Block Copolymer-Directed Assembly of Bare Metal Oxide Nanocrystals for Energy-Related Devices

Brett A. Helms, Evelyn L. Rosen, Raffaella Buonsanti, Teresa E. Pick, Lina Zhu and Delia J. Milliron

1The Molecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720

INTRODUCTION

The properties of metal oxide nanocrystals in energy-related devices are strongly dependent on the presence and chemical nature of ligands at their surface, and the architectures they assume in electroactive layers. A comprehensive strategy to control these aspects of the electrode’s design will be presented. First, we will describe an exceptionally versatile class of reagents, trialkyloxonium salts, for stripping carboxylate-, phosphate- and amine-based ligands from the surfaces of transition metal oxide nanocrystals, resulting in either bare or BF4-/DMF-passivated surfaces depending on the material used. These reagents were effective for either thin films of nanocrystals or their dispersions. Significantly, no etching of the nanocrystals was observed. Dispersions of bare nanocrystals are useful as nanoinks for preparing electrodes free of insulating ligands. These nanoinks are also amenable to architecturing at the mesoscale using appropriately-designed macromolecular templating agents that make particular use of dynamic molecular interactions directed at the nanocrystal surface. Mesosstructed electroactive layers as such are poised to overcome ion/electron transport limitations associated with electrochemical reactions occurring at electrolyte-accessible interfaces.

EXPERIMENTAL

Reagents. Triethyloxonium tetrafluoroborate (Et3OBF4) was purchased from Aldrich and used as received.

Reactive Ligand Stripping of Nanocrystals. Ligand-stripping reactions were performed in a nitrogen dry box. Et3OBF4 (0.01-0.10 mmol) was dissolved in ACN (1 mL) and a hexanes solution of nanocrystals was then added to form a biphasic solution. After vortexing, the nanocrystals precipitated from solution. Chloroform was added and then the reaction mixture was centrifuged, and the supernatant discarded. The pelleted nanocrystals were then washed with additional chloroform. The resulting nanocrystals were then re-suspended in DMF, generally requiring gentle heating and sonication. A similar procedure could be conducted in a single phase using dry dichloromethane from nanocrystals similarly dispersed, as could a direct transfer from a dispersion in hexanes to DMF containing Meerwein’s salt. In rare cases, the presence of DMF (up to 10 equivalents with respect to Meerwein’s salt) during the ligand stripping served to mitigate undesirable fusing.

Analysis of Architectured Nanocrystalline Thin Films. SEM images were recorded on a Zeiss Gemini Ultra-55 Analytical scanning electron microscope with a beam energy of 5 kV and an In-Lens detector. An in-built EDS detector was used for elemental analysis. XRD was performed on a Bruker Gaddé-8 diffractometer with a CuKa source operating at 40 kV and 20 mA. FTIR spectra were obtained on a PerkinElmer Spectrum One FTIR Spectrometer on AgCl or doubleside-polished Si substrates or on a ZnSe prism by using an HATR sampling accessory. Atomic emission spectroscopy was performed on a Varian 720-ES ICP optical emission spectrometer by using an argon plasma. Absorbance spectra were recorded on a Varian Cary 5000 UV/Vis/NIR spectrophotometer. Diffuse-reflectance spectra were determined on an ASD Inc. Quality Spec Pro UV/Vis spectrometer with MugLite attachment and Spectralon reference. Film thicknesses were determined on a Veeco Dektak 150 Surface Profilometer. Dynamic light scattering (DLS) data were obtained with a Malvern Zetasizer Nano ZS instrument.

RESULTS

The TEM images of the initial and treated metal oxide nanocrystals (Figure 1) showed that their quality was retained after stripping. In general, no aggregation was observed by dynamic light scattering (DLS) of stripped nanocrystal dispersions in DMF. For example, oleylamine-passivated ITO nanocrystals with initial hydrodynamic size of 9 nm in hexanes exhibited a hydrodynamic size of 6 nm after treatment with Et3OBF4, consistent with loss of ligands with long carbon chains. Dispersions of stripped nanocrystals were found by FTIR to contain adsorbed BF4- and DMF, consistent with similar dispersions produced by using NOBF4. Together, these qualities make these dispersions of bare nanocrystals primed for templating into diverse 3-D architectures at the mesoscale for advanced energy devices (supercapacitors, electrochromics, batteries, etc).

Figure 1. Summary of TEM for ligand-passivated metal oxide nanocrystals (left column) and those stripped using Et3OBF4 (right column): a) Olate-passivated TiO2; b) Stripped TiO2; c) Oleate/oleylamine-passivated ITO; d) Stripped ITO. Scale bars are 20 nm.

Figure 2. Block copolymer-templating of metal oxide nanocrystal active layers.
DISCUSSION

Preliminary results with BCP templating of bare metal oxide nanocrystals suggest a highly efficacious process that is made possible by tuning the supramolecular interactions between the nanocrystal surface and the nanocrystal binding domain of the BCP templating agent (Figure 2). These results are qualitatively much improved over other schemes, whereby templating agents were used to direct the assembly of nanocrystals with non-optimized ligands at their surfaces. As such, we will discuss at length their use as cathodes for electrochemical energy storage, where the ability to control the volume fraction and architecture of the nanocrystal storage particles is expected to impact power density, etc in devices.

ACKNOWLEDGEMENTS

We gratefully acknowledge A. Dong for helpful discussions. This work was funded in part by the DOE Early Career Research program (D.J.M.). All work was completed at the Molecular Foundry, supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.

REFERENCES