EXCHANGE BIAS IN HYBRID NANOCRYSTALS OF ZINC OXIDE

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Introduction

In the recent years, development of magneto-optical nanomaterials has drawn rising interest due to their many perspective applications, ranging from spin-LEDs to multimodal imaging and therapeutic action. Bottom-up approaches to nanocrystals (NCs), such as colloidal chemistry methods, have paved the way towards such multi-functional nanoscale systems [1]. Especially promising are seeded-growth approaches for multi-component hybrid nanocrystals (HNCs), with which the technological potential is boosted beyond that of conventional nanoparticle of individual materials [2]. Engineering the interfacial regions of such HNCs represents a prerequisite to exchange coupling mechanisms that may modify the ultimate macroscopic response (e.g. exchange bias at the ferromagnetic – antiferromagnetic interfaces). Numerous protocols are available to synthesize HNCs built of a magnetic material and a chalcogenide semiconductor (MQ; M= Cd, Zn, Q= S, Se, Te) in various geometrical configurations. Less is known when the semiconductor is an oxide, like ZnO. One such type of magnetic-fluorescent HNC has been reported up to now, which consists of a core-shell type of architecture with the ZnO in the shell and FePt in the core regions, respectively [3]. An advantage of this system is related to the lower toxicity the oxide-based HNC. To make a step further, no work has demonstrated HNCs of ZnO associated with either Fe NPs or even with a $Fe@Fe_xO_y$ core-shell type of sections. Difficulties arise from the Fe metal sensitivity to oxidation. It is challenging though due to the interesting exchange coupling effects [4] originating from the interconnection between dissimilar magnetic property domains. Here we present some progress in this field by demonstrating a new highly asymmetric HNC based on ZnO nanorods (NRs) decorated with $Fe@Fe_xO_y$ core-shell magnetic domains and the study its magnetic and optical properties.

Experimental

Nanocrystal Synthesis
ZnO NRs were synthesised under anaerobic conditions via thermal decomposition (at 280°C) of Zn-acetate in hexadecylamine [5]. After the purification the NRs were used as core seeds onto which $Fe@Fe_xO_y$ core-shell nanocrystals were grown heterogeneously upon decomposition of the $Fe(CO)_5$ at high temperature (235°C) in liquid octadecene solvent under Ar-flow. The result was an initial nucleation and growth of metallic Fe nanoparticles onto the semiconductor NR surface without any ZnO facet preference. The formation of a polycrystalline Fe_xO_y shell occured over the Fe domains, at the same elevated temperature and acted as a protection to the core from complete oxidation. This colloidal chemistry pathway produced HNC architectures where the oxide semiconductor shared multiple small interfaces with the iron-based particles.

Apparatus and Procedures
X-ray diffraction (XRD) patterns of the HNCs powders were taken on a Rigaku D/Max-2000H rotating anode diffractometer, with Cu-Ka radiation. TEM images were recorded on a JEOL 2100 high-resolution transmission electron microscope (HRTEM) operating at an accelerating voltage of 200 kV. The magnetic properties of the samples were studied (T= 5-300 K) on a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design MPMS XL5). Photoluminescence (PL) experiments at 300 K employed a 325 nm He-Cd laser (35 mW max power). The PL signals were analysed through a double-grating monochromator and detected in a CCD camera.

Results and Discussion

Typical TEM images (Fig. 1) illustrate the morphology and the size of the bare NRs, as well as that of the HNCs. The ZnO nanorods have a “bullet like” shape and are grown in the same crystallographic direction, namely, along the c-axis [0001] of the wurtzite structure, with an average length of ~240 nm and a diameter of ~60 nm (Fig. 1a). During the seeded-growth synthesis, the NRs were employed as starting substrates to accommodate deposition of the magnetic material. High-resolution TEM images show that the magnetic entities have a core-shell type of structure, with an Fe core of ~20 nm and Fe_xO_y polycrystalline shell of ~4-5 nm thickness (Fig. 1b). The two possible candidates include the cubic spinels, maghemite and magnetite, which however display similar diffraction patterns that cannot be

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discriminated. On the other hand, we determined that the core has the *bcc* structure of the Fe-metal. Interestingly, the TEM study resolves a spatial separation (void) of ~1 nm between the core and the shell in the Fe@Fe_xO_y domains (Fig. 1). The void formed during the stage in which the solution was left open to air for 1 hr at 120°C. This structural discontinuity can be attributed to the Kirkendall effect, involving a faster migration of the Fe metal atoms from the core to the shell than that of the oxygen atoms inwards [1].

