

## **Polymer and Colloid Highlights**

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## Stable Ferromagnetic Nanoparticle Dispersions in Aqueous Solutions

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The combination of magnetism and chemistry brings many opportunities: magnetic particles can be influenced by external forces (magnetic separation) and additionally allow unique analytical methods with high specificity and low detection limits. As a result superparamagnetic iron oxide nanoparticles (SPIONs) have found several applications in biomolecule separation technologies and biomedical diagnostic devices. However, from a materials perspective SPIONs have several drawbacks including relatively weak magnetic properties and the chemically fragile nature of the surface chemistry (siloxane chemistry on oxidic surfaces). Carbon-coated metallic (iron or cobalt) nanoparticles on the other hand offer a superior magnetic saturation and covalent C–C surface chemistry, but the ferromagnetic properties induce particle aggregation, which impedes the utilization of these materials for many applications.

As the adsorption of polymers or simple surfactants on the surface of these carbon-coated particles was not effective in overcoming the strong attractive forces needed for the formation of stable (= non-aggregating) dispersions, a more elaborate approach was required. For this reason polymer brushes were grown from the surface of the carbon-coated metallic particles utilizing SI-ATRP chemistry (surface initiated atom transfer

A)

SI-ATRP
Monomer 2

SI-ATRP
Monomer 2

SI-ATRP
Monomer 2

SI-ATRP
Monomer 2

Ke

Br

RMIC

RM

Fig. 1. (A) Block copolymers are grown on the surface of carbon coated metallic nanoparticles *via* SI-ATRP. (B) The dispersions can be printed with a consumer off-the-shelf ink-jet printer, which allows the low-cost formation of magnetic patterns on paper.

radical polymerization) and methacrylic monomers (Fig. 1A). The direct, covalent attachment of highly charged polymer brushes on the graphene layers circumvents stabilizer detachment and permits the preparation of stable dispersions of ferromagnetic, graphene protected nanoparticles (Fig. 1B).<sup>[1,2]</sup> A minimal polymer length of six charged monomer units was required to achieve a full dispersability. The formed dispersions are stable over the long term and can even be printed by a conventional inkjet printer (Fig. 1B). If printed on paper, this 'ferromagnetic ink' enables rapid magnetic paper and ink recycling.<sup>[3]</sup>

The ATRP approach further allows the formation of block copolymers with a second monomer, which can serve as a platform for postmodification. This is essential for the attachment of (bio)chemical analytes and for application of the ferromagnetic particles in diagnostic detection devices. As an example we introduced epoxide functionalities, which can be used for the direct reaction with proteineous amines, or can be further modified to be compatible with the popular Huisgen 1,3-diploar cycloaddition ('click chemistry').<sup>[2]</sup>

Even with postmodification possibility, the ferromagnetic particles displayed an excellent dispersability in pure water, and also in biological relevant media (PBS, DMEM, Fig. 2), displaying the usefulness of the materials for biomolecule capturing and detection.

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<sup>[3]</sup> M. Zeltner, L. M. Toedtli, N. Hild, R. Fuhrer, M. Rossier, L. C. Gerber, R. A. Raso, R. N. Grass, W. J. Stark, *Langmuir*, 2013, 29, 5093.

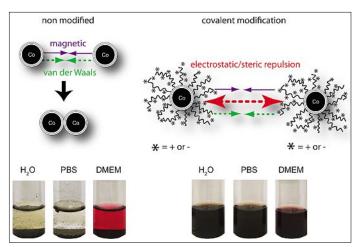


Fig. 2. While uncoated metallic particles rapidly agglomerate, the particles carrying highly charged polymer brushes remain in suspension, even at high salt concentrations in physiological solutions and cell culture media (PBS and DMEM).

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<sup>[2]</sup> C. J. Hofer, V. Zlateski, P. R. Stoessel, D. Paunescu, E. M. Schneider, R. N. Grass, M. Zeltner, W. J. Stark, *Chem. Commun.* 2015, 51, 1826.