

Polymer-Mediated Nanoparticle Assembly for Catalyst and Energy Applications

Jill Lowman

Chemistry, Old Dominion University

NNIN REU Site: Penn State Nanofabrication Facility, The Pennsylvania State University, State College, PA

NNIN REU Principal Investigator(s): Prof. Melik Demirel, Engineering Science and Mechanics, PSU

NNIN REU Mentor(s): Dr. Hui Wang, Engineering Science and Mechanics, The Pennsylvania State University

Contact: jlowm002@odu.edu, Mdemirel@engr.psu.edu, wanghuichem@yahoo.com

Abstract:

Polymer-mediated nanoparticle assembly offers applications ranging from catalyst to energy. We have recently demonstrated that nanostructured polymers of poly-(*p*-xylylene) (PPX) can be fabricated by an oblique-angle polymerization method. The nanostructured polymers offer the possibility of fabricating surfaces exhibiting tunable physical properties by systematically varying and controlling the surface chemistry and morphology at the same time. The nanostructured polymers were deposited on a micropatterned substrate from a directional vapor source in an evacuated chamber. The micropatterned substrate consisted of posts 10 μm in diameter with 10 μm spacing between each post. The substrate was oriented obliquely relative to the vapor flux, typically at an angle of 10°, which created a porous and low-density film of columns. The columnar components of our nanostructured PPX films constitute a carpet of densely-packed fibers. The nanostructured PPX film deposited on the top of the micropatterned posts created gaps in the film. We propose to create structured PPX-nanocomposite sandwich films and control the dispersity of the nanoparticles by controlling the porosity of the structured polymer film. In our approach, PPX films were immersed in ligand solutions, where ligands adsorb to the columns. The ligand adsorbate performed the function of binding both to the PPXs and nanoparticles. The adsorbate ligates nano-colloids in sufficient quantities. The ligand adsorbate was chosen from the group consisting of an alkylamine and a nitrogen-containing heterocycle capable of covalently binding the metal species. The micropatterned PPX-nanocomposite acted as a catalyst for electroless metallization.

Introduction:

We attempted to develop a catalyst using a nanostructured polymer surface deposited on a micropatterned silicon wafer substrate. The nanostructured polymer allows for more surface area of our metal catalyst which was deposited on the polymer. If using this catalyst for hydrogen release, the surface area of the catalyst is proportional to the hydrogen release rate [1]. In order for the metal catalyst to form on the nanostructured polymer, a metal nanoparticle seed must be present. The seed attached to the ligand, pyridine or a thiol containing arene, which adsorbed to the nanostructured polymer surface by aromatic interactions [2]. Palladium or copper were the seeds used in this experiment.

Experimental Procedures:

A micropattern was created on the surface of a silicon wafer by using photolithography. Silicon wafers were treated with 50/50 hydrochloric acid/methanol solution, then concentrated sulfuric acid, and finally washed with acetone before being placed in the allyltrimethoxysilane solution. Allyltrimethoxysilane self assembled into a monolayer on the surface of the silicon wafer. The wafers were then deposited with a nanostructured poly-(chloro-*p*-xylylene) (PPX-Cl)

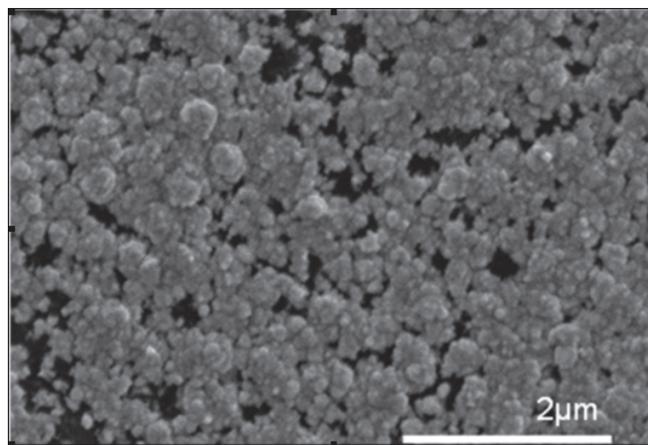


Figure 1: SEM of copper plated on PPX-Cl using palladium nanoparticles as catalysts for copper growth.

polymer by vapor deposition [3]. Planar deposition of the polymer on silicon wafers was also carried out to act as a control. The polymer was treated with a 1 M pyridine solution which served as the ligand for palladium nanoparticle adsorption. Palladium nanoparticles were synthesized using

