NANO LETTERS

2001
Vol. 1, No. 11
647−649

Fabrication of Two-Dimensional Assemblies of Ag Nanoparticles and Nanocavities in Poly(dimethylsiloxane) Resin

Serhiy Malynych, Holly Robuck, and George Chumanov*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634

Received August 15, 2001; *Revised Manuscript Received September 10, 2001*

ABSTRACT

Silver nanoparticles, self-assembled in two-dimensional arrays on quartz and silicon surfaces, were coated with poly(dimethylsiloxane) (PDMS). After peeling off the surface, resin films contained embedded nanoparticles in their original arrangement. Films with nanoparticles are transparent, flexible, and mechanically stable. The embedded nanoparticles were etched away, producing nanocavities in PDMS. The described method can be used to produce highly robust assemblies of metal, semiconductor, and dielectric nanoparticles on flexible substrates.

Growing interest in nanostructures and nanometer-scale patterning is driven not only by novel yet unexplored properties associated with nanoscale materials but also by continuously increasing demand for further miniaturization of electronic components, optical detectors, chemical and biochemical sensors and devices, etc. Many of these devices will require immobilization of nanoparticles in different assemblies on various substrates. To be functionally sound the nanoparticles should be stabilized on the surface and protected from chemical and mechanical effects.

A lot of ongoing studies relate to the properties and potential applications of two-dimensional nanostructures; however, little attention is paid to the development of efficient methods for their stabilization on surfaces. Two-dimensional self-assemblies of metal nanoparticles that exhibit a number of remarkable optical[1,2] and electronic[3,4] properties due to the excitation plasmon resonances are prone to surface aggregation that drastically alters their properties. Potential stabilization methods include the encapsulation of nanoparticles into protecting glass[5,6] or polymer shells,[7] and polymer matrix.[8−11] Even though these approaches helped to reduce aggregation and, in some cases, to protect from chemical environments, complete stabilization was not accomplished.

In this letter we present a simple, highly efficient method for complete stabilization of two-dimensional nanostructures by embedding them into an elastomer film. As a result, a new type of flexible nanocomposite film was produced. Unique properties of elastomers such as flexibility, large tunability range of the Young's modulus, ability to be easily molded (so-called "soft lithography"),[12,13] and conformability to complex shapes will be indispensable in many applications of nanomaterials.

The method consists of two steps. In the first step silver nanoparticles were self-assembled in two-dimensional arrays on poly(vinylpyridine) (PVP) modified silicon wafers.[11] The wafers were first cleaned in 1:3 mixture of 30% H_2O_2 and H_2SO_4 (piranha solution) for 30 min and rinsed with ultrapure water (Milli-Q, Millipore) under continuous sonication. *Caution! Piranha solution is a very strong oxidizing agent and reacts violently with organic compounds. It should be handled with extreme care.* After drying in the stream of the nitrogen gas, the wafers were exposed to 1% of PVP ($M_W = 160\,000$, Aldrich) solution in reagent alcohol. Pyridyl groups on PVP molecules are capable of simultaneously forming hydrogen bonding with silanol groups on the oxidized silicon surface and binding metal (silver) nanoparticles via the lone electron pair on the nitrogen atom. After the exposure to the PVP solution for several hours, wafers were thoroughly rinsed with alcohol to remove polymer molecules that are not directly attached to the surface. A thin (∼2 nm) monolayer of PVP adsorbed on the surface was further annealed at 120 °C for 2 h to produce more uniform polymer film. Finally, modified wafers were exposed overnight to an aqueous suspension of silver nanoparticles (ca. 100 nm in diameter), resulting in the formation of nanoparticle layer. At saturation limit, nanoparticles assembly into two-dimensional, semiregular arrays with interparticle distance comparable to their diameter. The electrostatic repulsion between double layers surrounding nanoparticles

* To whom correspondence should be addressed. Phone: (864) 656-2339. Fax: (864) 656-6613. E-mail: gchumak@clemson.edu.

