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X-RAY LITHOGRAPHY OF METAL AND SEMICONDUCTOR NANOPARTICLES

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Introduction

In the last few years, a considerable amount of research has focused on the three-dimensional fabrication of contacts and electronic devices.¹ Most techniques, however, are essentially based on photoreduction, and are limited to noble- and semi-noble metals. We present here a general method that allows patterning of porous matrices in 3D with metal, but also with semiconductor nanoparticles which is of potential relevance for microfabrication applications. In our method, the pore-filling solvent of a sol-gel material is exchanged with a solution of precursors. The precursors are photodissociated and nanoparticles are formed when the monoliths are irradiated. In a series of previous publications²⁻⁶ we showed that noble metals but also semiconductor quantum dots can be produced with our technique. Here we focus on the X-ray variation of our technique and show that monoliths can be patterned with metals and also with semiconductor nanoparticles. The patterns have the same resolution than the masks, i.e., around 10 μm , and extend into the bulk of the monoliths for up to a depth of 12 mm.

Our method possesses several attractive features. Sample preparation is very simple; the technique has a bottom-up character; it allows access to a wide number of materials, such as noble metals and II-VI semiconductor materials; and it has a 3D character. With additional developments, our technique could be possibly used to complement more established techniques such as LIGA and multiphoton fabrication techniques which are currently used for 3D microfabrication.

Experimental

Silica hydrogels were prepared following a conventional base-catalyzed route. The hydrogels were then immersed in a solution of a group II and a group VI precursor. The bathing solution contained $\text{Cd}(\text{NO}_3)_2$ or $\text{Pb}(\text{NO}_3)_2$ in a concentration between 0.01 and 0.05 mol/l (M), and 2-mercaptoethanol or thioglycerol in a concentration of 1 M. To pattern with Ag, the precursor solution contained AgNO_3 in a concentration of 1 M, and 2-propanol, in a concentration of 0.1 M. Precursors diffused inside the gels in 1-2 hours, and after this time the samples were removed from the solution and exposed. Unreacted precursors were removed after exposure by washing the samples in distilled water. Irradiations were carried out at the Materials Research Collaborative Access Team (MRCAT) bending magnet beamline, at Argonne National Laboratory's Advanced Photon Source. The beamline has a beam-defining mask upstream of an 880 mm long in-vacuum platinum coated mirror held at an angle of 8 mrad used as a low pass energy filter. The beam dimensions are approximately 100 mm by 6 mm. The mean beam energy was 8.5 keV, and the fwhm of the energy distribution was around 6 keV. To prevent heating and damage to the gel structure, gels were translated vertically in front of the beam at a typical speed of 20mm/s. X-Ray masks were fabricated by electrodepositing a 50 μm thick Au absorber layer on a 0.5 mm graphite sheet.

Samples were characterized with UV-Vis and Raman spectroscopies. Due to the challenges of Raman spectroscopy of PbS, a reference PbS powder was prepared by adding 0.1 M Na_2S to a 0.1 M $\text{Pb}(\text{NO}_3)_2$ solution. The

precipitate was filtered and washed several times with water, methanol, and ethanol.

Results and Discussion

X-Ray Figure 1 shows patterns obtained by X-ray lithography. Figure 1 (a) shows Ag patterns, and figure 1(b) shows PbS patterns. The features' size coincided with the size of the features on the mask, which had a resolution of about 10 μm .

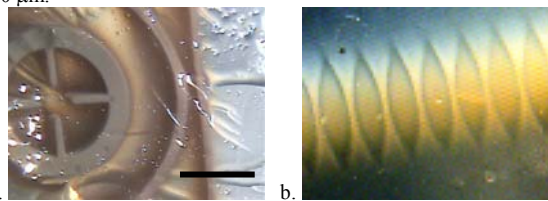
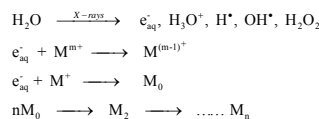


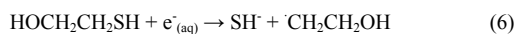
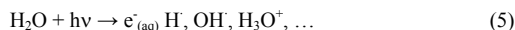
Figure 1. Sample PbS patterns obtained with X-Ray lithography. (a) Ag, (b) PbS. The scale bar represents 300 μm .

Mechanism The mechanism of Ag pattern formation is closely related to the gamma radiolysis process⁷⁻⁹. In gamma radiolysis, reduction of metal ions to form homo- and heteronuclear clusters of transition metals is initiated by formation of solvated electrons, e_{aq}^- (eq 1), which reduce metal ions M^{m+} to metal atoms (eqs 2, 3). Metal atoms eventually form aggregates, M_n (eq 4).



