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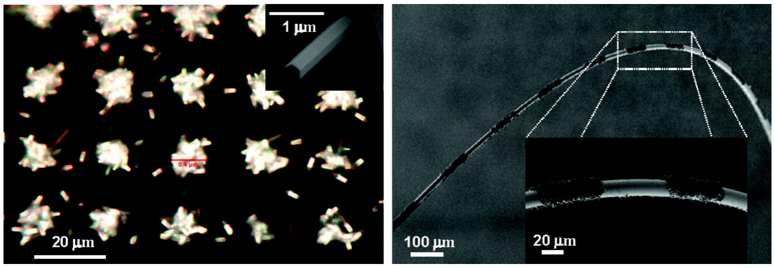
J. Am. Chem. Soc., **2007**, 129 (45), 13776-13777• DOI: 10.1021/ja074856g • Publication Date (Web): 19 October 2007



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Biomimetic Assembly of Zinc Oxide Nanorods onto Flexible Polymers

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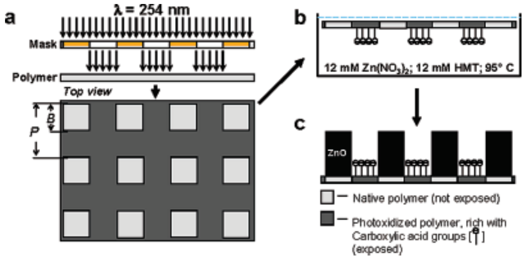
Received July 2, 2007; E-mail: jin@chem.wisc.edu

In nature biological organisms employ sophisticated strategies to achieve nanoscale assembly with complexity unmatched by manmade systems. Though these assemblies typically involve soft materials such as DNA, lipids, and proteins, inorganic−organic composites created through biomineralization processes are also common.[1] In biomineralization, complex nanoscale organization is orchestrated by "matrix" macromolecules that promote the nucleation and growth of inorganic crystals in specific locations while simultaneously controlling their size and morphology. Driven by the need to assemble functional nanomaterials for applications in macroelectronics and sensor arrays,[2] we have developed a bottom-up, biomimetic assembly strategy which borrows key principles from biomineralization; in particular the use of organic functional groups to direct nucleation. Specifically, our strategy involves the selective functionalization of polymer surfaces to create regions of differing surface energy which promote heterogeneous nucleation in designated regions but suppress it in others. The feasibility of this strategy has been previously demonstrated using self-assembled monolayers (SAMs) to create ordered arrays of calcium carbonate,[3a] anthracene,[3b] and zinc oxide (ZnO).[4] While SAMs are effective at dictating the location and orientation of crystals, the metallic film substrates employed limit their device applications. In contrast, we utilize functionalized engineering polymers as templates to nucleate and organize nanomaterials into microarrays directly out of solution, making our biomimetic strategy more technologically applicable.

ZnO, a direct, wide band gap semiconductor with numerous applications in optoelectronics,[5a,b] sensing,[5c] photovoltaics,[5d] and piezoelectrics[5e] was chosen as the model system. ZnO nanorod or nanowire arrays can be created using patterned gold catalysts,[6a] seed layers,[6b,c] and SAMs.[4] Here a simple photoresist/catalyst-free process is employed. Commodity polymers such as polycarbonate (PC) films and polyester (PET) filaments are selectively functionalized through UV oxidation and then used as templates to control the nucleation and growth of ZnO nanorods and microplates forming periodically ordered microarrays directly out of aqueous solution. This method enables direct integration of functional inorganic nanomaterials with polymeric substrates whose temperature/chemical stability is often incompatible with conventional semiconductor processing conditions.

Illustrated in Scheme 1, our approach consists of two steps. The first relies on transferring a photomask pattern onto a polymer substrate through UV ($\lambda = 254$ nm) oxidation (Scheme 1a).[7] Previous research on the oxidation of various engineering polymers[8] shows that UV exposure in air easily generates carboxylic acid groups on polymer surfaces. Here PC films were UV irradiated through a variety of quartz plate photomask patterns including grid, block, and checkerboard patterns of varying periodicities (P) and sizes (B). To verify the selective surface functionalization post UV exposure, a fluorescent tag 5-(aminoacetamido)fluorescein, that selectively binds to carboxylic acid groups, was used to label the surface of the films.[8a,9] Fluorescence microscopy imaging (Figure 1) of the tagged PC films show that carboxylic acid groups are patterned with resolution capable of creating well-defined ZnO microarrays.

Scheme 1. Schematic Illustration of the Process Employed to Produce Ordered Microarrays of ZnO



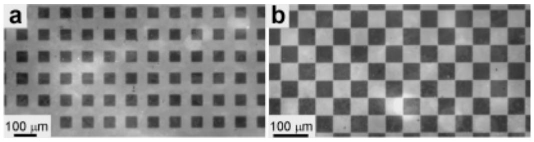


Figure 1. Fluorescent micrographs of photopatterned PC with block (a) and checkerboard (b) patterns. The bright regions reveal the location of carboxylic acid groups fluorescently labeled with 5-(aminoacetamido) fluorescein (the dark regions are native polycarbonate).

In the second step of our strategy (Scheme 1b), nanorods of ZnO are nucleated out of mild aqueous solution and directly grown (assembled) onto the chemically patterned polymers. We intentionally avoid synthetic approaches that use organic solvents[10a] or CVD/thermal annealing steps[10b] that would degrade the polymer substrate and vacuum processing that is costly, instead utilizing a previously reported aqueous synthesis.[11] Specifically, the photo-oxidized polymers were exposed to growth solutions containing equimolar concentrations of hexamethylenetetramine (HMT) and zinc nitrate at 95 °C. The key here is that instead of random growth on the substrate well-organized ZnO nanorods are assembled only onto the *unexposed* polymer regions (Scheme 1c).