10.1021/nl015604v CCC: $20.00
Published on Web 09/27/2001

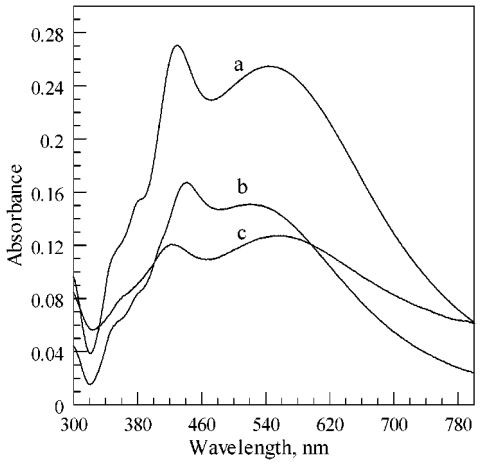

Figure 1. UV−vis absorption spectra of a suspension of silver nanoparticles in water (a), silver nanoparticles self-assembled on PVP modified quartz surface from this suspension (b), and the self-assembled nanoparticles embedded into PDMS resin (c).

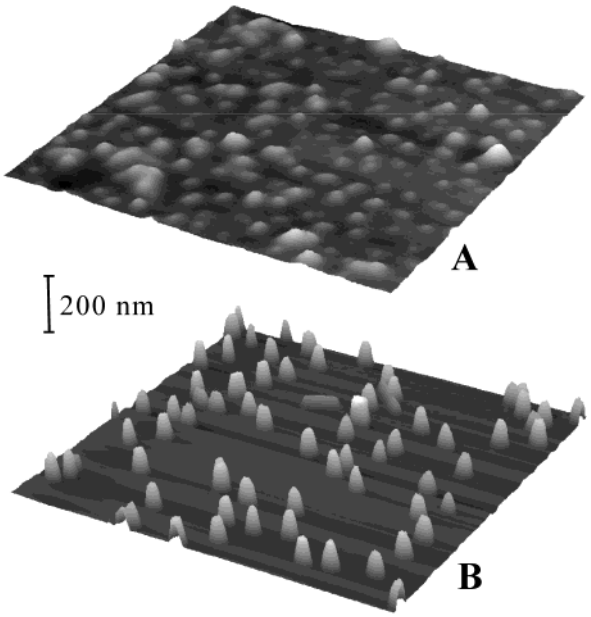

Figure 2. AFM images of INA film (A) and silver nanoparticles immobilized on PVP modified silicon wafer (B). The vertical scale is the same for both images, and the scan range is 5 × 5 μm. Note that silver nanoparticles, otherwise nearly spherical, appear in (B) as elongated objects because the vertical scale was artificially expended in order to emphasize the small height variations in (A).

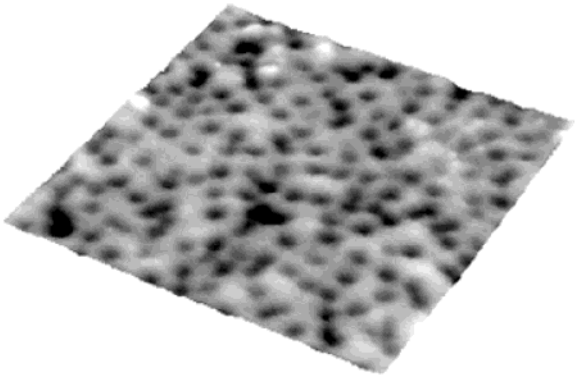

Figure 3. AFM image of nanocavities obtained after etching of INA film. Scan range is 3 × 3 μm.

is the driving force for such assembly. The reduction of exposure time and/or the concentration of particles in the suspension decreased the density of nanoparticles on the surface. These assemblies were very stable in pure water and in alcohol; however, drying of the substrates induced aggregation of nanoparticles presumably due to the dragging force of evaporating solvent and disappearance of the double layer.

