Au/Titania Composite Nanoparticle Arrays with Controlled Size and Spacing by Organic-Inorganic Nanohybridization in Thin Film Block Copolymer Templates

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A simple approach to prepare arrays of Au/TiO₂ composite nanoparticles by using Au-loaded block copolymers as templates combined with a sol-gel process is described. The organic-inorganic hybrid films with closely packed inorganic nanodomains in organic matrix are produced by spin coating the mixtures of polystyrene-block-poly(ethylene oxide) (PS-b-PEO)/HAuCl₄ solution and sol-gel precursor solution. After removal of the organic matrix with deep UV irradiation, arrays of Au/TiO₂ composite nanoparticles with different compositions or particle sizes can be easily produced. Different photoluminescence (PL) emission spectra from an organic-inorganic hybrid film and arrays of Au/TiO₂ composite nanoparticles indicate that TiO₂ and Au components exist as separate state in the initial hybrid film and form composite nanoparticles after the removal of the block copolymer matrix.

Key Words : Au/TiO₂ nanoparticle, Block copolymer, Sol-gel, Organic-inorganic hybrid, Photoluminescence

Introduction

Metal/semiconductor oxide composite nanoparticles are extremely attractive because they exhibit novel optical, electrical, magnetic, and chemical properties that are not found in the individual components.1-3 The possible applications include nanoelectronics device, catalysis, nonlinear optical devices, etc.5-7 Titanium dioxide (TiO₂) is one of the most widely studied semiconductor materials due to the wealth of useful applications.1,2,6,8 Recently, TiO₂-based systems containing transition metal ions and noble metals have been investigated extensively to improve the efficiency of the photocatalytic and photoelectrochemical responses.1,2

Several routes to the fabrication of thin films containing nanocrystals of semiconductors and metals have been suggested including physical techniques,9,10 chemical methods,11,12 or a two-step method consisting of Au(III)-complex chemisorption and subsequent photoreduction.13 Microstructured Au/TiO₂ model catalysts are also produced by combining optical lithography methods for microstructuring with ultrahigh vacuum deposition for Au nanoparticle deposition.14,15

In many applications, the ability to use nanoparticle properties for device fabrication will require the formation of highly ordered arrays of nanoparticles.12 Several approaches have been reported to generate arrays of composite nanoparticles.13 However, it is challenging to control the final morphology and composition of the produced nanostructures. There is still a strong demand for simple, facile routes to fabricate arrays of the metal/semiconductor composite nanostructures with different size, spacing or composition.

The self-assembly of diblock copolymers has been recognized as an attractive platform toward highly ordered, periodic nanoscale structures.14-17 An increasing number of novel functional nanostructures have been reported from this unique class of polymers,18-22 for instance, magnetic storage media,24 resist in microelectronics,25 photonic band gap materials,26 planar optical waveguides,27 etc. In particular, it has also been shown that hexagonally ordered 2-dimensional (2D) arrays of metallic, inorganic, semiconductor, and metal/ semiconductor nanoparticle arrays could be generated using block copolymer templates.28-31

Recently, thin films of amphiphilic poly(styrene-block-ethylene oxide) copolymer (PS-b-PEO) with cylindrical PEO microdomains aligned perpendicular to the substrate surface have attracted increasing attention as scaffolds to produce arrays of inorganic nanostructures.32-35 Combining sol-gel (SG) process, organic-inorganic hybrid nanostructures can be fabricated with TiO₂ selectively incorporated into the PEO microdomains.31 In this work, we extend this methodology to produce arrays of composite Au/TiO₂ composite nanoparticles using Au precursor-loaded block copolymer micelles as templates. Although sol-gel chemistry using block copolymers as structure-directing agent has been extensively exploited to generate highly ordered mesoporous materials,36 no experimental reports have yet been made concerning arrays of metal/semiconductor composite nanoparticles. The present approach involves the fabrication of organic-inorganic hybrid nano composite films with TiO₂ and Au precursors incorporated into PEO microdomains. Specifically, we show that the lateral scale of the arrays of composite nanoparticles, i.e., the size of each nanoparticle and spacing, as well as the composition can be finely tuned on the nanometer scale by controlling the relative amount of sol-gel precursor to block copolymer and the loading ratio of HAuCl₄ to EO units in
Hybrid inorganic-organic films were produced simply by spin coating the common solution on a piece of Si substrate in toluene. The obtained films were dried under ambient condition to induce crosslinking of the sol-gel precursor. The film thickness was about 48 nm as measured by a surface profiler (Tencor-10).

