

A Generic Single-Step Synthesis of Monodisperse Core/Shell Colloids Based on Spontaneous Pickering Emulsification**

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Monodisperse core-shell colloids are widely applied in various fields such as biomedicine, catalysis, and optics, and are also important for fundamental studies in colloid and interface science.^[1–4] The synthesis of particles with a well-defined core-shell morphology still comprises several separate steps such as core preparation, its subsequent functionalization with a coupling agent and the deposition of one or several shells.^[5–11] This multi-step approach towards composite colloids has some serious drawbacks. First, both coupling chemistry and synthetic pathways need to be specifically designed for the materials involved. Second, multi-step reactions often require intermediate purifications or separations that not only reduce the net yield but also hamper the up-scaling of composite-colloid synthesis for applications such as those referred to above.^[1–3] In this communication we report a novel single-step synthesis of monodisperse latex-based core-shell colloids that completely relies on self-assembly of the components involved (Fig. 1).

Recently we discovered that nano-particles may induce spontaneous emulsification of oil in water to thermodynamically stable, monodisperse Pickering emulsions.^[12] This novel emulsification phenomenon, first observed for magnetite (Fe_3O_4) nano-particles, turns out to be quite generic since also cobalt ferrite (CoFe_2O_4) and commercial silica particles (Ludox) lead to stable Pickering emulsions.^[13] It was also shown that using the chemically reactive oil (methacryloxypropyltrimethoxysilane, TPM), Pickering emulsions could be polymerized by addition of a radical initiator (potassium persulfate, KPS) resulting in stable colloidal dispersions (Fig. 2a and b).

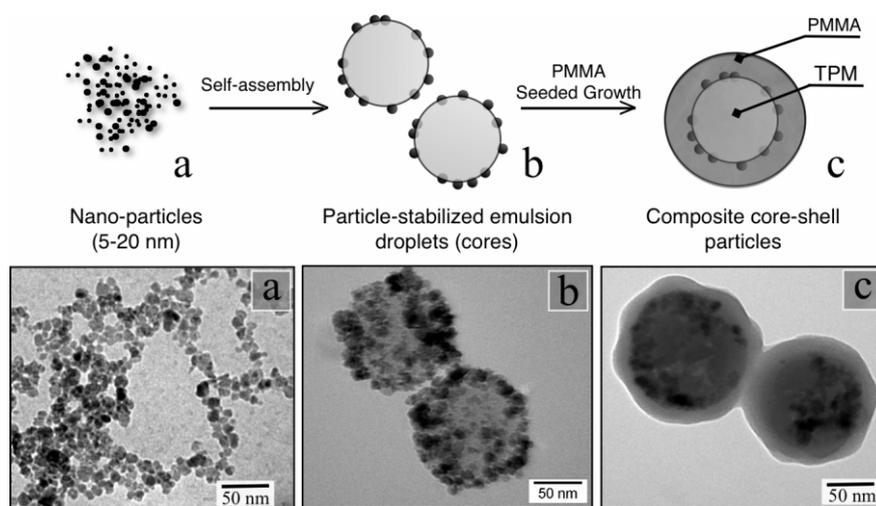


Figure 1. Scheme for core-shell particles self-assembly (above) and corresponding TEM images (below). Nano-particles (a) self-assembly into polymerizable Pickering emulsion droplets (b) which are incorporated into PMMA shells (c). Core polymerization and shell formation occurs simultaneously upon addition of the initiator KPS.

Here we investigate the use of such particle-stabilized emulsions (hereafter TPM-emulsions) in a seeded growth polymethylmethacrylate (PMMA) polymerization, to obtain in one single and simple step, PMMA colloids with various inorganic cores. Initially we focused on TPM-emulsions merely as a source for monodisperse inorganic cores to seed a surfactant-free PMMA polymerization.^[14] However, exploring what would happen when TPM-emulsions are prepared directly in the presence of methylmethacrylate (MM) we noticed that, surprisingly, MM does not interfere at all with the TPM emulsification. In fact, during the latter emulsification, MM remains present as a separate oil phase (Fig. 2c insert). Addition of a water-soluble radical initiator, however, not only induces polymerization of the TPM-emulsion droplets to solid spheres, but simultaneously also triggers the polymerization of PMMA shells onto these spheres. Thus the floating MM phase (Fig. 2) acts as a monomer source for this PMMA shell formation and, indeed, the shell thickness continues to grow until the whole MM phase is consumed.