The second step involved coating the surface with poly(dimethylsiloxane) (Sylgard 184, Dow Corning Corp.) for the stabilization of nanoparticle assemblies. To avoid drying, substrates were submersed into alcohol and the resin mixed with the curing agent (10:1) was directly pored on the surface of the substrate. Because the resin is heavier than alcohol, it sunk and spread on the bottom covering the immobilized nanoparticles. The resin replaced the alcohol layer from the surface and, in this way, drying of the substrate was completely avoided preserving the assemblies of nanoparticles in their initial state. Excess alcohol can be removed; however, alcohol does not interfere with the polymerization process. The polymerization was allowed to continue for 10 h at ambient temperature and finally for 30 min at 120 °C. After polymerization, the PDMS films containing embedded nanoparticles were peeled off the substrate. UV−vis absorbance measurements of nanoparticle assemblies on a quartz substrate prior to PDMS deposition and the same assembly embedded into the resin revealed only minor changes in the spectra due to different dielectric environment, thereby confirming that the initial arrangement of nanoparticles was completely preserved (Figure 1).

Such "frozen" nanoparticles comprise a very stable and robust immobilized nanoparticle assembly (INA). INA films can be easily handled, stretched, and, after overcoating with another PDMS layer, exposed to different chemical environments. Also, the resin substrates exhibit excellent transparency down to 300 nm, which is an essential property for many photonic and spectroanalytical applications.

To determine whether the PVP layer used for the immobilization of nanoparticles remained on the substrate or was transferred to the resin film, UV absorbance spectra were measured of PVP modified quartz substrates before and after assembly of silver nanoparticle and PDMS deposition. The presence of the characteristic band around 260 nm in the spectrum of quartz substrate after the resin was pilled off indicated that the PVP did not adhere to PDMS, although it is not clear whether some PVP molecules remained adsorbed to embedded silver nanoparticles.

INA films were studied with an atomic force microscope (AFM) (AutoProbe CP, ThermoMicroscope) using both tapping and noncontact modes and ultrasharp tips with ca. 3 N/m force constant. An AFM image of a typical densely packed INA film is shown in Figure 2A.

Silver nanoparticles adsorbed on PVP modified silicon wafer (without PDMS resin) are presented in Figure 2B. Note that the same nanoparticle suspension was used in the preparation of both films. As can be clearly seen from the

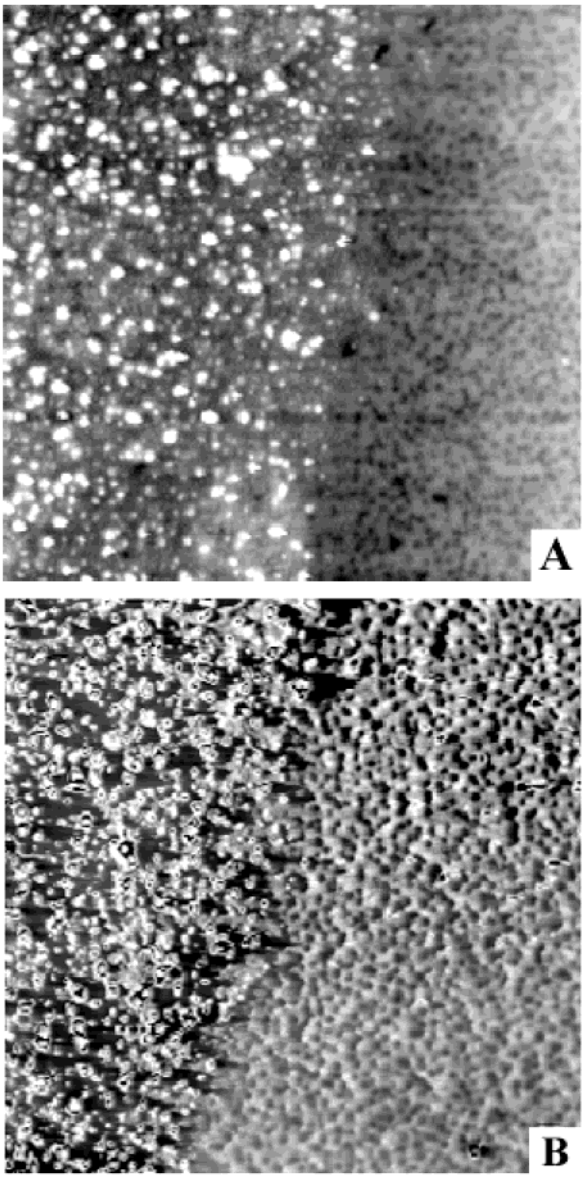

Figure 4. Topography (A) and phase (B) AFM images of boundary region between original and etched INA films. Scan range 10 × 10 μm.

