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Research articles

Beating the macroscopic quantum tunneling limit by man-made magnetic dead layers

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ABSTRACT

Magnetic dead layers (MDLs) are always undesirable in practical applications due to their highly frustrated spin configurations and severe degradation of host magnetism. Here we provide new insights in MDLs and unravel their attractive prospect for ferrimagnetic hybrid of Fe_3O_4 and γ-Fe_2O_3 (denoted as Fe_3O_4@γ-Fe_2O_3 in the main text) to exhibit macroscopic quantum tunneling (MQT) phenomena in measureable kelvin range. The 3 nm-sized negatively-charged Fe_3O_4@γ-Fe_2O_3 nanoparticles were immersed in various metal chloride solutions containing Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, and Fe^{2+} cations to form cationic MDLs via electrostatic attraction. These man-made MDLs, if being of positive enough zeta potentials, greatly disordered the magnetic dipole interactions among Fe_3O_4@γ-Fe_2O_3 nanoparticles and induce extra energy barrier to yield pronounced MQT effect in Fe_3O_4@γ-Fe_2O_3 nanoparticles even though they were dispersed neither in water nor in oil. Their crossover temperatures dividing MQT and purely thermal relaxation were found to be one order of magnitude higher than reported values in other MQT systems, and more strikingly, they could be tailored by altering the soak period in our facile and scalable route.

1. Introduction

Macroscopic quantum tunneling (MQT) effects include quantum tunneling of magnetization in nanoscopic magnets [1], quantum nucleation of magnetic bubbles [2] and quantum depinning of domain walls from defects in bulk ferromagnets [3]. MQT is of fundamental importance because it not only presents a chance to deal experimentally with a single quantum object of nanoscopic size, but also offers a very exciting possibility for computers using nanoscopic magnets for memory in the field of information and computation applications [4].

In the absence of an external magnetic field, the magnetic moments of a ferromagnet align along with the anisotropy axis with two equivalent but opposite orientations that are separated by an energy barrier. At low temperatures, the magnetic moments have a certain probability to tunnel through this energy barrier due to the quantum tunneling effect. That means, the "north" and "south" magnetic poles inside the ferromagnet may suddenly interchange. As the temperature rises, the thermal transitions dominate the energy barriers. In this scenario, the most important parameter to evaluate the MQT ability of a material is thought to be a crossover temperature T_C, below which quantum under-barrier transitions dominate. During the last decade or so, many materials with T_C values being of few kelvins are successively discovered, such as the polynuclear cluster compounds (e.g., Mn_{12}-ac [5,6]), mesoscopic particles of ferritin protein [7], and granular rare earths (e.g., Dy imbedded in a Cu matrix [4]). However, unlike their ferrite counterparts (e.g., $CoFe_2O_4$ and $NiFe_2O_4$ with T_C values above 2 K [4,8]), the crossover temperatures of both magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) nanoparticles have not yet been found either dispersed in water or oil [9,10]. It is reported that quantum relaxation in these particles should not be expected above 0.3 K [9]. Therefore, it is of both scientific and commercial aspiration to have a facile and scalable route to leapfrog this MQT limit due to the well balance between cost and performance of these ferrimagnetic (FiM) iron oxides.

Considering antiferromagnetic (AFM) materials feature the merits of significantly higher tunneling rates and crossover temperatures than those of ferromagnets, a design of AFM/FiM nanocomposites may greatly enhance the T_C values of FiM Fe_3O_4 and γ-Fe_2O_3 materials from the assumed millikelvin range to the observable kelvin range. Besides, this material design will certainly mitigate the formerly insurmountable problem that relaxation measurements on AFM materials are much more difficult than those on ferromagnets due to their extremely low net magnetic moment. However, the understanding and tuning of spin structures at AFM/FiM interfaces is a really big hurdle, so that facile

