

One-pot synthesis of $\text{Fe}_{3-x}\text{O}_{4-x}@\text{MnO}$ nanoparticles allowing high control of the shell thickness and physicochemical properties

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The synthesis of novel nanomaterials with controlled structure and composition that show desired physicochemical properties is one of the most promising goals in the field of advanced materials.

We developed a one-pot synthesis of core@shell nanoparticles (NPs) having a single-crystal iron oxide ($\text{Fe}_{3-x}\text{O}_{4-x}$, $0 \leq x \leq 1$) ferrimagnetic (FM) core, and a polycrystalline MnO antiferromagnetic (AFM) shell. This protocol allowed us to control the shell thickness and, therefore, the magnetic properties of the NPs. In particular, we modified a standard solvothermal synthesis of manganese ferrite [1], based on the high-temperature (~ 300 °C) decomposition of $\text{Fe}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ in the presence of oleic acid (OIAc), replacing $\text{Mn}_2(\text{CO})_{10}$ with manganese(II) dioleate MnOl_2 , a Mn precursor we previously used for the synthesis of the MnO NCs.[2] We studied the synthetic outcome as a function of the reaction time using the reactants with the Mn:Fe:OIAc = 1:2:6 molar ratio.

We investigated the chemical composition of the core-shell NPs with nanometric resolution by means of two microanalytical techniques: STEM/EDX and EELS/ESI. The atomic ratio Mn:Fe is 1:2 independently of the reaction time but the distribution of the metal ions inside the NPs significantly changes during the reaction

Reaction time (min)	Shell thickness (nm)				
	Median	Mean	S.E.M.	Std Dev	Disp %
10	0.61	0.48	0.12	0.47	77%
30	0.38	0.35	0.04	0.25	66%
60	0.25	0.24	0.02	0.18	72%
90	0.04	0.03	0.01	0.12	300%

Tab. 1 Thickness of the MnO shell in the $\text{Fe}_{3-x}\text{O}_{4-x}@\text{MnO}$ NPs at different reaction times. Disp = Median/(Std Dev) measures the thickness dispersity of the sample.

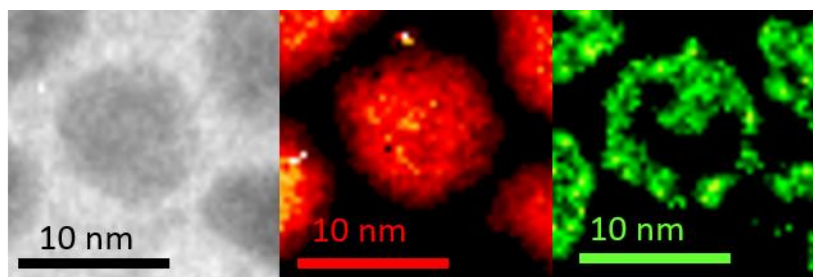


Fig.1 ESI elemental maps of a Core@Shell NP (time:10 min). Left ref. TEM image, Fe (red), right: Mn (green).

At the early stage of the reaction Mn is mainly located in the external shell, this is a clear sign that the iron precursor decompose faster than the manganese one, generating the seeds on which the $\text{Mn}(\text{oleate})_2$ starts to grow. As the reaction proceeds, Mn diffuses into the iron oxide core. At reaction time ≥ 60 min, the core-shell NPs were transformed into homogeneous single-crystal MnFe_2O_4 NCs having stoichiometric composition and equivalent diameter 19.2 ± 1.8 nm.

These NPs have interesting magnetic properties due to the changing exchange coupling across the FM/AFM interface influenced by the changing of the shell thickness. In fact the large exchange bias field is detected in the early core-shell NPs, vanishes in the late MnFe_2O_4 NCs where the chemical inhomogeneity disappeared. Moreover, this protocol allowed us to easily control the shape and size of the NPs.

In summary, we developed a synthetic method where the nanostructure, composition, and magnetic properties of the NPs could be modulated by just changing the reaction time, during which cation diffusion occurs in the nanosystem.

[1] E.Kang *et al.*, *J. Phys. Chem B*, **2004**, 108, 13932.

[2] A.Puglisi *et al.* *Chem. Mater.* **2010**, 22, 2804–28133.