In order to remove the block copolymer template and reduce HAuCl₄ into metallic Au, the films were treated with deep UV irradiation in air (λ = 254 nm, 30W) for 2 days.\textsuperscript{33}

**Characterization.** AFM height and phase contrast images were obtained using a Digital Instruments Dimension 3100 scanning force microscope in the tapping mode with Olympus cantilever with spring constants ranging between 33.2 and 65.7 N/m and a resonant frequency of 277.3-346.3 Hz (as specified by the manufacturer). Field emission scanning electron microscopy (FESEM) images were obtained with a LEO 1530 “Gemini”. The average diameters of the inorganic domains containing titania and gold were determined Image J program (NIH). The center-to-center distance between domains were calculated from AFM images using Nanoscope software (Nanoscope III 5.12r1). XPS measurements were performed on a Perkin-Elmer-Physical Electronics 5100 with Mg Kα excitation (400 W). Spectra were obtained at a take-off angle of 15°. Photoluminescence (PL) spectra were measured using a SPEX FLUOROLOG II (212) instrument at an excitation wavelength of 350 nm and 260 nm. The hybrid films were treated at 90°C for 1 h in vacuum or with UV light for 2 days in air before PL measurement.

**Results and Discussion**

The AFM height images of the hybrid films spin-coated from the initial PS-b-PEO/AuCl₄/SG mixed solutions with different amount of SG precursor are shown in Figure 2. The
and the center-to-center distance ($d_{4}$) study. With the addition of Au precursor HAuCl$_4$ micelles in a non-polar solvent (such as toluene used in this study), isopropanol and small amounts of water are easily absorbed into the micellar cores due to the existence of HAuCl$_4$ in the PEO domains. Since this effect would cause the aggregation number of the block copolymer micelles to increase, it is reasonable to deduce that the micelle size increases with increasing $\phi$. On the other hand, the Au precursors uniformly distribute inside PEO domains to form composites with the SG precursors that help to prevent the SG precursors from self-aggregation. This effect may preclude the macro-phase separation of SG precursors from the BCP domains. Therefore, the domain size of the TiO$_2$ nanoparticles increases with increasing $\phi$ after SG incorporates into the PEO domains selectively due to strong interaction between the SG precursor and the PEO domains containing HAuCl$_4$ precursor. With the assumption that the SG precursor is uniformly distributed in the micelles domains, the center-to-center distance ($d_{cc}$) will also increase due to the increase of the micelle size with increasing $\phi$. When the SG content is less than $\phi$$\sim$20%, the PEO domains could include all the SG precursor molecules, while macro-phase separation occurred with a further increase of $\phi$ to 30%.

The chemical identity of the surface of a spin-coated PS-b-PEO/HAuCl$_4$/SG10 film was investigated by XPS analysis. The survey spectrum clearly reveals that Ti, O, C, and Au elements exist in the hybrid film, as shown in Figure 4a. Figure 4b is the high resolution Ti$_2$p spectrum and the characteristic peaks of Ti$_{2p3/2}$ and Ti$_{2p1/2}$ in TiO$_2$ were observed at 459.4 eV and 465.2 eV, respectively. The peaks at 457.6 eV and 455.3 eV due to other titania species such as Ti$_{2p3/2}$ in Ti$_2$O$_3$ or TiO were not observed. Therefore, it is concluded from the XPS results that the titania nanoparticles in the hybrid film are mainly composed of TiO$_2$.

In order to generate arrays of pure Au$_x$TiO$_2$ composite nanoparticles on the silicon substrate from the initial hybrid organic-inorganic films, the block copolymer templates were removed by deep UV irradiation. HAuCl$_4$ is reduced simul-