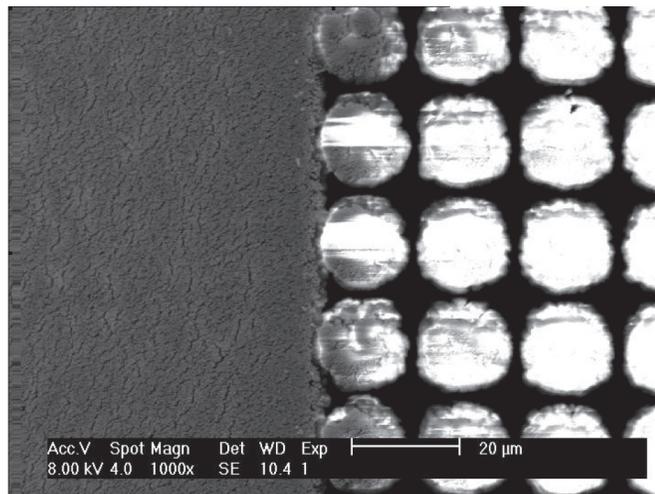


Figure 2: SEM of micropatterned nickel plated on PPX-Cl using palladium nanoparticles as catalysts for nickel growth.

the procedure described by Brandow, S.L. et al. [4]. Copper electroless metallization was performed according to Ma, Z.H. et al. [5]. The wafers were observed under scanning electron microscopy (SEM) as shown in Figure 1. Nickel electroless metallization was performed according to Demirel, M.C. et al. [2]. The SEM image can be seen in Figure 2. Various ligands were tested with copper nanoparticles to determine the optimal ligand for copper nanoparticle attachment.

Results and Conclusions:

Copper metallized on the nanostructured polymer surface better than on the planar polymer surface. This was due to the fact that the ligand has more adsorption on the nanostructured polymer due to its increased surface area compared to the planar polymer. Therefore, there was more binding between the palladium nanoparticles and the ligand on the nanostructure polymer which led to more seeds for metallization.

Nickel metallized on the micropatterned substrate which contained a helical nanostructured polymer. The polymer was deposited at an angle of 25° so that none would be deposited between the columns. Figure 2 shows that there was no nickel plating between the columns which confirms that there was no polymer between columns.

For this experiment the optimal ligand was pyridine because the nanoparticle seed used was palladium. Palladium binds

to the nitrogen in pyridine. When using copper nanoparticles as seeds, 1,2-benzenedithiol is the best ligand compared to benzenethiol and hydroxyl functionalized benzenes. Thiol is a more liable ligand than hydroxyl because sulfur is softer than oxygen. Images were taken with a triple-laser confocal microscope with a $40\times$ objective to assess the ligand's ability to bind with the nanoparticles. It was observed that thiols are better than hydroxides and multiple ligand sites are better than one site. It was also observed that a ligand must be present for nanoparticle attachment to occur.

Future Work:

The copper and micropatterned nickel catalysts need to be tested for their ability to release hydrogen from an aqueous sodium borohydride solution kept in alkaline conditions.

Acknowledgements:

I would like to thank Dr. Melik Demirel and his group, National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program, NSF, and PSU MRI staff.

References:

- [1] Malvadkar, N., Park, S., Urquidi-MacDonald, M., Wang, H., Demirel, M.C. "Catalytic activity of cobalt deposited on nanostructured poly(*p*-xylylene) films", *J. Power Sources*, Vol. 182, pg. 323-328, (2008).
- [2] Demirel, M.C., Cetinkaya, M., Singh, A., Dressick, W.J. "Noncovalent deposition of nanoporous Ni membranes on spatially organized poly(*p*-xylylene) film templates", *Adv. Mater.*, Vol. 19, pg. 4495-4499, (2007).
- [3] Demirel, M.C. "Emergent properties of spatially organized poly(*p*-xylylene) films fabricated by vapor deposition", *Colloid. Surface. A*, Vol. 321, pg. 121-124, (2008).
- [4] Brandow, S.L., Chen, M., Wanq, T., Dulcey, C.S., Calvert, J.M., Bohland, J.F., Calabrese, G.S., Dressick, W.J. "Size-controlled colloidal Pd(II) catalysts for electroless Ni deposition in nanolithography applications", *J. Electrochem. Soc.*, Vol. 144, pg. 3425-3434, (1997).
- [5] Ma, Z.H., Tan, K.L., Kang, E.T. "Electroless plating of palladium and copper on polyaniline films", *Synthetic Metals*, Vol. 114, pg. 17-25, (2000).