Supplementary Material (ESI) for Chemical Communications

Sacrificial layer electrophoretic deposition of free-standing multilayered nanoparticle films

Electronic Supplementary Information

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I. Iron oxide nanoparticles (NPs): synthesis and characterization

a. Method

Iron oxide NPs were synthesized using the method of Park et al.[28] Iron oleate precursor was formed by reacting 2.16 g $FeCl_3 \bullet 6\ H_2O$ (Sigma Aldrich, 98% Reagent Grade) with 7.33 g sodium oleate (TCI) in a solvent comprising 12 ml deionized water, 16 ml ethanol, and 28 ml hexane at 70°C for 4.5 h. The upper layer containing iron oleate was rinsed with deionized water several times and removed using a separatory funnel. Iron oleate was heated further at 75°C for 24 h under vacuum. NPs were then grown by decomposition of 1.36 mmol iron oleate with 0.8 mmol oleic acid in 10 ml 1-octadecene. The mixture was heated to 320°C at a rate of 3.3°C/min and allowed to reflux for 40 minutes, then cooled to room temperature.

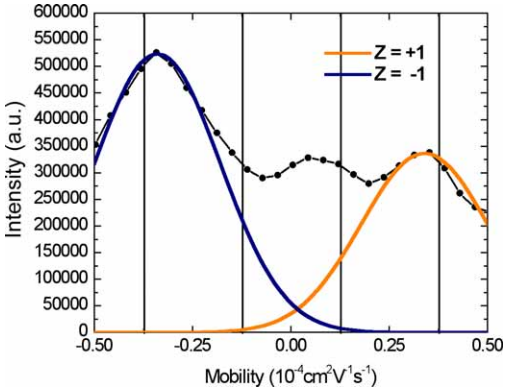
b. Electrophoretic mobility

We prepared the EPD suspension by combining 1 ml of the NP synthesis product with 5 ml hexane and 15 ml acetone, and then centrifuging the resulting mixture for 45 min at 3500 rpm. After pouring out the supernatant, the NPs were suspended in hexane at a concentration of ~2.5×10^{13} ml^{-1} to perform EPD.

The charge states present in a colloidal system may be probed by measuring the electrophoretic mobility of the constituent particles. The relation between charge and mobility is detailed in the following passage from *Electrophoretic deposition of CdSe nanocrystal films onto dielectric polymer thin films* (S. A. Hasan, D. W. Kavich, S. V. Mahajan, S. V. and J. H. Dickerson, *Thin Solid Films,* 2008, **517,** 2665):

> Generally, the mobility μ gauges the velocity v of a particle in an applied electric field E.
>
> $$\mu \equiv \frac{v}{E} = \frac{Ze}{3\pi\eta d}$$
>
> μ may be calculated for a colloidal particle using the surface charge number Z, in units of elementary charge e, the solvent viscosity η, and the particle's hydrodynamic diameter d. For suspensions measured using a constant electric field, the sign of the electrophoretic mobility corresponds to the sign of the particle's charge.

The mobility distribution shown below, measured by laser Doppler velocimetry using a Malvern Zetasizer NanoZS instrument, affirms the presence of iron oxide NPs both positively and negatively charged in hexane suspension.



Electrophoretic mobility distribution of iron oxide NPs in hexane suspension.

II. Electrodes: preparation and characterization

a. Evaporation of metals

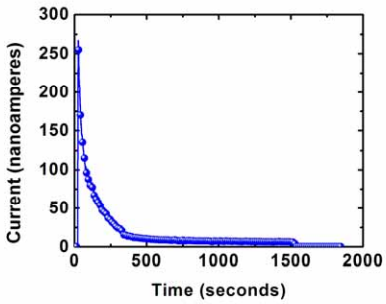
On Si wafers (as-delivered), we evaporated ~20 nm Cr adhesion layer and ~125 nm Au. These thicknesses were verified by ellipsometry.

b. PLGA characterization

The thickness uniformity of the spun cast PLGA layer was verified by ellipsometry, using the parameters described in "Adsorption of serum albumin to thin films of poly(lactide-co-glycolide)" (S. M. Butler, M. A. Tracy and R. D. Tilton, *J. Control. Release,* 1999, **58,** 335).

III. Electrophoretic deposition current

A representative plot of current during EPD of NPs is shown below.



Current for ~25 min EPD of NP film, followed by 5 min drying.