

A Rapid Prototyping Approach to Ag Nanoparticle Fabrication in the 10–100 nm Range**

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The fabrication of metal nanoparticles has drawn considerable attention because of both fundamental interest and the potential for applications.^[1–5] Depending on the exact particle size to be synthesized, elaborate and often time-consuming processes can be required to achieve highly uniform particles. Herein, we demonstrate a simple, inexpensive, and rapid method for making metal nanoparticles ranging between 10 and 100 nm in size. The process can be completed in approximately 11 min without the use of a clean-room environment or vacuum techniques. The method works by using a thin supported TiO₂ film as a photocatalyst and an alumina membrane as a template. The nanoparticle array formed in this manner is nearly monodisperse and the particle surface density and geometry are uniform over large areas. The templates are reusable and the technique may be amenable for biosensing as well as catalytic applications.

Metal nanoparticles possess unique physical, magnetic, optical, electrical, and catalytic properties.^[1–5] Gaining control over their size and geometry during the fabrication process is of central interest. This has led to remarkable achievements in the preparation of nearly monodisperse particles up to approximately 10 nm in diameter by employing synthetic methods.^[6–10] Moreover, photolithographic methods now make it possible to precisely control geometries down to the 100 nm scale.^[11–14] There are, however, fewer methods for easily fabricating highly uniform metal nanoparticle arrays on an intermediate length scale.

Previous fabrication efforts on the 10 to 100 nm scale have included reduction synthesis and nanolithography.^[15–18] Also, template approaches have been used to synthesize nanotubes,^[19–28] nanorods,^[29,30] nanoelectrodes,^[31] and nanoparticles.^[32,33] Some of these techniques depend on wet electrochemical methods to deposit metal onto a uniform nanoporous template,^[20–29] while others apply thermal or electron-beam evaporation followed by etching procedures.^[32,33] Anodic aluminum oxide (AAO) templating has been widely exploited in these applications because of its uniformity, rigidity, and size-controllable properties.

It should be noted that the approaches described above require a vacuum chamber for evaporating metal, a clean-room environment, sophisticated preparation, relatively specialized equipment, and/or etching steps. It was therefore deemed desirable to design a bench-top technique that could be performed rapidly with minimal equipment and without specialized facilities, while still achieving large arrays of highly uniform particles. Herein, a simple templating method is described for photoreducing metal from aqueous solutions onto TiO₂ thin films through a nanoporous filtration membrane.

TiO₂ has well-studied photocatalytic properties, which makes it an excellent choice for reducing metal ions from solution by UV illumination.^[34,35] Most often it has been used in the form of nanoparticles for reducing metal ions in solution.^[36–39] More recently the process has been demonstrated with a thin TiO₂ film on a silica substrate.^[40] In both cases the metal particles that are synthesized are typically 50 to 200 nm, where the average size can be tuned to some extent by the solution conditions. Although the particles are not monodispersed, it should be emphasized that the process can be performed under mild conditions (i.e., at room temperature in aqueous solution and neutral pH).

Our strategy for forming uniform size arrays of metal nanoparticles is outlined in Figure 1. In the first step, a TiO₂ precursor was deposited onto the surface of a Pyrex slide in a dropwise fashion from an alcohol solution. The precursor solution consisted of 1 g of titanium(IV) isopropoxide, 0.15 g of HCl, and 8.0 g of isopropyl alcohol. Approximately 150 μ L of this mixture quickly and completely wetted the surface of a 2.5 cm \times 2.5 cm planar Pyrex substrate. Next, a circular nanoporous alumina filtration membrane with 18 nm diameter pores was placed on top of the wet glass slide and the system was allowed to dry under ambient conditions for 6 min. As the isopropyl alcohol evaporated, the TiO₂ film formed spontaneously on the Pyrex and its presence was directly verified using X-ray photoelectron spectroscopy (XPS). Profilometry measurements showed that the film was approximately 200 nm thick. Atomic force microscopy (AFM) measurements revealed that the coating was very flat with a root-mean-square roughness of 0.72 nm over a 1 μ m \times 1 μ m area (Fig. 2a). This surface roughness was identical to a control experiment where the precursor solution was allowed to evaporate from the substrate in the absence of the alumina membrane. Indeed, no evidence of TiO₂ pillar formation caused by the nanoporous template could be detected. Moreover, only trace amounts of TiO₂ could be found on the alumina surface using XPS. It should be noted that the alumina template was

