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Supporting Information

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Control of Nanoparticle Assembly Using DNA-Modified Diatom Templates[**]

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Functionalization of Diatom Surfaces.

Diatoms were cultured from a freshwater silicate-rich growth medium for two weeks under ambient cool-white fluorescent light (Carolina Biological Supply Company). The cultures (typically ~1000 mL total) were collected via centrifugation (3000 rpm) and washed (3X) with nanopure water (NANOpure, Barnstead/Thermolyne Corp.; 18 MΩ). A Pirahna solution (0.34 M $K_2Cr_2O_7$, 1 mL; conc. H_2SO_4, 5 mL; 30% H_2O_2, 1.5 mL) was used to digest the organic portions of the diatoms as well as to activate their cell walls for silane functionalization. Isolation of the activated diatom cell walls was accomplished via filtration with a 0.45 μm Teflon filter (Millipore Corp.) followed by copious washing with nanopure water. The cell walls were collected into a plastic centrifuge tube (15 mL) and suspended in a mixture of nanopure water (5 mL), 3-aminopropyltrimethoxysilane (0.500 mL), and glacial acetic acid (5 μL). The mixture was allowed to react for two days on an inverting rotation device (Rotoshake Genie; Scientific

Industries, Inc.) after which unreacted silane was removed via centrifugation. The amino-functionalized diatoms were washed with nanopure water (3X) followed by acetone (3X) to dry and remove excess water, and then reacted with succinimidyl 4-[*p*-maleimidophenyl]butyrate (SMPB, Pierce Biotechnology, Inc.) (2 mM solution in 1 mL dimethyl sulfoxide/4 mL absolute ethanol) for 1 day. The excess reagents were removed via centrifugation, the unreacted amine groups were capped with acetic anhydride (2.5 mL CapA mix and 2.5 mL CapB mix; Glen Research Corp.), and the diatoms were finally washed and dried with acetone (3X). Lastly, the SMPB-functionalized diatoms were suspended in buffer (1 mL 0.3 M PBS; pH ~7.0) and reacted with 2 OD thiolated, Cy3-labeled DNA (3′-HS-C_3H_6-Cy3-AATATTGATAAGGAT-5′). After 1 day on the inverting rotator, the DNA-functionalized diatoms were filtered using a Centricon 100 centrifuge filter (100K MW cut-off; Millipore, Inc.) to remove unreacted DNA and rinsed with 0.3 M PBS (3X). The DNA-functionalized diatoms were stored as a suspension in 1 mL 0.3 M PBS. They appeared pink and fluoresced (563 nm) upon excitation with a mercury lamp.

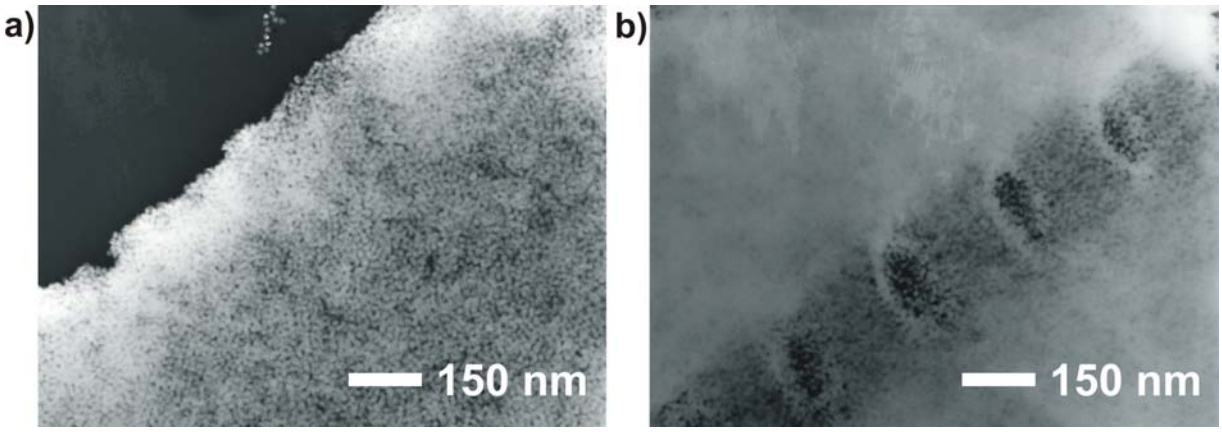
Coating Diatoms with layers of DNA-modified Nanoparticles

A sample of DNA-functionalized diatoms (typically ~250 µL) was exposed to 13 nm Au particles (Particles **A′**) functionalized with complementary 3′-propylthiol-capped oligonucleotide strands

(3′-HS-C_3H_6-ATCCTTATCAATATT-5′; **a′**) until, after brief centrifugation (3000 rpm), the color of the solution changed from deep red to clear and the color of the diatoms changed from pink (from the Cy3) to deep red, thus indicating that the particles had assembled onto the diatom surfaces. Fresh colloid was added iteratively until the solution remained red for at least 24 h in order to fully saturate available surface binding sites on the diatoms.

Additional layers of nanoparticles were added by exposing the diatoms to particles modified with DNA that was complementary to the outermost layer of DNA on the diatoms. Again, Fresh colloid was added iteratively until the solution remained red for at least 24 h.

TEM Images of Multiple Nanoparticle layers



Supporting Figure 1. TEM images of four layers of nanoparticles on Navicula (a) and Synedra (b).

Instrumentation

All TEM images were acquired using a Hitachi H-8100 TEM. All SEM images were acquired using a Leo Gemini 1525. Both instruments are housed in the Electron Probe Instrumentation Center (EPIC) at Northwestern University.

Fluorescent microscopy images were acquired using a Zeiss Axiovert 100A optical microscope equipped with a Zeiss Attoarc 2 mercury lamp for fluorescence.