In previous publications^{2,9} we showed that noble metal nanoparticles formed inside hydrogel monoliths irradiated with gamma- or X-rays. In the experiments with gamma rays, masking was clearly impossible, and hydrogels were obtained which were homogeneously loaded with metal particles. In our preliminary experiments with X-rays, relatively primitive patterns were obtained by translating a monolith in front of a small beam-defining aperture. Figure 1 shows, instead, that patterns of any complexity could be obtained by masking; the patterns are transferred faithfully to the hydrogels and were seen to penetrate inside the monoliths for up to 12 mm. Patterns were formed readily with X-ray lithography. Typically, an exposure to 85 mA \cdot minute was sufficient to generate clearly visible patterns. This exposure is very low when compared to more conventional X-ray lithography processes such as LIGA. These processes are usually based on radiation-induced cross-linking of polymers like poly(methyl methacrylate) (PMMA) which require extremely lengthy exposures. On our apparatus, PMMA structures were obtained after exposures on the order of 40000 mA \cdot minute.

For chalcogenide formation, the mechanism is probably of indirect nature. The chalcogenide precursors were aliphatic alcohols carrying a thiol group such as 2-mercaptoethanol. These compounds are dissociated and liberate SH^- when they react with the solvated electrons and the radicals produced when water is ionized by X-rays.^{10,11} The overall reaction is reported in Eqs. (5-7). Reduction of the metal ions by solvated electrons, Eq. (8), was prevented by working in excess RSH, typically 10-100 times the metal ion concentration.



The composites were characterized in our previous reports with techniques such as Raman spectroscopy, transmission electron microscopy, X-Ray diffraction, and X-Ray photoelectron spectroscopy. All these techniques showed that the nanoparticles were free of contamination, and that they had a bulk crystalline structure. In this work we characterized the nanoparticles with Raman spectroscopy, and the results were in agreement with our previous research. Fig. 4 reports Raman spectra for CdS and PbS patterns obtained with

X-Ray lithography. A peak at 303 cm^{-1} was measured for CdS. This frequency is in good agreement with previous measurements of CdS/silica composites, and corresponds to the first-order longitudinal optical (LO) phonon.^{4,5,12} The interpretation of the Raman results for PbS is more complex. The LO phonon of crystalline PbS at $\sim 205\text{ cm}^{-1}$ in normal Raman scattering is forbidden. However, by using an excitation source close to the intergap energies allows the forbidden Raman bands through the Fröhlich interaction mechanism.¹³ The Raman spectrum of bulk PbS contains mainly three peaks at $154, 204, \text{ and } 454\text{ cm}^{-1}$.¹⁴ The 154 cm^{-1} peak is a combination of a transverse acoustic (TA) and a transverse optic (TO) phonon; the 204 peak is the first-order LO phonon and the 450 is the first overtone of the LO phonon (2LO). Our Raman measurements from a PbS powder show the first-order LO phonon at 200 cm^{-1} and a peak at 143 cm^{-1} which probably arises due to a combination of TA and TO phonons. The Raman spectrum from monoliths patterned with PbS shows the second and the third order LO phonons peaks at 440 and 610 cm^{-1} , respectively. Observation of overtones which are not detected in the bulk appears to be a common phenomenon in nanocrystals,¹² and has been reported for PbS nanoparticles with a mean size of 1.5 nm .¹⁴ The origin of the 240 cm^{-1} is still under investigation; this could be the first-order LO phonon that has an enhanced peak position due to the size of the nanocrystal. In 2 nm PbS nanocrystals, for example, the forbidden LO phonon appears at 230 cm^{-1} .⁵³ We notice that a shoulder around 240 cm^{-1} is evident also in the spectra of the PbS powder.

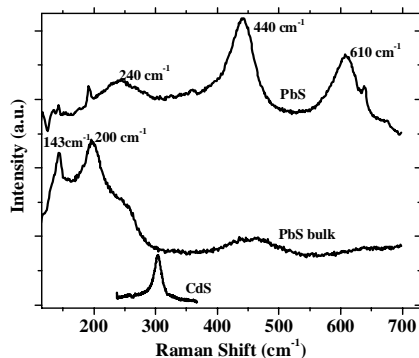


Figure 2. Room temperature Raman spectra of PbS and CdS produced by X-ray lithography in silica hydrogels. The Raman spectrum of a PbS powder is also shown for reference.

Conclusions

In conclusion, we have shown that metal and chalcogenide nanoparticles can be produced by X-ray lithography in the bulk of porous sol-gel materials such as silica hydrogels. The features lithographed on the surface and in the bulk of the hydrogels reproduce faithfully those of the masks, and penetrate inside the bulk of the monoliths for up to 12 mm . The technique is very simple and robust, and does not present issues typically encountered in X-ray lithographic processes, such as polymer foaming. Therefore, with additional developments, the technique might be employed to complement X-ray lithographic techniques such as LIGA.

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