Nature and Enhancement of the magnetic surface contribution in model NiO nanoparticles

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Abstract – We report an alternative synthesis method and novel magnetic properties of Ni-oxide nanoparticles (NPs). The NPs were prepared by thermal decomposition of nickel phosphine complexes in a high-boiling-point organic solvent. These particles exhibit interesting morphology constituted by a crystalline core and a broad (~ 80 % *vol.*) disordered superficial shell. Our results suggest that the magnetic behavior is mainly dominated by strong surface effects, which become evident through the observation of shifted hysteresis loops (~5.0 kOe), coercivity enhancement (~10.9 kOe) and high field irreversibility ($\geq$ 50 kOe). Both exchange bias and vertical shift in magnetization can be observed in this system below 35 K after field cooling. Additionally, the exchange bias field shows a linear dependence on the magnetization shift values, which elucidate the role of pinned spins on the exchange fields. The experimental data are analyzed in terms of interplay between the interface exchange coupling and the core antiferromagnetically ordered structure.

Ni-oxide nanoparticles were synthesized by adapting a procedure described by Tang *et al.*, for silver monodisperse nanocrystals [1]. Firstly, the Ni-metallic precursor ($C_{54}H_{45}P_3ClNi$) was prepared from the stoichiometric amount of $Ni(NO_3)_2.6H_2O$ (0.1 mmol, 0.029g), triphenylphosphine (0.3 mmol, 0.078g) and tetraethylammonium chloride hydrated (0.03 mmol, 0.016g), which were mixed in 40 mL of warm acetonitrile (ACN) and heated at 75^oC for 3-4 hours under continuous Ar flux with intermediate stirring. Crystals of desired size can be achieved by cooling the solution slowly to room temperature. Thereafter, 20 mL of 1-octadecene and 3 mL of oleyamine (OLA) were slowly added to this solid solution (keeping the molar ratio of Ni/OLA=1:20). The above mixture was slowly heated up to a final temperature of 225^0C for 1 hour under Ar flux with heating rate of $3^oC/min$.

Our structural results show that our colloidal NiO NPs with interesting morphology constituted by a crystalline core and a broad disordered superficial shell (~ 80 % in *vol.*) as confirmed from an excellent correlation using TEM, SAXS and XRD data. The magnetic behavior mainly dominated by a large surface effect, which play a major role particularly at low temperatures. This is responsible for the observed exchange bias field, vertical shift, high field irreversibility and a large coercivity in the hysteresis loop after FC process. The strong bias-interaction between the core and shell magnetic structures was quantified. The *H*-dependence of the H_{EX} (*T* = 5 K), gave a maximum value of 5.0 kOe after FC mode in an applied field of 15 kOe, whereas the *T*-dependence, H_{EX}, vanished for temperatures *T* > 35 K. These characteristics make these particles an excellent model system to study the finite size effect and the magnetic surface contribution in nanostructured systems.
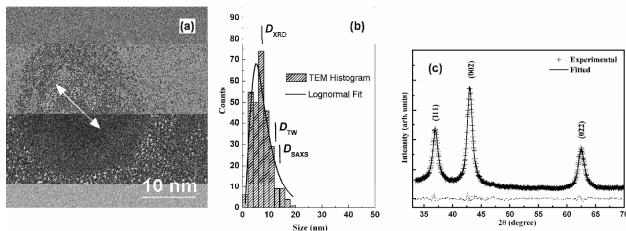

Figure 1: Figure 1 (a) HRTEM image for the NiO nanoparticle sample, (b) histograms of the particle size distributions calculated from TEM, and (c) (color online) XRD pattern for the NiO nanoparticle along with the Reitveld fits.
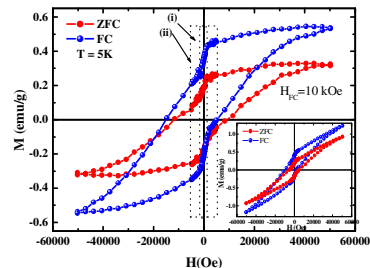

Figure 2: a) Figure 3 (color online) ZFC and FC hysteresis loops taken at 5 K for the NiO nanoparticle after subtracting the high field linear magnetization region. Inset showing the corresponding loops at 5 K.

References [1] Yun Tang and Min Ouyang, Nature materials, **6**, 754 - 759 (2007).