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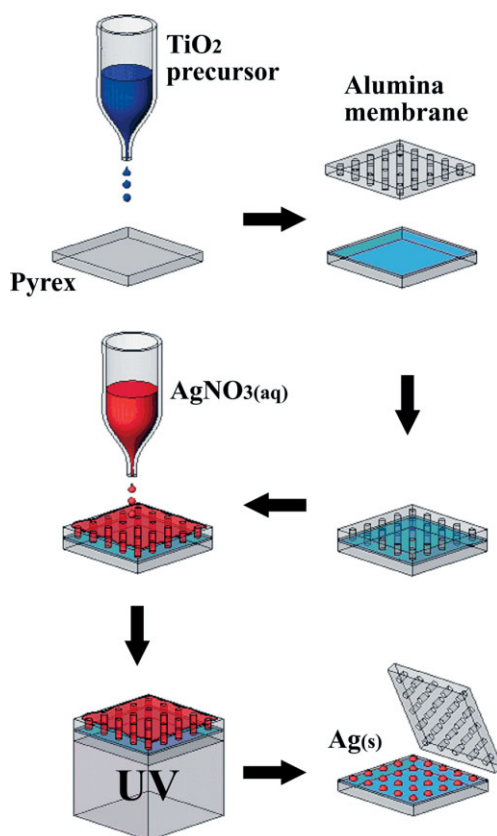


Figure 1. Schematic diagram of the process for fabricating silver nanoparticle arrays.

gently peeled off the substrate using a pair of tweezers before AFM and XPS data were obtained.

When forming a silver nanoparticle array, the alumina membrane was left in place on the Pyrex substrate and a 0.1 M AgNO_3 aqueous solution was introduced dropwise above it ($\sim 150 \mu\text{L}$) after waiting 6 min for the precursor solution to dry. This essentially immersed the hydrophilic alumina membrane in bulk aqueous solution. UV radiation was then illuminated onto the alumina/glass interface through the Pyrex substrate to reduce metal from solution for 5 min. Finally, the alumina template was gently peeled away from the glass surface and washed with ethanol and deionized water. XPS measurements confirmed the deposition of Ag onto the Pyrex support.

AFM was performed over a $2 \mu\text{m} \times 2 \mu\text{m}$ area in order to access the size, shape, and density of the Ag nanoparticles. The results indicated that the metal nanoparticles were approximately 19 nm in diameter (Fig. 2b). This compares favorably with the known template size of the alumina filtration membrane specified by the manufacturer (18 ± 3 nm). Next, several control experiments were performed. For example, the above conditions were repeated exactly, but the surface was left in the dark for 5 min instead of being illuminated with UV light. This demonstrated that no nanoparticles were formed on the substrate (Fig. 2f). Also, a control experiment

was performed with UV illumination, but without AgNO_3 in the aqueous solution. Again, no evidence for nanoparticle formation was found. A final control without a TiO_2 thin film, but with a AgNO_3 solution and UV illumination also showed no evidence for metal deposition (AFM data looked identical to Fig. 2f).

The photoreduction of Ag nanoparticles was repeated with alumina filtration membranes that contained 35, 55, and 75 nm diameter nanopores. The corresponding AFM images are provided in Figure 2c–e. Again, the sizes of the nanoparticles were determined using AFM. The results closely corresponded to the known pore diameters in the alumina template (Table 1).

Table 1. Template pore sizes and resultant mean nanoparticle diameters.

Template pore size (nm)	Mean nanoparticle diameter (nm)
18 ± 3	19
35 ± 3	34
55 ± 6	55
73 ± 7	72

To determine information about the particle size distribution, the AFM data were employed to assemble histograms from the arrays of nominally 18, 35, 55, and 73 nm Ag nanoparticles. The number of particles analyzed was 590, 309, 216, and 117, respectively. The bin sizes were 2 nm and the results, normalized to 100 total counts, are shown in Figure 3. As can be seen from the data, the particle distributions were quite narrow. In each case the vast majority of particles fit into just two bins. Indeed, between 73 and 83 % of the nanoparticles were within this range for the three smallest pore sizes, and 61 % of particles fit within it for the largest filter. In all cases the distributions were slightly skewed toward the low end. This should be expected because the templates provide an upper bound to particle size, while it should be possible to grow nanoparticles on the TiO_2 surface that do not completely fill the pore. This effect is most pronounced for the largest pore size where the average particle size would be only modestly larger than 73 nm even in the absence of a template under otherwise similar conditions. It should be emphasized, however, that these results represent some of the narrowest particle distributions achieved to date using any technique.