It turns out that, in addition, polymerized TPM-emulsions are also excellent seeds dispersions for growing polystyrene shells via surfactant free emulsion polymerization, as well as silica shells via the classical Stöber synthesis, showing that the spontaneous Pickering emulsification allows for the preparation of polymeric as well as inorganic composite model colloids.^[15]

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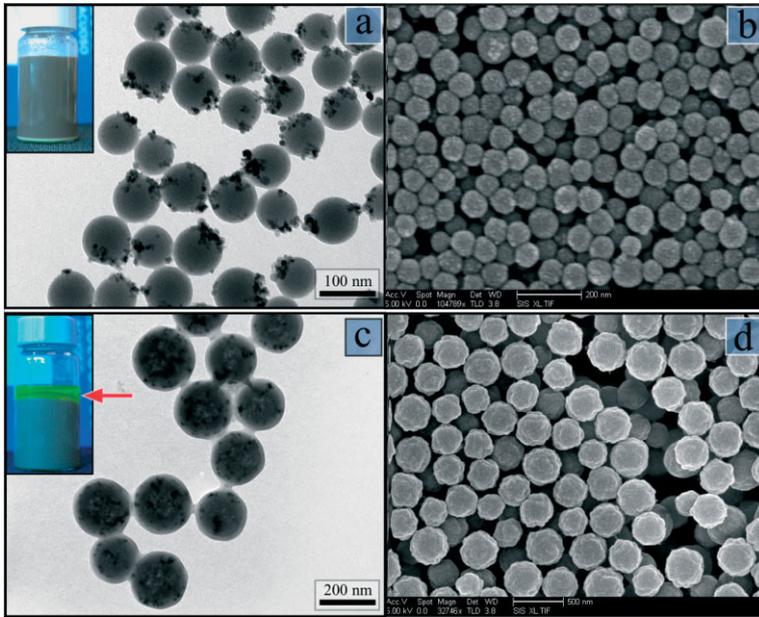


Figure 2. Morphology of cores and core-shell particles. Magnetite-stabilized TPM-emulsion polymerized with (c,d) and without (a,b) MM present. EM pictures show that when no MM is present the TPM-emulsion polymerizes leaving magnetite exposed on the droplet surface (visible as dark spots on the TEM image (a) and as bright spot on the droplet surface in the SEM image (b)). Conversely, when MM is added, the emulsion droplets are embedded into a smooth PMMA latex shell (c,d). Inset of figure (c) shows the excess of MM floating on top of the emulsion (the yellowish color is due to the presence of a fluorescent dye).

EM analysis shows a narrow size distribution (the polydispersity is about 10%) for the resulting core-shell particles (Fig. 2c and d), which partially reflects the low polydispersity of the starting emulsions (Fig. 2a and b). TEM and SEM pictures clearly show (Fig. 2) that when no MM is added to the TPM-emulsion, the inorganic nano-particles remain exposed on the particle surface even after polymerization (Figs. 1b, 2a and b). In contrast, when an excess of MM is present (Fig. 2c and d) polymerized particles have an outer shell of PMMA which covers the whole emulsion droplet.

Fluorescently labeled core-shell particles for confocal microscopy studies can also be prepared via the same single-step method. When a small amount (about 1% of the total oil volume) of fluorescent dye 7-nitrobenzo-2-oxa-1,3-diazol (NBD) covalently coupled with a methylaminoethylmethacrylate (NBD-MAEM) is added to the initial mixture, it mixes with both TPM and MM, yielding, after polymerization, homogeneously fluorescent particles.^[16] When polymerized in absence of MM, TPM-emulsions can be transferred in Stöber mixtures of ammonia (or tetramethyl-

ammonium hydroxide) in ethanol, where the growth of a silica shell can be carried out by addition of TEOS (an example of silica deposition on colloidal seeds can be found in Ref. [17]).

Figure 3d shows a sample containing such emulsion droplets (stabilized by adsorption of cobalt ferrite nanoparticles) incorporated into a 22 nm thick silica shell, resulting in magnetic core-shell colloids which rapidly crystallize when exposed to a magnetic field gradient (Fig. 3d).

Some distinctive advantages of the synthesis procedure in this communication are as follows. Particles design is simplified by the fact that size and numbers of cores are reproducibly controlled by the initial amount of TPM and nano-particles, whereas the relative amount of MM sets the latex shell thickness. Moreover, because the formation of TPM-emulsion droplets is thermodynamically favorable, and because of the high adsorption energy of the nano-particles at the TPM/water interface (up to 200 kT for magnetite), no purification steps are needed once the polymerization is completed to remove any free inorganic particles.^[12] Finally, polymerized TPM-emulsions are also suitable substrates for the growth of other polymers (e.g., polystyrene) or silica shells.

