^+$ Ion Concentration. Although the morphology of silver clusters can be modified to a certain degree by pH adjustment and the use of surfactant, the control of deposited cluster size and deployment intervals is still limited. To obtain even smaller silver clusters and further control its dispersion morphology, one possible approach is to further lower the bulk and local concentration of Ag$^+$ ions on the illuminated TiO$_2$ surface. It is estimated that a steady low concentration of Ag$^+$ ions (i.e. <10 μM) would yield deposits/clusters with more desirable size and dispersion distribution. Maintaining such a low steady Ag$^+$ concentration through conventional methods such as continuous external injection, obviously, is impractical. An alternative solution is to convert Ag$^+$ into silver oxide which shall serve as a reservoir to provide a steady low concentration of Ag$^+$ ions. When the pH value of the solution is controlled in the alkaline region away from the IEP of TiO$_2$ particles, silver ions will precipitate out of solution as silver oxide or hydroxide. To validate this model, experiments were carried out in the pH region 11−12. The results showed that the formation of silver oxide not only decreased the steady-state Ag$^+$ ion concentration. The low steady state concentration inhibited the rapid growth of silver clusters. The silver hydroxide/oxide particles may have also partly occupied the surface active site of TiO$_2$ (shown in Figure 2b) and thus modified the deposition patterns of the silver clusters. Figure 2a showed the result of this effect in TEM with smaller size of silver clusters and shorter distance among particles compared to those shown in Figure 1d.

Control of Silver Ion Source. Encouraged by the success of using silver oxide as a reservoir for a low steady concentration of silver ions, we then explored other forms of silver source. More specifically, to further lower the local concentration of Ag$^+$ ions near TiO$_2$, Ag$^+$ ions were converted into other forms of silver with even lower K_{sp} (solubility product constant) than that of silver oxide. For example, a predetermined amount of bromide (NaBr) or chloride (NaCl) was introduced at the experimental condition mentioned above to form silver bromide or silver chloride, respectively. Due to the difference in K_{sp} (K_{sp}(AgCl) = 1.8×10^{-10}, K_{sp}(AgBr) = 5.0×10^{-13}, K_{sp}(AgOH) = 2×10^{-8}), AgCl or AgBr will provide a local concentration of Ag$^+$ ions of about 10^{-7} or 10^{-10} M, respectively, which is significantly lower than that from silver oxide (10^{-5} M). The deposition experiments carried out using either AgCl or AgBr as the source of silver in the pH region 10−12 showed even finer silver clusters on the TiO$_2$ surface, as shown in Figure 3. The morphology of silver clusters can be easily observed from the TEM, which showed that, compared to AgOH, when AgCl was used as the silver source, smaller size and better dispersion clusters were obtained. Even smaller size and better dispersion of silver clusters were obtained when AgBr was used as the source of silver ions. This is in perfect consistency with the hypothesis that a lower steady concentration of silver ion is more effective in producing small and highly dispersed silver clusters on TiO$_2$.

