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Regiospecific Assembly of Gold Nanoparticles around the Pores of Diatoms: Toward Three-Dimensional Nanoarrays

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The fundamental theory in photonic crystal engineering is that the propagation of light as well as the interaction of light and matter is modified due to the presence of lattice-periodic photonic modes with characteristic dispersion relations. Recent advances in the field involves the use of nanoparticles to self-assemble into superlattices, of a higher level of hierarchy, and eventually to 3D crystals.[1,2] The template directed self-assembly approach is the nanochemical analogue of lithography and a nanoengineering route for patterning and templating advanced structures with 3D patterns.[3] Nanoporous structures are one of the most interesting classes of materials, potentially providing a well-defined architecture at the nanometer scale that can be used as a template for nanoparticle assembly. However, regulating the porous architecture at the nanometer scale is a difficult task in terms of fabrication. Nevertheless, a most interesting example provided by nature is the intricately and precisely fabricated porous architectures of the unicellular algae called diatoms.[4,5] Diatoms are microscopic organisms found in both fresh and salt water ecosystems comprising about a quarter of autotrophic biomass and are believed to be responsible for 25% of the total oxygen production on Earth.[6] Diatoms are encased by an amorphous silica frustule "shell" which is perforated with unique pores that vary greatly depending on the species. For example, the diatom sample we report here had four dominant frustule morphologies present as shown in Figure 1. The frustule is made up of two tightly overlapping halves called thecae which fit together much like a Petri dish.[7] They can be from several micrometers to a millimeter in size with the pores ranging from less than 50 nm to in excess of a micrometer. This suggests that there is a range of suitable structures for a range of applications. The structures created by diatoms would be extremely difficult, expensive, and time-consuming to reproduce; therefore diatoms are being utilized directly rather than mimicked. Diatoms can reproduce rapidly with one single diatom having 100 million descendents within a month with exactly the same frustule structure, thereby providing a very high output of exact replicas for down stream applications. Diatomaceous earth has already been recognized for its utility in filters, abrasives and insecticidal dust.[8,9] For optical applications, for example, the cell can be regarded as a photonic crystal slab waveguide with moderate refractive-index contrast. Optically rich nanoparticles, for example gold, can be further combined with the regularly repeating structure of the frustule pores in the formation of ordered gold particle arrays. The deposition of gold and silver on a diatom frustule surface has been achieved by thermal evaporation and using a DNA mediated binding.[7] Furthermore self-supporting 3D nanoparticle assemblies have been synthesized using diatom frustules.[7] Herein we demonstrate that the ordered pores of diatom frustule can be effectively used as templates to mediate gold nanoparticle growth by a facile method.

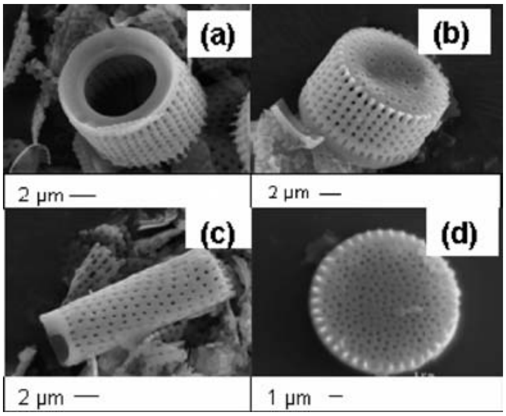

Figure 1. (a−d) SEM images showing the four major silica frustule morphologies of the diatoms used in the current study.

An important criteria in template-directed assembly of nanoparticles is an effective route to immobilize nanoparticles on these substrates. The immobilization is often achieved by surface modification on various oxide surfaces with functional groups such as thiol, pyridyl, amino, and carboxy to provide attraction to nanoparticles.[10] Herein, poly(vinylpyridine) (PVP) is an attractive polymer for immobilization of nanoparticles because of the strong affinity of pyridyl group to metals and because of its ability to undergo hydrogen bonding with polar species. The ability of one polymer molecule to interact simultaneously with the surface through many pyridyl groups provides an entropic advantage for the quasi-irreversible adsorption of this molecule to the surface even in the presence of highly polar solvents. Following the adsorption to substrates, PVP molecules still have numerous unbound pyridyl groups that do not participate in the interaction with the surface which are capable of binding nanoparticles.[11] Consequently, only one type of functionality (pyridyl group) is required for the adhesion to surfaces and the binding of nanoparticles. Because of the strong adhesion of PVP to many metal and nonmetal surfaces, this compound has been suggested as a universal monofunctional surface modifier for the immobilization and assembling of different nanoparticles on Si/SiO_2 surfaces.[10] Furthermore, a unique property of PVP that makes it ideal in the current application is the ability of PVP thin films deposited onto a silicon substrate with native oxide layers to dewet reversibly upon exposure to different pH solutions.[11] The dewetting pattern depends on the deposition