Figure 3. FESEM images of the spin-coated PS-b-PEO/HAuCl$_4$/SG films with different amount of sol-gel precursors: (a) 7.0%, (b) 10.0%, (c) 15.0%, (d) 20.0%. The film thickness is about 12 nm. (e) The average diameter of the inorganic domains, $D$, and the center-to-center distance between them, $d_{cc}$, as a function of the amount of sol-gel precursors. The scale bar at lower left of each SEM image represents 100 nm.
taneously into metallic Au during this irradiation process. \[^{33,37}\]
It should be noted that arrays of composite nanoparticles could be obtained only from hybrid micellar films of PS-\(b\)-PEO/HAuCl\(_4\)/SG of the order of one monolayer thickness because the inorganic domains in thicker films (e.g. 48 nm), which do not form cylinders perpendicular to the substrate surface, collapse to form irregular arrays after matrix removal. Figure 5 shows the SEM image of arrays of Au/TiO\(_2\) composite nanoparticles obtained from the hybrid films of about 12 nm thickness obtained by UV exposure in air for 2 days. The average particle size is measured to be 15.7 ± 3.5 nm, 18.1 ± 2.8 nm, 20.9 ± 2.8 nm, and 20.2 ± 4.5 nm for samples with \(\phi\) values of 7.0, 10.0, 15.0, and 20%, respectively. XPS measurement was also performed to determine the chemical composition of the resulting composite nanoparticles. The spectrum of Ti\(_{2p}\) from the film after removal of the block copolymer is similar to that from the hybrid film (Figure 3b). Characteristic peaks of Au\(^0\) were observed at binding energies of 87.5 eV (Au4f\(_{5/2}\)) and 84.0 eV (Au4f\(_{7/2}\)). \[^{36}\]
Therefore, it is concluded that these nanoparticles contain metallic Au. More in-depth analysis of the individual nanoparticle is in progress by high-resolution transmission electron microscopy.

We explore the photoluminescence (PL) properties of the hybrid PS-\(b\)-PEO/HAuCl\(_4\)/SG films and arrays of Au/TiO\(_2\) composite nanoparticles with an excitation wavelength of 350 nm and 260 nm, respectively. Figure 6 shows the representative PL spectra from a spin-coated film and arrays of Au/TiO\(_2\) nanoparticles with \(\phi\) value of 10.0%. It can be seen from Figure 6a and b, that the initial hybrid samples exhibit the broadband PL with main peak located at about 420 nm under photocexcitation at 350 nm, which can be attributed to

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Figure 4. XPS survey (a) and high-resolution XPS Ti\(_{2p}\) spectra (b) of the surface of a spin-coated PS-\(b\)-PEO/HAuCl\(_4\)/SG10 film.

Figure 5. FESEM images of arrays of Au/TiO\(_2\) nanoparticles obtained from the hybrid PS-\(b\)-PEO/HAuCl\(_4\)/SG films after removal of the block copolymer matrix by exposing the samples to UV light for 2 days in air: (a) 7.0%, (b) 10.0%, (c) 15.0%, (d) 20.0%. (e) The average diameter of Au/TiO\(_2\) nanoparticles, \(D\), and the center-to-center distance between them, \(d_{CC}\), as a function of the amount of sol-gel precursors. The scale bar at lower left of each SEM image represents 100 nm.
process. Sol-gel precursors could be selectively incorporated into the PEO/HAuCl₄ domains in the Au-loaded PS-b-PEO solution. After spin coating, organic/inorganic hybrid films with dense arrays of inorganic domains containing TiO₂ and Au embedded in an organic matrix were generated. The size of each nanoparticle and the characteristic spacing of the arrays could be controlled by varying the relative amounts of the SG precursors versus block copolymers. By removing the organic template with deep UV irradiation, arrays of pure Au/TiO₂ composite nanoparticles could be obtained with controlled lateral scale on a substrate surface. The initial organic/inorganic hybrid film and the Au/TiO₂ composite nanoparticles array exhibit different fluorescence emissions spectra, indicating that the TiO₂ and Au keep their respective domains in the as-cast, initial films. This work demonstrates a simple, low-cost method with potential applications in photocatalysis, as energy conversion sensors, or as a model system to study the mechanism of photochemistry in nanopatterned media.

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Conclusions

We presented a simple route to produce arrays of Au/TiO₂ composite nanoparticles using Au-loaded micelles of PS-b-PEO block copolymers as templates combining with sol-gel synthesis. The PL spectra of TiO₂ nanoparticles exhibited only a broadband with a main peak localized within TiO₂ octahedra and oxygen vacancies. Therefore, PL peak of Au nanoparticles can be shift to plasmon resonance, and charge separation occurs by the transfer of photoexcited electrons from the Au particle to the TiO₂ conduction band. In comparison with TiO₂ nanoparticles, no noticeable difference was found from Au/TiO₂ composite nanoparticles, which is consistent with the previous results. 20-21

Figure 6. (a) and (b): PL spectra of the hybrid PS-b-PEO/HAuCl₄/SG10 film. (c) and (d): PL spectrum from arrays of Au/TiO₂ composite nanoparticles obtained after removal of the PS-b-PEO template by deep UV irradiation. The excitation wavelength used in (a)-(c) is 260 nm and 350 nm in (b) and (d), respectively.

References