On the basis of the results described above, at a given silver loading, the morphology of silver clusters can thus be controlled by a combined use of surfactant, proper pH, and appropriate source of silver such as silver oxide, AgCl, and AgBr. The distribution intervals of silver clusters (i.e. the distance between two adjacent silver clusters) increase in the order AgCl ∼ AgBr < Ag$_2$O < surfactant alone, and the size of silver clusters increases as the steady-state concentration of Ag$^+$ ion increases, in the order K_{spAgBr} <
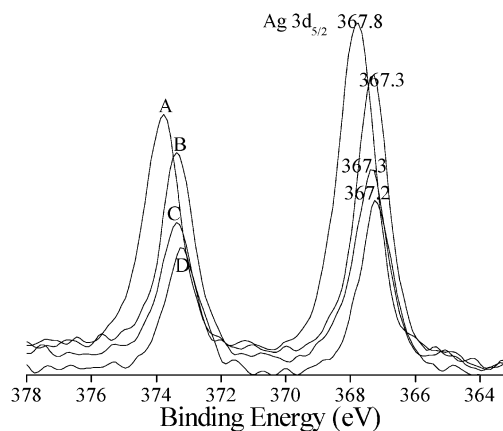
Figure 4. Ag XPS spectra of Ag/TiO$_2$ particles: (A) prepared using AgBr as the Ag$^+$ ion source at pH = 10−12; (B) prepared using AgCl as the Ag$^+$ ion source at pH = 10−12; (C) prepared by adjusting the pH to 11−12; (D) prepared by using SDS as a surfactant and adjusting the initial pH to ∼4.
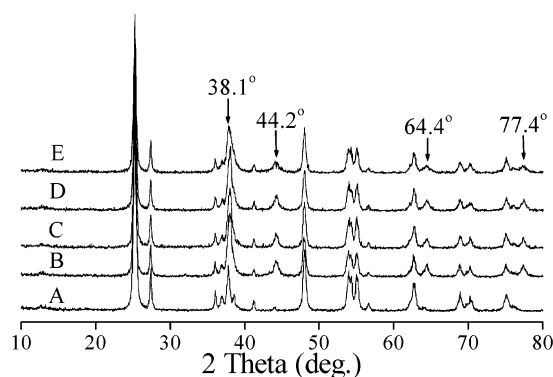
Figure 5. XRD patterns of untreated P-25 TiO$_2$ (A) and Ag/TiO$_2$ particles prepared under various conditions: (B) with the presence of SDS and pH adjusted to ∼4; (C) by adusting the pH to ∼11−12; (D) by using AgCl as the Ag$^+$ ion source at pH = 10−12; (E) by using AgBr as the Ag$^+$ ion source at pH = 10−12.

$K_{spAgCl} < K_{spAg2O}$ < surfactant alone. The results demonstrate that cluster size may be mainly controlled by the local concentration of silver ions. The deployment interval or spacing among clusters may be directly influenced by the transient particles that temporarily occupy the TiO$_2$ surface as well as the local silver ion concentration.

Characterization of Silver Deposits

Though the photodeposition of various noble metals onto semiconductor particles has been extensively reported, little attention was focused on the valence state of a coated metal, which has extensively been considered to have a great impact on the catalytic activity for some reactions. For affirming the existing state of silver deposits on the surface of TiO$_2$, four samples of as-synthesized Ag/TiO$_2$ particles, prepared by the above-mentioned four different methods, respectively, were characterized by XPS and XRD measurements. Figures 4 and 5 showed the XPS profiles and XRD patterns of them, respectively. On the basis of the binding energy, the metallic state of coated silver can be estimated. The powder XRD patterns of the pure TiO$_2$ substrate (Figure 5) confirmed the presence of rutile and anatase with the proportions as described in the Experimental Section. For Ag/TiO$_2$ particles, four additional peaks, 2θ = 38.1°, 44.2°, 64.4°, and 77.4° are assigned to the *silver-3c syn* crystals, which not only further confirm the metallic state of the coated silver

cluster but also show their existed state as stable silver crystals, which may be promising for improving the performance of the material as a catalyst. The average size of the silver phase of the Ag/TiO_2 particles was estimated according to the following equation:

$$D = [k\lambda/(\beta_c - \beta_s)] \cos \theta \qquad (6)$$

where D is the grain size; λ is the X-ray wavelength; β_c and β_s are the fwhm of the calculation phases and the standard (single-crystal silicon), respectively; the number $K = 0.89$ is a coefficient; and θ is the diffraction angle. The calculated results showed that the average size of silver modified by surfactant, pH, AgCl, and AgBr was 3.3, 2.7, 2.4, and 2.2 nm, respectively, in agreement with the size order of silver observed in the TEM.

Conclusion

We have demonstrated an innovative approach in controlling the coating morphology of silver clusters on TiO_2 particles during photocatalytic deposition. In addition to a balance of surface adsorption, particle dispersion, and metal clusters growth rate, the control of local silver ion concentration via a water-insoluble form was employed for the first time. The working principle of this new approach is thought to include two aspects of the intermediate silver source such as AgBr, AgCl, or Ag_2O: (1) the depositions partly occupied the surface site of titanium dioxide and (2) acted as the reservoir for the deposition of Ag^+ ions and keeping the concentration of Ag^+ ion in the solution extremely low. The size and dispersion of supported silver clusters can be controlled by the choice of precursor of silver. Both XPS and XRD characterized the coated silver clusters as existing as the metal state. The approach that has been validated in this study can be easily extended to other metal deposition onto reactive surfaces, and it has the potential to be applied in larger scale manipulation or synthesis.

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