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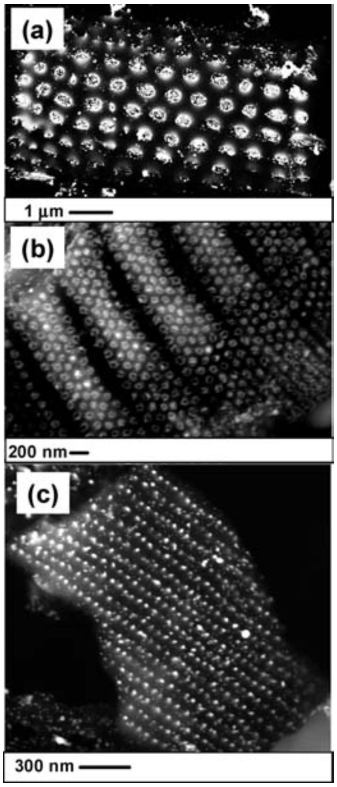

Figure 2. (a−c) Backscatter electron images showing gold nanoparticles around the pores of diatoms.

method, the film thickness, the nature of the substrate, and the polymer molecular weight. It was reported that although PVP is insoluble in basic aqueous solutions, it can show significant plastic deformation; consequently, its enhanced mobility under the experimental conditions resulted in dewetting.[11] The dewetting process was also found to be reversible, and the film wetted the surface in pH 4 solutions. We herein hypothesize that a PVP coated diatom on exposure to a basic solution will undergo instantaneous dewetting from the diatom surface localizing the polymer around the pores. The localized polymer will thereby direct regiospecific growth/assembly of gold nanoparticles mimicking the periodicity of the porous diatom architecture. In the current article, the polymer coated diatoms (coating confirmed by FTIR analysis and SEM, see Supporting Information) were exposed to a solution of $HAuCl_4$ under constant agitation to achieve an ion interaction with the nitrogen of the pyridine ring in the polymer under basic conditions, following which they were reduced by exposure to hydrazine hydrate solution (see Supporting Information for detailed procedure).

Basic conditions (pH 11) resulted in the growth of the gold nanoparticles specifically around the pores of the diatoms, Figure 2. The gold nanoparticles around the larger pores (>150 nm) were in the size range 10−50 nm (Figure 2a,b). It was also evident that if the pores are sufficiently small (<40 nm) it was possible for them to be completely filled with single nanoparticles (Figure 2c). The presence of gold was also confirmed by energy dispersive X-ray spectroscopy (EDS), and the crystallinity of the gold nanoparticles was confirmed using X-ray diffraction (see Supporting Information). It is noteworthy that acidic conditions (pH 4) resulted in growth of the gold nanoparticles randomly on the diatom frustule. Under basic conditions the silicon dioxide surface bears a significant negative charge, −60 mV with PVP being reported to have a charge of −20 mV above its isoelectric point.[12] Indeed these negative charges result in a nonfavorable interaction resulting in the polymer film to dewet the surface and relocate on the pores. Furthermore, although the polymer is insoluble under basic conditions it has been reported to show significant plastic deformation, which accelerates the dewetting phenomenon. Under acidic conditions, the polymer is positively charged while the silicon dioxide still has a negative charge. This coupled with the significant swelling of the polymer under acidic conditions favors the formations of a PVP film on the diatom surface rather than the pores. It is also noteworthy that the immobilization of nanoparticles to the PVP significantly decreases the polymer mobility, stabilizing the film following dewetting.[11] Indeed, the growth of the gold nanoparticles occurred selectively at pores under basic conditions and on the diatom surface under acidic conditions, and the composite structures remained stable following multiple washing.

In conclusion, in this report we have established a novel technique of using diatom frustules as a template for the formation of three-dimensional gold nanoparticle arrays. The in situ synthesis of gold nanoparticles in basic conditions has been shown to consistently yield gold particle arrays. The different species of diatom present, as well as their different pore size and structure, had little effect on the success of the technique. This indicates that the process can be universally applied to varying diatom species regardless of size or structure and in general for the regiospecific growth of optically active nanomaterials. We believe that harnessing the ordered structure of the diatom pores for gold nanoparticle attachment gives rise to numerous applications in electronics alone, such as further miniaturization of photonic and electrical circuits, new forms of data transfer using plasmons, and as sensors.

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Supporting Information Available: Materials and Methods, Analysis data: SEM, TEM FTIR, EDS, and XRD. This material is available free of charge via the Internet at http://pubs.acs.org.

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