Although the void may be common in metal-metal oxide HNCs, it plays a crucial role as it can be exploited for tailoring the magnetic response in a hybrid nano-architecture. In the present case, magnetic hysteresis loops of the ZnO HNCs (Fig. 2) indicated a ferromagnetic (FM) behavior with coercive field, H_c~ 302 and 46 Oe, at 300 K and 5 K, respectively. The diamagnetic contribution of the bare ZnO NRs was measured as negligible. It is worth noting that the zero-field cooled (ZFC) M-H (5 K) shows an abrupt jump at low-field (Fig. 2a). Having taken into account the core-shell type of structure of the magnetic motif, we suggest that such features are due to low-field switching behavior of spins, which is attributed to the depinning of the moments of the polycrystalline ferri-magnetic (FiM) shell. In the case of the ZnO HNCs no shift of the hysteresis loop along the field axis after field-cooling (10 kOe) is observed, which could have otherwise indicated exchange-bias (H_{EB}), expected in binary systems made of a FM core interfaced with a FiM shell. As the associated exchange coupling across interfaces decays exponentially with the distance, the lack of H_{EB} in our ZnO-based HNCs is in accord with the presence of the ~1 nm void in the Fe@Fe_xO_y domains.

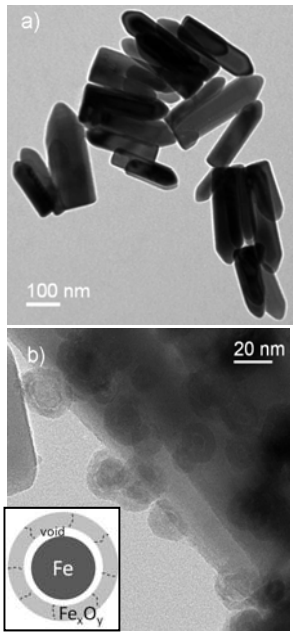

Fig. 1 TEM images of (a) the ZnO NRs and (b) the HNCs; inset: sketch of the core-shell magnetic domain.

Comparative PL measurements (Fig. 2b) of the same HNCs demonstrate the structural quality of their ZnO semiconductor component, with a pronounced near-band-edge (NBE) UV emission and very low contribution in the visible due to deep-level trap states. Furthermore, having modified the synthetic conditions (e.g. employ a bi-surfactant mixture for ZnO seeds), smaller magnetic particles were obtained, either with or without a void. For example, the hysteresis loop for ZnO HNCs with smaller Fe@Fe_xO_y domains (8 nm Fe core and 1 nm Fe_xO_y shell, no void) exhibits exchange-bias and shift of the loop, ~200 Oe, along the field axis after (10 kOe) field-cooling at 5 K. We postulate that size-control, associated with interface engineering, can give the opportunity to study cross coupling effects, like exchange bias and profit from enhanced magnetic anisotropy, both of which represent advantageous properties for magneto-electronic devices.

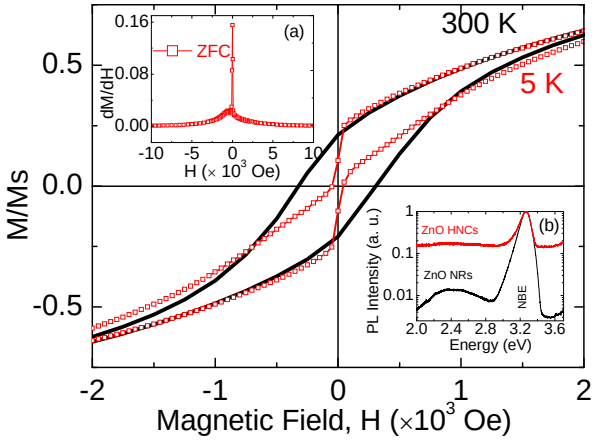

Fig. 2 Normalized M-H hysteresis loop for the ZnO HNCs at 300 K and ZFC at 5 K. Inset: (a) dM/dH plot at 5 K during the negative sweep direction (from 10 to -10 kOe), (b) ZnO HNCs normalized PL spectra at 300 K.

Conclusion

In summary, we have demonstrated a colloidal chemistry protocol for the development of hybrid nanocrystals with magnetic and optical functionalities. The core-shell structure of the magnetic components, their tailored exchange coupling and the strong UV emission suggest that this system holds promising technological prospects.

Acknowledgments

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