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Layer-by-layer Assembled Molecular Films—II: Monolayers of Metal Nanoclusters from Photochemical and Sonochemical Conversion of Multilayered Ionic Films

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Layer-by-layer Assembled Molecular Films – II: Monolayers of Metal Nanoclusters from Photochemical and Sonochemical Conversion of Multilayered Ionic Films

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Monolayer of uniform gold (Au) and platinum (Pt) nanoparticles were prepared from photochemical and sonochemical conversion of layer-by-layer assembled $\{R^+|AuCl_4^-\}_n$, $\{R^+|PtCl_4^{2-}\}_n$ and $\{R^+|PtCl_6^{2-}\}_n$ films, respectively, where R^+ is a cationic surfactant or a cationic polymer.

Keywords layer-by-layer; photochemical; sonochemical; nanoclusters

INTRODUCTION

Because of their unique chemical and physical properties, metal and semiconductor nanoparticles were widely chosen as the building blocks of various functional films[1]. The most commonly adopted approach to construct nanocluster films is to synthesize the metal nanocluster colloids in solution phase, and followed by electrostatic-driven assembling[1]. In this paper, we report an alternative approach in which the ionic precursors, instead of the metal colloids, were used as the building blocks to construct the primary film. The primary film was then converted to a film of monolayer metal nanoclusters by

photochemical or sonochemical reactions. The general idea of this approach is illustrated in Figure 1.

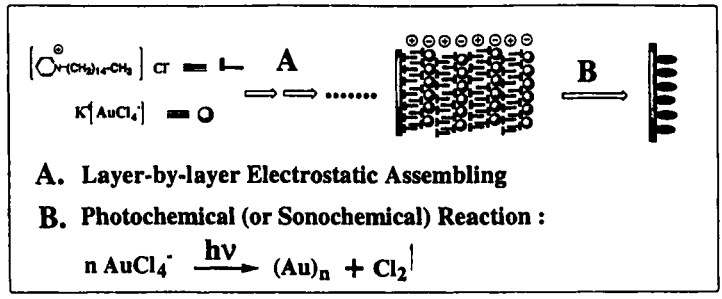

FIGURE 1. The primary multilayer film containing photolabile or sonolabile metal complexes was constructed by a layer-by-layer assembling (A). The primary film was then exposed to either an UV radiation or a supersonic wave to induce its conversion into a monolayer of metal nanoclusters (B).

EXPERIMENTAL

The chemicals used in this study, including $HAuCl_4$, $KAuCl_4$, K_2PtCl_6, K_2PtCl_4, cetyl-trimethylammonium bromide (CTA^+Br^-), cetyl-pyridium chloride (CPY^+Cl^-), were all purchased from Aldrich and used as received. UV-Vis absorption, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to characterize the films in the assembling process and before and after the photochemical or sonochemical reactions. Triply distilled water was used to prepare all the solutions. The layer-by-layer assembling of each primary film was achieved by alternatively inserting a substrate in solutions containing either cationic or anionic species. The substrate was either a Pyrex, a quartz, or an ITO glass slide.

RESULTS AND DISCUSSION

Figure 2 shows the growth of two primary films containing $AuCl_4^-$ and $PtCl_6^{2-}$ precursors, respectively, and monitored by UV-Vis absorption spectrometry. On the left side are the UV-Vis spectra of alternatively assembled CPY^+ and $AuCl_4^-$. On the right side are the UV-Vis spectra of alternatively assembled CTA^+ and $PtCl_6^{2-}$. The linear increase of the absorption maxima with the number of layers (the insets) in both films indicates that the amount of species assembled in each layer is roughly the same for each film.

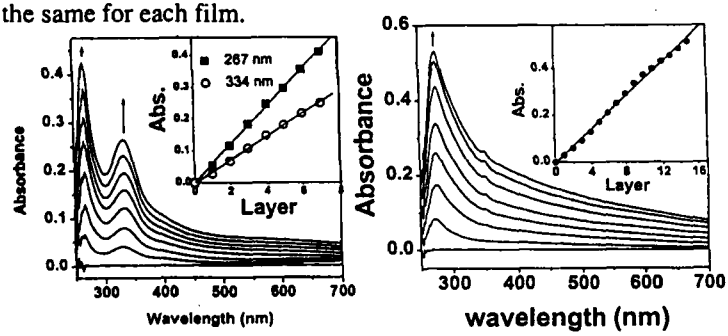

FIGURE 2. UV-Vis spectra of the layer-by-layer assembled $\{CPY^+|AuCl_4^-\}_n$ (the left) and $\{CTA^+|PtCl_6^{2-}\}_n$ (the right) films on Pyrex slides.

Figure 3 displays the XRD of the primary film $\{CTA^+|PtCl_6^{2-}\}_n$ (the left) and the XPS spectra of the $\{CTA^+|PtCl_6^{2-}\}_n$ and $\{CTA^+|PtCl_4^{2-}\}_n$ films before and after their exposure to UV radiation for four hours or to an ultrasonic wave for 20 min. in the presence of $NaBH_4$ solution (the right). As can be seen from the XRD pattern, the as-synthesized $\{CTA^+|PtCl_6^{2-}\}_n$ film has a very well ordered structure with a layer-by-layer spacing of ~ 27 A. Unlike $\{CPY^+|AuCl_4^-\}_n$ and $\{CTA^+|AuCl_4^-\}_n$ films which are readily converted to a monolayer of uniform Au^0

nanoclusters upon the exposure to UV light[2], the exposure of $\{CTA^+|PtCl_6^{2-}\}_n$ and $\{CTA^+|PtCl_4^{2-}\}_n$ films to UV light convert both of them into a special type of $[PtCl_2]_n$ nanoclusters with unifrom size[2]. However, both $\{CTA^+|PtCl_6^{2-}\}_n$ and $\{CTA^+|PtCl_4^{2-}\}_n$ films were converted to Pt^0 nanoclusters when the films were inserted in a solution containing 2.0 mM $NaBH_4$ and sonicated for 20 minutes[2]. The as-prepared Pt^0 and Au^0 nanoclusters display very good electrocatalytic activity in the oxidation of nitric oxide[2].

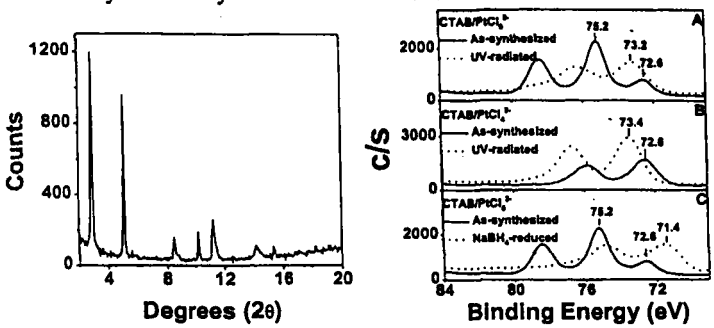

FIGURE 3. XRD pattern of $\{CTA^+|PtCl_6^{2-}\}_n$ film (the left) and the XPS spectra of $\{CTA^+|PtCl_6^{2-}\}_n$ and $\{CTA^+|PtCl_4^{2-}\}_n$ films (the right) before and after UV radiation or sonication.

CONCLUSION

Layer-by-layer assembled films $\{CPY^+|AuCl_4^-\}_n$, $\{CTA^+|AuCl_4^-\}_n$, $\{CTA^+|PtCl_6^{2-}\}_n$ and $\{CTA^+|PtCl_4^{2-}\}_n$ can be converted to a monolayer of metal nanoclusters photochemically or sonochemically.

Acknowledgement

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References

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