Supplementary Material (ESI) for PCCP

Supplementary Material

Controlling the Anisotropic Magnetic Dipolar Interactions of PbSe Self-Assembled Nanoparticles on GaAs

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Synthesis of the nanoparticles:

Lead acetate trihydrate (Pb-Ac, $Pb[CH_3COO]_2 3H_2O$, GR) was purchased from Merck. PhEt ($C_6H_5OC_6H_5$, 99%,), oleic acid (OA, $CH_3(CH_2)_7CHCH(CH_2)_7COOH$, 99.8%), trioctylphosphine (TOP, $(C_8H_{17})_3P$), and selenium (Se, 99.995% purity) were all purchased from Aldrich.

The synthesis of a PbSe nanoparticle (NP) core covered with organic surfactant followed a modified procedure reported earlier[1] and included the following stages: 1) 0.71 g of lead acetate trihydrate [Pb-AC] was dissolved in a solution that was composed of 2 mL of PhEt, 1.5 mL of oleic acid (OA), and 8mL of trioctylphosphine (TOP), under standard inert conditions in the glove box, which was inserted into a three-necked flask (flask I) ; 2) 10 mL of PhEt was inserted into a three-necked flask (flask II) under the inert conditions of the glove box; 3) both flasks were removed from the glove box and were placed on a Schlenk line and then heated under a vacuum to 100-120 ^{0}C for an hour;

4) flask I was cooled to 45 ^{0}C, and flask II was heated to 180-210 ^{0}C, both under stream of argon gas; 5) 0.155g of selenium powder was dissolved in 2.0 mL of TOP, forming a TOP:Se solution, under standard inert conditions of a glove box; then, 1.7 mL of this solution was injected into flask I on the Schlenk line; and 6) the contents of flask I, containing the reaction precursors, was rapidly injected into the PhEt solution in flask II, reducing its temperature to 100-130^{0}C, leading to the formation of PbSe NPs within the first 15 min of the reaction. The procedure described produced nearly monodispersed NPs with a <5% size distribution, and with an average size between 3 nm and 9 nm, controlled by the temperature and by the duration of the reaction.

Adsorption of the nanoparticles and their characterization

The PbSe NPs, with diameters of 4.5 nm, were attached to a p-type GaAs (AXT company) surface through self-assembled monolayers of 1,8-octanedithiol and 1,4-benzenedimethanethiol (Sigma–Aldrich Co). The process followed that described in reference 2. The GaAs slides were cleaned, prior to the adsorption, by acetone, n-hexane and ethanol and by an ultraviolet ozone cleaning system (UVOC model T10/OES/E) for 25 min, after which, they were immersed in a concentrated HCl solution for 1 min followed by a 3%NH_4OH solution for 30 s to remove the oxides. The slides were then immersed in a 1mM solution of the specific compound in ethanol (overnight deposition) and then washed with ethanol. A WVASE32 spectroscopic ellipsometer was used to obtain the effective thickness of the monolayer at an incident angle of 70^0. The measurements were performed at wavelengths between 250 and 1100 nm, with sampling steps of 5 nm.

In addition to ellipsometry, the quality of the monolayer was also verified by atomic force microscopy (P47 SolverAFM NT-MDT Ltd., Russia), using AC240 probes (Olympus, Japan) and contact potential difference measurements (CPD) using a Kelvin Probe (Besocke Delta Phi GmbH). The AFM measurements provided the nanoparticle density (about 6.0 x 10^{10} cm^{-2} for both monolayers) and distribution on the surface (Fig. 3). Zero-field-cooled (ZFC) and field-cooled (FC) measurements were performed with a SQUID (superconducting quantum interference device) magnetometer MPMS2 (magnetic property measurement system 2) with an absolute sensitivity of 10^{-7} emu with the magnetic field applied either parallel or perpendicular to the sample plane. The

samples were then placed in plastic straws, which have a low background contribution to the magnetic moment (about 10^{-6} emu at 1 T).

References:

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(2) Aqua, T.; Cohen, H.; Vilan, A.; Naaman, R. *J. Phys. Chem. C.* **2007,** *111*, 16313.