It was found that the particle arrays were highly uniform over large regions of the Pyrex sample. Data were gathered from multiple $25 \mu\text{m} \times 25 \mu\text{m}$ scan regions on different samples and over areas that were several millimeters apart on single samples. Representative area images are shown as insets in each histogram in Figure 3. Of equal significance, we found that the membrane templates could be used repeatedly. To do this, each alumina template was washed with water and ethanol after being peeled away from the surface. The template was then used with a new precursor solution and Pyrex substrate. The results revealed no perceptible loss in fidelity of the array even after several uses. The alumina membranes

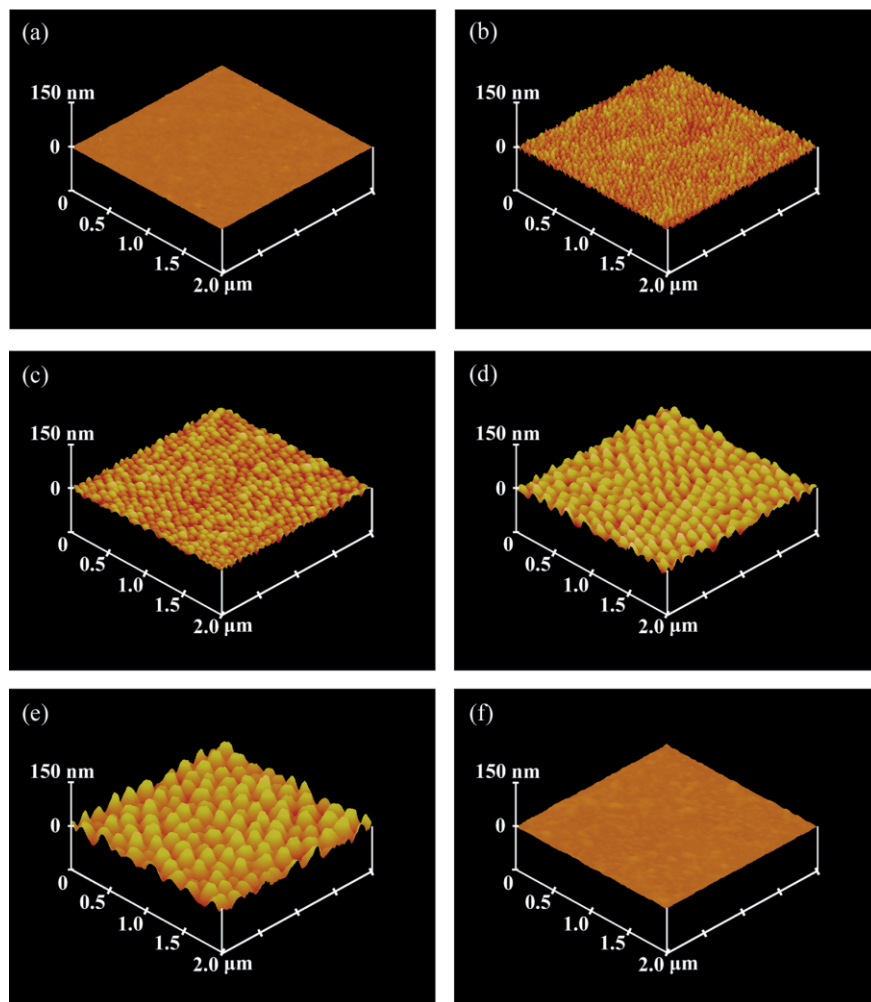


Figure 2. AFM microscopy images of Ag nanoparticle arrays fabricated by using different pore size templates: a) bare TiO₂/Pyrex surface, b) 18 nm template, c) 35 nm template, d) 55 nm template, e) 73 nm template, and f) a control experiment without UV illumination of the sample.

were checked for the presence of Ag by using XPS and the peak corresponding to Ag was extremely weak (barely above the noise level), when it could be found at all.

In summary, we have demonstrated a reliable and simple method for the rapid prototyping of metal nanoparticles onto thin TiO₂ films on Pyrex substrates by using UV illumination. All experiments could be performed at a laboratory bench top with commercially available and relatively inexpensive materials. Moreover, the entire process could be performed from start to finish in about 11 min. The uniform size and shape control of the nanoparticles over large areas suggest that this approach could be employed for biosensor development as well as in catalytic applications. Finally, it should be straightforward to apply this method for producing arrays of other metal nanoparticles such as Au, Pd, and Cu.

Experimental

Porous alumina filtration membrane templates were purchased from Synkera Technologies (Longmont, CO). The templates were 1.3 cm in diameter and 50 μm thick. Four different pore diameters were employed: 18, 35, 55, and 73 nm. The template with the smallest pores contained approximately 5×10^{10} pores cm⁻². The others had 1×10^{10} , 5×10^9 , and 4×10^9 pores/cm², respectively. We independently verified the manufacturer's pore size and density by using scanning electron microscopy. Ethanol was obtained from AAPER Alcohol and Chemical (Shelbyville, KY), while AgNO₃ was purchased from Sigma-Aldrich (Milwaukee, WI). Polished Pyrex 7740 wafers (25.4 mm², 0.5 mm thick) were supplied by Precision Glass and Optics (Santa Ana, CA). Purified water (≥ 18.2 MΩ cm) was prepared with a NANOpure Ultrapure Water System (Barnstead, Dubuque, IA).

