ADVANCED MATERIALS

Supporting Information

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Nanocomposite Microcontainers

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Supplementary Information

Materials: Polyvinyl alcohol (PVA) with a molecular weight of MW ≈ 70,000, Selenium powder (Se), Cadmium Oxide (CdO), trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), hexadecylamine (HDA), stearic acid, trichloro(3,3,3-trifluoropropyl)silane, chloroauric acid, sodium citrate, n-hexane, chloroform and methanol, were purchased from Sigma-Aldrich and used as received. Poly(dimethylsiloxane) (PDMS) Sylgard 184 was purchased from Dow Corning (Michigan, USA). Na+-montmorillonite (MTM) powder was purchased from Southern Clay Products (Gonzales, TX) and was exfoliated via extensive stirring in aqueous solution. The average diameter of the platelets is 110 nm and thickness is approximately one nm as described by the supplier.

PDMS mold preparation: A silicon wafer containing 64 squared 0.18μL wells with 3 mm edges and a depth of 20 μm (Lurie Nanofabrication Facility, UofM), was vapor-coated with Trichloro(3,3,3-trifluoropropyl)silane. PDMS pre-polymer was mixed with a curing agent in 10:1 proportion and poured onto the specified Silicon wafer in order to form 1 cm thick mold. The PDMS was cured at 80ºC overnight. A flat PDMS (without pattern) mold was similarly produced on a glass substrate. Both PDMS templates were removed from their substrates and washed with acetone before using for layer by layer deposition (LBL).

Microcontainer fabrication: The patterned and non-patterned PDMS molds were sequentially immersed in a 1wt% aqueous solution of PVA for 5 minutes and in a 1wt% aqueous dispersion of MTM. Each polymer and clay adsorption step was followed by a rinse in deionized water for two minutes followed by drying under an air stream for two minutes. The deposition procedure was realized with a robotic manipulator (DR-1, R&K Technologies, Germany) programmed to carry out all the operations automatically for a number of cycles, n, to produce a $(PVA/MTM)_n$ film. Both the patterned and planar molds were coated with n = 1000 bilayers, with fresh solutions of each component used

after every 20 bilayers. After multilayer fabrication, the PVA/MTM films were gently pealed from the PDMS molds. The microcontainer was produced by combining the planar and patterned LBL nanocomposite films with a droplet of water in between and applying gentle pressure to allow for hydrogen bonding to seal the planar lid in place. In some cases, prior to sealing, the microwells were filled with a CdSe or gold nanoparticle solution by micropipetting. The samples were analyzed by scanning electron microscopy (Philips XL30 Environmental Scanning Electron Microscope and FEI Nova 200 Nanolab) after gold coating and confocal microscopy (Olympus LEXT Interferometer).

Synthesis of CdSe nanoparticles (NPs): Based on the previously reported procedure*[1]* a three necked rounded bottom flask 0.04g of CdO and 6g of stearic acid were combined and heated under argon to 250ºC, at which point the mixture became colorless. The solution was then cooled to room temperature and 5.67g of HDA and 5.67g of TOPO were added while stirring. The solution was heated up again to 250ºC and a solution of Se powder (0.025 g) and TOP prepared under an inert atmosphere was added drop wise. In order to control the NP growth, the fluorescence of aliquots of dispersed NPs in chloroform was measured. The reaction was stopped when a maximum of 650nm absorbance was reached. After the reaction reached room temperature, the NP's were purified by dispersion in a 1:1 hexane/methanol solution followed by centrifugation for 15 minutes at 6000 rpm and repeated three times. Fluorescence was realized based on photography in the presence of a UV light source.

Synthesis of Gold NPs: As previously reported,*[2]* citrate stabilized gold NPs were fabricated by bringing chloroauric acid (0.005M) to boil before adding sodium citrate (1% w/w) under vigourous stirring. Heat and stirring was applied for an additional 15 minutes before cooling.

[1] D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase, H. Weller, *Nano Lett.* **2001**, *1*, 207.

[2] J. Turkevich, P. C. Stevenson, J. Hillier, *Discussions of the Faraday Society* **1951**, 55.