

Assembly of iron oxide nanocrystal superstructures

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Self-organization of colloidal magnetic nanocrystals (NCs) into ordered superstructures is of significant interest as an opportunity for the controlled design and fabrication of mesoscopic magnetic materials that could find use in magnetic data storage, sensors and biomedicine. For example, an assembly of monodisperse magnetic NCs with controlled interparticle spacing can allow a fine tuning of spin-dependent transport which is particularly important when single electron tunneling (SET) and spin-dependent transport (SDT) are targeted in nano-sized devices [1, 2].

Using ad-hoc self-assembly procedures, highly ordered supercrystal structures have been prepared in recent years, with interesting collective magnetic properties that are different from those exhibited by their isolated NC building blocks, corresponding disordered ensembles or their bulk materials counterpart. In large superstructures of colloidal iron oxide NCs, the interplay of magnetic dipole-dipole interactions with the NC magnetocrystalline anisotropy can lead to enhanced saturation magnetization and coercivity, while dilute assemblies exhibit superparamagnetic behaviour [3, 4]. Collective magnetic properties are indeed extremely sensitive to mutual interactions among NCs, depending on the superlattice structure and interparticle spacing. This calls for efficient design of NC arrays with different dimensions for integration into functional device structures.

Here, we report on the magnetic field-assisted assembly of iron oxide NCs with inverse spinel cubic structure of mixed-phase half-metallic magnetite (Fe_3O_4) /insulating maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [5]. Self-assembly was carried out by subjecting toluene solutions of purified NCs to slow solvent evaporation in a quasi toluene-vapour-saturated ambient. A perpendicular to plane magnetic field (0.5 T) was applied to facilitate growth of superlattices.

Two common procedures were employed for NC self-assembly, namely dip coating and drop

casting. In the former approach, a substrate was dipped into a NC solution with a permanent magnet positioned below and kept there over a period of 3 days maintaining a saturated toluene vapour ambience. Then the substrate was extracted, washed and dried. In the drop-casting method, few drops of NC solution were placed over the substrate and the solvent was allowed to slowly evaporate. NC concentrations were varied in the range of 0.3-7 μM .

Self-assembly was investigated on two kinds of surfaces: (100 nm thick) Au and (3nm/100nm) SiO_2/Au , prepared on SiO_2/Si substrates using thermal evaporation and electron beam techniques. The template surfaces were also modified with organic ligands to evaluate the effect of NC-substrate interactions on the self-assembly. The superlattices could be tailored in a versatile way, from thin films up to macroscopic supercrystals in the millimeter range, by acting on NC solution concentration and the mode of casting. Although NC self-assembly into superlattices is largely entropically driven, beyond crystal size distribution and NC density, ordering is also governed by NC-NC and NC-substrate interactions, and the presence of external forces. Interparticle interactions may include van der Waals attraction, steric repulsion, dipole-dipole interactions and Coulomb interactions between charged ligands. Changing these interactions can significantly modify the self-assembly process. In particular, the organic ligands passivating the NC surface or the specific substrate chemistry were found to change the extent of the mutual interactions between neighbouring particles as well as the strength of NC adhesion on the substrate, thereby modifying the surface mobility which plays a critical role [5].

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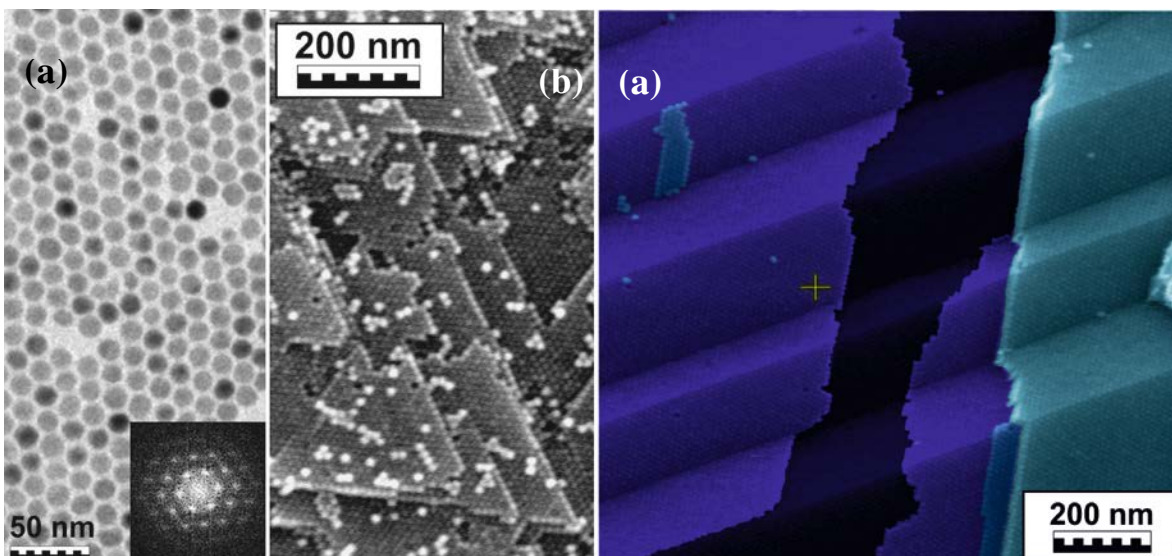


Figure 1. (a) TEM image of 13 nm iron oxide NCs. Inset shows the FFT pattern for the assembly, which is compatible with that expected for a cubic phase viewed down the [111] orientation or a hexagonal phase lattice down the [001] orientation. (b) SEM image of superlattice triangular structures of iron oxide NCs formed on SiO₂/Au surface by entropy driven diffusion process. (c) Superlattice structures formed on SiO₂/Au surfaces by drop casting 10 μ M NC solution.

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