As stated above, the precursor solution consisted of 1 g of titanium(IV) isopropoxide (Sigma-Aldrich, Milwaukee, WI), 0.15 g of HCl (EM Industries, Gibbstown, NJ), and 8.0 g of isopropyl alcohol (Acros, Geel, Belgium). The solution was prepared by first adding titanium(IV) isopropoxide followed by the acid. All solutions were used within two weeks. A TiO₂ film was made by depositing approximately 150 μL of the TiO₂ precursor solution onto the Pyrex sample as described above. The reduction of silver from a 0.1 M aqueous silver nitrate solution was performed with a standard 100 W Hg Arc lamp as the UV source. The light was illuminated onto the TiO₂ interface through the Pyrex side of the sample (Fig. 1). The Pyrex sample is transparent in the near UV (~ 365 nm), which is the critical wavelength region from reducing silver ions from solution.

AFM measurements of nascently formed Ag nanoparticle arrays were performed by using a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA). All measurements were made by tapping mode in air with a type E scanner employing etched silicon tips, NSC15/No Al (Mikro Masch, Wilsonville, OR). TiO₂ film thickness was measured with a Dektak 3 Stylus profilometer (Veeco Tucson Inc., Tucson, AZ). XPS was performed on a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer (Kratos Analytical Inc., Chestnut Ridge, NY).

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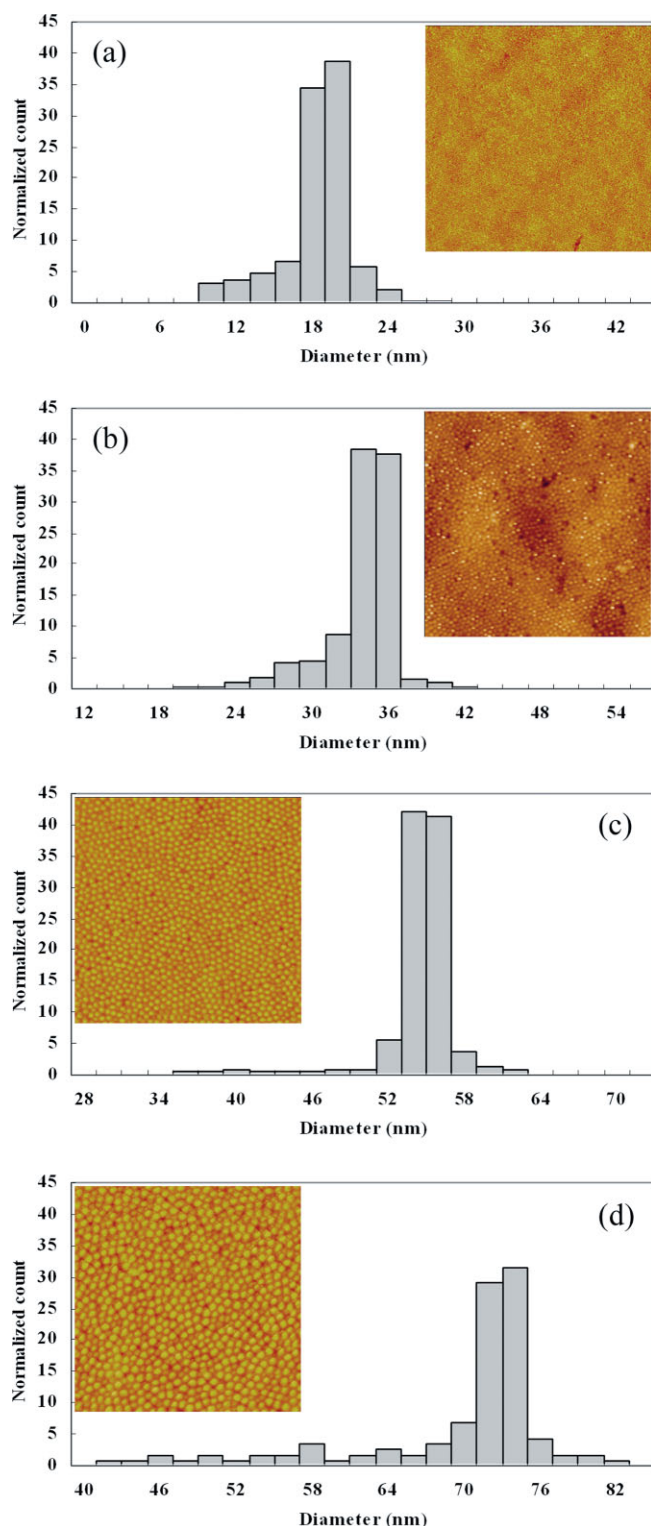


Figure 3. Histograms of Ag nanoparticle diameters formed with a) 18 nm, b) 35 nm, c) 55 nm, and d) 73 nm alumina templates. The insets show representative 5 $\mu\text{m} \times 5 \mu\text{m}$ AFM images.

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