The resulting ZnO assemblies were observed using optical microscopy and scanning electron microscopy. Representative images of the ZnO microarrays on PC films are shown in Figure 2, together with the images of the corresponding photomasks. Large areas (at least 1 cm^2) of checkerboard, grid, and block patterns have been generated using our technique. The smallest features patterned were 10 μm blocks (Figure 2d), and 4 μm grids (Figure 2f). Larger pattern area, smaller feature size, and more intricate assemblies can be realized in the future using more sophisticated photomasks and/or growth schemes. In addition the ZnO morphology can be changed from nanorods to microplates (Figure 2h) by adding small concentrations of citric acid to the normal growth solution.[4,12] This tunability highlights another advantage of our biomimetic strategy.

Directed growth of calcium carbonate crystals on planar substrates using SAMs has been investigated thoroughly.[3a] Because the rate of heterogeneous nucleation depends on surface function-

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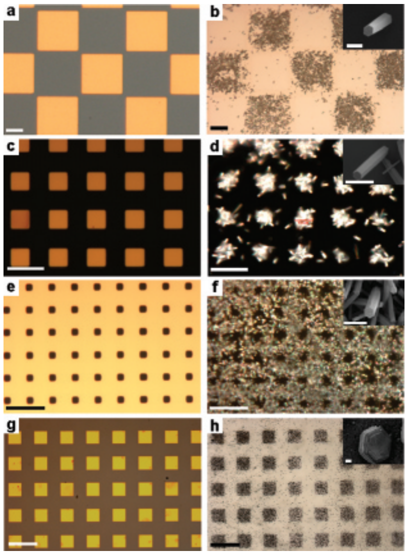

Figure 2. Optical micrographs of the mask patterns (a, c, e, and g) used in Scheme 1 and the resulting patterned microarrays of ZnO nanorods (b, d, f) and microplates (h). Insets show higher magnification SEM images of the ZnO nanorods or plates. Scale bars are 20 μm for panels a−f, and 300 μm for panels g and h. All insets have 1 μm scale bars.

alities and their associated interfacial energies,[1d] patterned SAMs can create regions where nucleation is faster. As crystal growth begins over the faster nucleated regions concentration depletion wells form as diffusion tries to equalize concentration. These wells suppress nucleation and growth for a specific length[13] around the faster nucleating region allowing pattern generation.[3a] Though we have replaced SAMs with selectively oxidized polymer substrates the mechanism for patterning crystal growth is analogous. Here the *native* polymer regions are where nucleation/growth occur faster, eventually suppressing growth on the photoxidized surface. Since surface carboxylic acid (−COOH) groups were thought to be more favorable for nucleation this result is somewhat unexpected. It has been suggested previously that protonated HMT species may complex with surface −COOH groups blocking nucleation in these regions,[4] but further work is needed to confirm this.[7]

We found that two geometric parameters of the patterns heavily influence the quality of the resulting arrays on PC films: (i) percentage of total area exposed to UV radiation and (ii) pattern periodicity (*P* from Scheme 1a). When exposure percentage is $\lesssim$75% quality patterns are easily produced regardless of periodicity. This is best illustrated by quality grid patterns (Figure 2f) which have exposure percentages well below 75% and show little dependence on periodicity. As exposure percentage is increased above 75%, pattern periodicity becomes more important. At this exposure percentage periodicities (*P*) twice the feature size (*B* from Scheme 1a) usually yield good patterns as seen in Figure 2d. Checkerboard patterns satisfy both pattern parameters and thus usually work very well (Figure 2b). These findings reflect the influence of the diffusion and depletion processes discussed above, as shown more explicitly in the Supporting Information.

The advantages of our approach also lie in its generality. Although discussion so far has focused on the formation of microarrays on *PC films*, our assembly strategy can be easily extended to many polymer materials and polymers of *any arbitrary shape*. As a demonstration, we have used a procedure analogous to Scheme 1 to assemble segments of ZnO nanorods along polyester (PET) filaments (Figure 3).[7] Such versatile assembly of functional nanomaterials on filaments can enable applications in smart textiles and wearable macroelectronics.

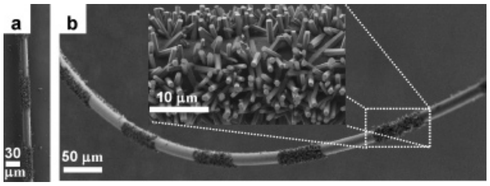

Figure 3. Scanning electron micrographs of patterned ZnO nanorods assembled on flexible PET filaments.

In conclusion, we have demonstrated a biomimetic assembly approach for selective nucleation and growth of patterned ZnO assemblies directly out of aqueous solution onto flexible polymer films or filaments that does not rely on photoresist or SAMs. This strategy can be expanded to other inorganic and polymer materials with complex substrate geometries to enable many macroelectronic applications. In the future, the fundamental concepts shown here can be further applied to self-assembled block copolymer nanostructures to achieve truly bottom-up nanoscale assembly of nanomaterials.

Acknowledgment. This research was supported by a SEED grant through the UW-Madison NSEC (NSF Grant DMR0425880). S.J. is a 3M Non-tenured Faculty Grant Awardee and a DuPont Young Professor. We thank Professor R. J. Hamers for access to various instruments.

Supporting Information Available: Experimental conditions, the effects of diffusion, and HMT complexation. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA074856G