A simple aminoalkyl siloxane-mediated route to functional magnetic metal nanoparticles and microspheres

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The synthesis of superparamagnetic metal nanoparticles has been previously described, *e.g.*, by applying $Co_2(CO)_8$ with organometallic precursors (aluminium trialkyls),[1] or polysiloxane micelles.[2] Besides the control of size, structure, and composition, surface properties and functionalities of nanoparticles are an important issue of research, *e.g.*, for further preparing functional multicomponent nanostructures or nanocomposites.

We use amino-functionalized siloxanes not only to directly control particle nucleation and growth by coordinating to the metal surface but also to provide reactive siloxane groups on the particle surface as a functional interface for further deposition of oxides, such as SiO_2 and TiO_2. This procedure permits the synthesis of Co and Fe nanoparticles of various sizes by thermolysis of $Co_2(CO)_8$ or $Fe(CO)_5$ in solution, respectively, and the preparation of magnetic microspheres.

As show by UV-visible and FTIR spectrometry the reaction proceeds via a homomolecular disproportionation in which the uncharged $Co_2(CO)_8$ initially disproportionates into cobalt(II) cation and cobalt carbonylate anion. There are several key parameters that control the growth aspects including type and concentration of metal precursor and siloxane, metal to siloxane ratio, reaction temperature, heating rate, etc. The delicate choice of these key parameters allows to tune, *e.g.*, the size of the particles. After surface passivation with low doses of oxygen (*smooth oxidation*), the nanoparticles show a good resistance to oxidation. The presented procedure can be also applied for the synthesis of iron nanoparticles by decomposing $Fe(CO)_5$ in the presence of APTES. The size, structure, and magnetic properties of the particles were characterized by TEM, EDX, XPS, Mössbauer spectroscopy, XRD, AES-ICP, and magnetic measurements.

The applied bifunctional siloxane compound not only controls particle formation by complexation of cobalt but also serves as a coupling agent for SiO_2 and TiO_2 deposition, resulting in functional magnetic microspheres. Such magnetic microspheres are typically based on magnetic iron oxide nanoparticles. Microspheres equipped with magnetic metal nanoparticles are interesting since they exhibit a much higher M_s and magnetophoretic mobility. However, Co is easily oxidized which is probably among the reasons why much less examples of Co@SiO_2 microspheres exist in the literature. Magnetic Co@SiO_2 microspheres are obtained by adding and heating TEOS in water/ethanol in the presence of the APTES-functionalized Co nanoparticles. The Co@SiO_2 microspheres can be further functionalized with a molecular Rh precursor via formation of a phosphine complex and used as a magnetically recyclable catalyst in hydroformylation reactions (hydroformylation of 1-octene). Magnetic Co@TiO_2 microspheres are obtained by hydrolysis of titanium (IV) n-butoxid in the presence of the Co nanoparticles. TiO_2 is typically applied as photocatalytic system for the treatment of various biological, organic, or inorganic pollutants in water.[3]
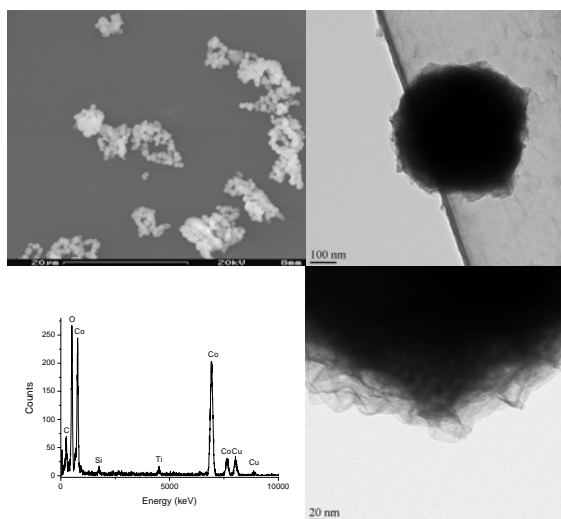
Fig. 1. SEM and TEM images and EDX spectrum of magnetic TiO$_2$ microspheres.

References

[1] H. Bönnemann, W. Brijoux, R. Brinkmann, N. Matoussevitch, N. Waldöfner, N. Palina, and H. Modrow, *Inorganica Chimica Acta*, **2003**, 350, 617.

[2] J. Stevenson, M. Rutnakornpituk, M. Vadala, A. Esker, S. Charles, S. Wells, J. Dailey, and J. Riffle, *J. Magn. Magn. Mater.*, **2001**, 225, 47.

[3] X.M. Song, J.M. Wu, and M. Yan, *Thin Solid Films*, **2009**, 517, 4341.