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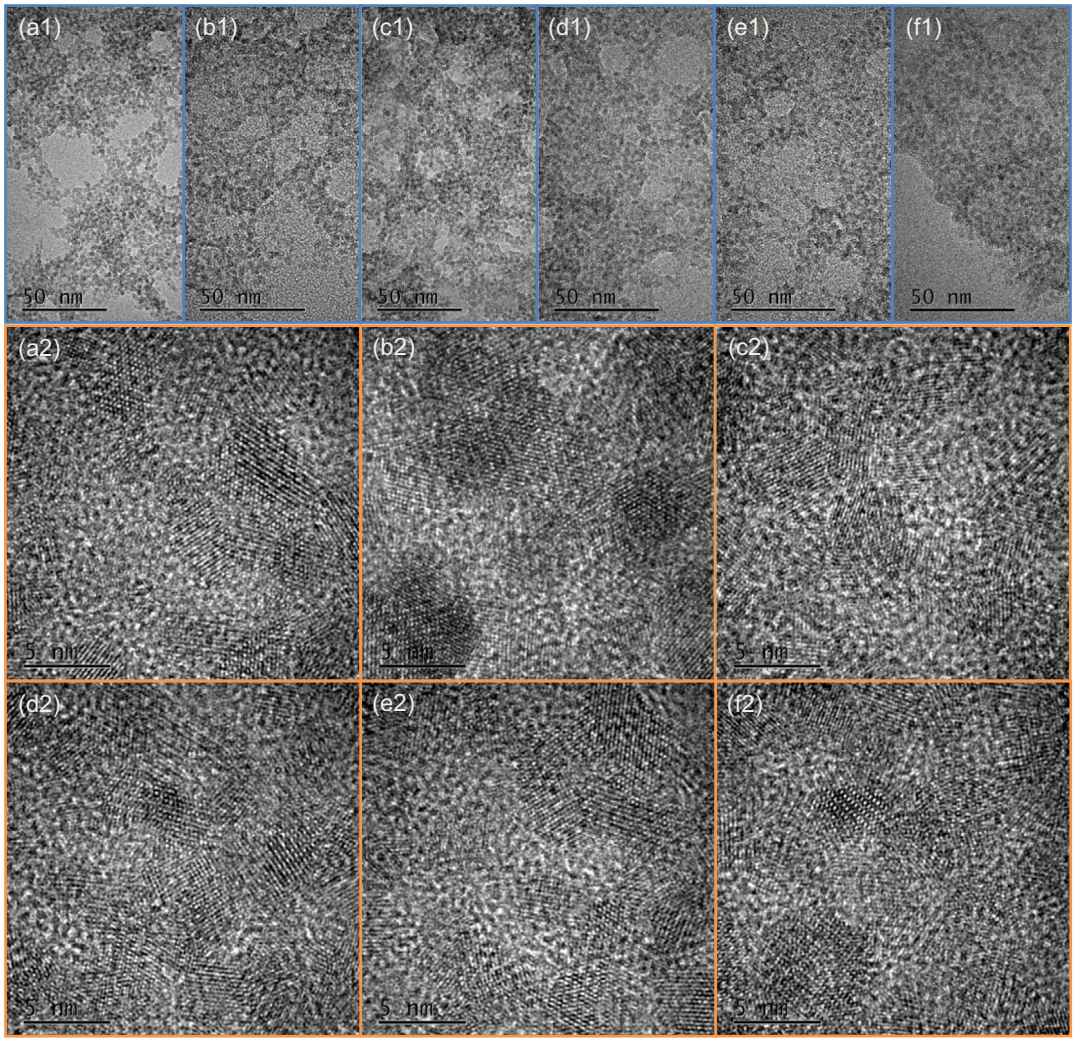

Fig. 1. TEM and HRTEM images of (a) bare Fe_3O_4@γ-Fe_2O_3 nanoparticles and their adsorption of (b) Mn^{2+}, (c) Co^{2+}, (d) Ni^{2+}, (e) Fe^{3+}, and (f) Fe^{2+} cations.

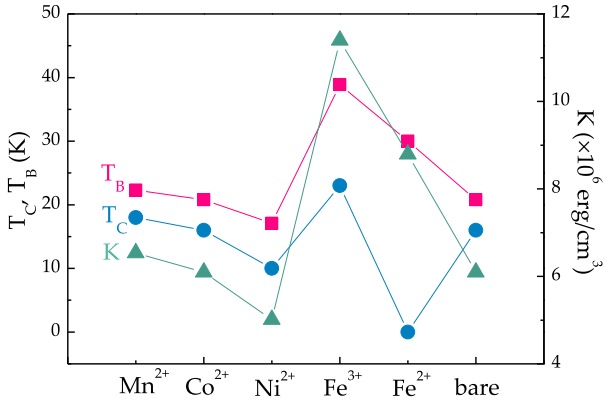

Fig. 2. T_C, T_B and K values for bare and cation-adsorbed Fe_3O_4@γ-Fe_2O_3 nanoparticles.

and economical fabrication for easily repeatable AFM/FiM interfaces with well-defined spin configuration remains elusive. In this work, we intentionally construct various cationic MDLs on bare Fe_3O_4 and γ-Fe_2O_3 nanoparticles to bypass this cumbersome issue. MDL refers to a common surface spin-disordered region of a ferromagnet, wherein the magnetic couplings are highly frustrated and hence leading to a severe degradation of host ferromagnetism. In this sense, MDLs are believed to be useless and always undesirable in practical applications [11]. In our experiments, we utilize a simple electrostatic adsorption method to effectively graft various paramagnetic metal cations (i.e., Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+} and Fe^{2+}) on the pre-synthesized negatively charged Fe_3O_4@γ-Fe_2O_3 nanoparticles. The adsorbed metal cations are proved to be magnetically coupled with FiM host lattice with few angstroms thick, and behave like man-made MDLs. These MDLs are expected to heighten the inherently-low anisotropy energies of Fe_3O_4@γ-Fe_2O_3 cores, and hence greatly enhance their crossover temperatures to the observable kelvin range.

2. Experimental

In our experiments, Fe_3O_4@γ-Fe_2O_3 nanoparticles with four different sizes are synthesized according to our previous report [12] with little modification. Typically, 2 mmol of $FeCl_3 \cdot 6H_2O$ was dissolved into 50 mL of deionized water. Then, 10 mL of Na_2CO_3 aqueous solution (0.6 mol L^{-1}) was added with vigorous stirring. Five minutes later, 0.5 g of ascorbic acid was added into the above solution and stirred for another ten minutes. Finally, the mixture was transferred into a Teflon-lined stainless-steel autoclave with the capacity of 100 mL for hydrothermal treatment at 160 °C for 3 h,