comparison of both images, only a small part of each silver nanoparticle protrudes the surface of elastomer in the INA film, indicating that particles are embedded into the resin and do not simply adhere to the surface of PDMS. Protruded heights were always measured to be below 30 nm, which was smaller than the average radius of silver nanoparticles (55 nm). This result implies that nanoparticles were physically entrapped by PDMS resin that covers more than half of their diameter. Because silver nanoparticles themselves are fairly monodispersed, the distribution of protruded heights in Figure 2A is due to the fact that different nanoparticles are buried into the resin to different extents.

Since silver nanoparticles in INA films were not completely covered with the resin, they were etched with nitric acid, resulting in an assembly of nanosize cavities in the PDMS film. It is reasonable to assume that the size, shape, and distribution of nanosize cavities in PDMS were the same as those for nanoparticles in the corresponding INA film. These nanocavities can be used as templates for synthesis of nanoparticles from other materials. AFM images of nanocavities and the boundary between etched and original INA films are presented in Figure 3 and Figure 4, respectively. We were not able to determine the actual depth of the cavities because AFM tips could not penetrate down to the bottom.

In conclusion, two-dimensional assemblies of various nanoparticles can be simply and efficiently stabilized by embedding in PDMS matrix. Prepared in this way, INA films exhibit excellent mechanical and optical properties and present a new valuable system for many applications. In addition, PDMS films with embedded metal nanoparticles can be easily converted into films with spherical nanocavities, which are unattainable by using nanoimprint lithography.[14] Properties of these films are yet to be explored and exploited.

Acknowledgment. The research was supported by the National Institutes of Health (GM35108). The authors thank Ames Laboratory (U.S. Department of Energy) for the equipment used for this work.

References

(1) Chumanov, G.; Sokolov, K.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 5166.
(2) Gotschy, W.; Vonmetz, K.; Leitner, A.; Aussenegg, F. R. *Appl. Phys.* **1996**, *B 63*, 381.
(3) Ito, K.; Ohyama, S.; Uehara, Y.; Ushioda, S. *Surf. Sci.* **1995**, *324*, 282.
(4) Downes, A.; Welland, M. E. *Appl. Phys. Lett.* **1998**, *72*, 2671.
(5) Liz-Marzan, L. M.; Giersig, M.; Mulveney, P. *Langmuir* **1996**, *12*, 4329.
(6) Attempts to stabilize glass coated silver nanoparticles on poly(vinylpyridine) modified glass surface were unsuccessful in that the aggregation always appeared after drying the substrates.
(7) Quaroni, L.; Chumanov, G. *J. Am. Chem. Soc.* **1999** *121*, 10642.
(8) Fritzsche, W.; Porwol, H.; Wiegand, A.; Bornmann, S.; Köhler, J. *Nanostruct. Mater*. **1998**, *10*, 89.
(9) Spatz, J. P.; Eibeck P.; Mössmer, S.; Möller, M.; Herzog, T.; Ziermann, P. *Adv. Mater.* **1998**, *10*, 849.
(10) Kunz, M. S.; Shull, K. R.; Kellock, A. J. *J. Colloid. Interface Sci.* **1993**, *156*, 240.
(11) Malynych, S.; Luzinov, I.; Chumanov, G. *J. Phys. Chem. B* **2001**, submitted.
(12) Quake, S. R.; Scherer, A. *Science* **2000**, *290*, 1536.
(13) Xia, Y.; Whitesides, G. M. *Angew. Chem. Int., Ed. Engl.* **1998**, *37*, 550.
(14) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *J. Vac. Sci. Technol. B* **1996**, *14*, 4129.

NL015604V