Thought at this stage the molecular details of the TPM-emulsification are still unclear we have identified some general guidelines for preparing stable

Pickering emulsions. First of all, the nano-particles which has been used, were charge-stabilized by means of ammonia or quaternary ammonium hydroxides. Moreover, those particles were wetted by both water and TPM, and they always had radii smaller than 15 nm. We also found no influence of the particle shape and polydispersity with respect to the emulsion formation. Magnetite and cobalt ferrite dispersions had a

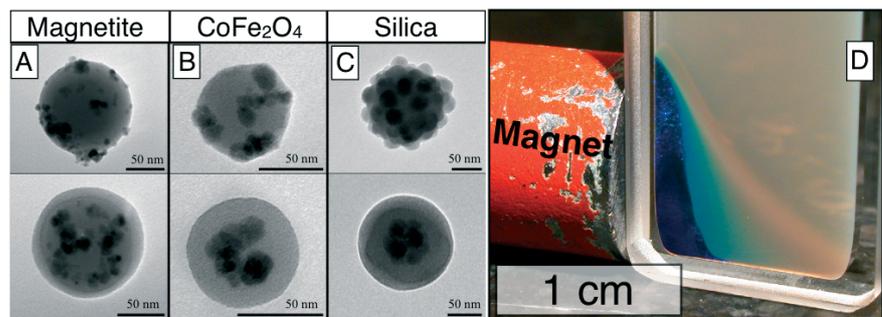


Figure 3. Example of composite core-shell colloids with and without PMMA outer shell. Our method is potentially suitable for preparation of a large variety of core-shell composite colloids. Shown are three different examples where the particle cores consist of polymerized TPM-droplets stabilized by (A) magnetite, (B) cobalt ferrite, and (C) silica nanoparticles. Polymerized TPM emulsion droplets also form stable dispersions in ethanol, where they are excellent seeds for silica deposition. In (D) 50 nm TPM emulsion droplets with adsorbed cobalt ferrite nanoparticles are embedded into a 22 nm silica shell. Such outer shell confers optical properties such that Bragg-reflections can be visually observed when the particles crystallize under influence of gravity or (D) by a magnetic field gradient.

polydispersity up to 30 % with rather irregular particle shapes whereas Ludox silica colloids were nicely spherical with a polydispersity of 18 %.

In conclusion, we have shown that complex core-shell colloids with a centered inorganic core and a PMMA latex shell can be easily prepared via a clean one-pot reaction. In contrast to other preparative methods, our synthesis does not require coupling agents or surfactants and only employs thermodynamically stable Pickering emulsions that coexist with an excess phase of MM. Both core polymerization and shell growth occurs simultaneously upon addition of a radical initiator. We have used the procedure disclosed in this letter to obtain PMMA spheres with a core of magnetite, silica and cobalt ferrite (Fig. 3a–c). This clearly suggests a generic procedure and in future work we will investigate the encapsulation of other inorganic nano-particles such as gold, silver, platinum or CdS quantum dots.

Experimental

In a typical preparation 5 mL of TPM (Acros) and 2 mL of MM (Acros) are mixed to a water based ferrofluid (7 mL of a 2.9 wt % dispersion diluted in 80 mL of demi water) consisting in 12 nm (diameter) Fe_3O_4 (or CoFe_2O_4) particles prepared according to Massart et al. [18,19]. For silica cores 1.5 mL of AS-40 Ludox dispersion (DuPont, used as received) was diluted with 20 mL of demi-water and then mixed with 1 mL of TPM and 100 μL of MM. The average silica particles diameter was determined by dynamic light scattering to be $25 \text{ nm} \pm 18 \%$. Gentle stirring immediately causes emulsification of TPM whereas MM ($d = 0.94 \text{ g cm}^{-3}$) forms a separate oil phase on the top of the reaction vessel (Fig. 2c insert). When the concentration of nano-particles is insufficient to emulsify all TPM, the system spontaneously expels the excess oil. Since TPM ($d = 1.04 \text{ g cm}^{-3}$) is slightly denser than water, this expulsion leads to a three-layer system in which the TPM-emulsion is sandwiched between an upper pure

MM-phase and a lower pure TPM-phase. The latter is easily removed when the reaction vessel is a separation funnel. Core polymerization and shell growth occur simultaneously by addition of KPS at 70°C (KPS concentration 0.65 mM).

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