Nanotechnology

Colloidally Stable Amphibious Nanocrystals Derived from Poly{[2-(dimethylamino)ethyl] Methacrylate} Capping**

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We present a general protocol for the capping of nanocrystals (NCs) with poly{[2-(dimethylamino)ethyl] methacrylate} (PDMA) brushes to render NCs soluble in both water and organic solvents. The PDMA-capped NCs are not amphiphilic and do not absorb at interfaces but remain in bulk phases in water/oil two-phase systems. We therefore refer to them as amphibious NCs. Recently, NCs have been extensively investigated because of their unique size-dependent, electronic, magnetic, and optical properties.[1] A number of wet-chemical strategies have been well established to generate NCs in either aqueous or organic phases. One of the problems of water-based NCs is their tendency to agglomerate on changing the pH value, the temperature, and/or the ionic strength of the aqueous solution.[2] Their stability may be improved by capping with hydrophilic ligands as stabilizers, but the excess stabilizer is generally difficult to remove. One can transfer hydrophilic NCs to organic solutions with the aid of surfactants with long hydrocarbon chains based on direct covalent bonding or electrostatic interactions to improve the colloidal stability or to organize particles into ordered arrays.[3] The efficiency of the phase transfer, however, is generally low. High-quality NCs, with well-defined size, shape, and crystallinity, can be prepared in organic media.[1c,4] Nevertheless, their water immiscibility limits their usage in aqueous milieu. Such hydrophobic NCs may be transferred into aqueous phases by replacing surface capping agents with multi- or monolayers of surfactants with short hydrocarbon chains.[5] However, the colloidal stability of the transferred NCs remains poor. Although the coating by hydrophilic polymers and silica can improve the colloidal stability, there are difficulties in avoiding aggregation of NCs during the coating procedures.[6] Overall it remains a challenge to direct NCs into specific physicochemical environments without the loss of properties and colloidal stability.

Herein, we present a new, efficient and versatile process to transfer hydrophobic or hydrophilic NCs into a specific milieu by coating them with shells of PDMA brushes. These brushes

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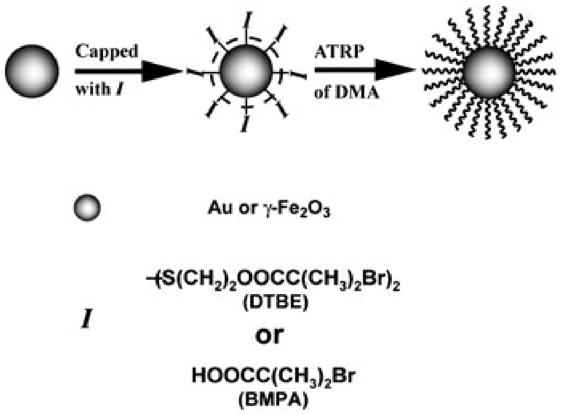
were capped on organic γ-Fe_2O_3 and aqueous Au NCs through surface-initiated atom-transfer radical polymerization (ATRP). Because of the unique solubility of PDMA, the coated NCs can be well dispersed in both water and organic solvents. This report is the first step towards the fabrication of amphibious NCs. We were encouraged by the success of surface-initiated ATRP on colloidal particles.[7] A number of hydrophobic polymers such as polystyrene and poly(methyl methacrylate) have been recently grafted onto colloidal particles of sizes ranging from nanometers to submicrometers.[7a–e] Armes and co-workers have created hydrophilic brushes on silica spheres.[7f] All these reports mainly focus on the synthesis and structural characterization of polymer grafted NCs. So far there are few reports on the use of surface-initiated ATRP as a phase-transfer means to direct NCs into specific physicochemical media. Our protocol benefits from several recent developments in both polymer chemistry and materials synthesis. First, surface-initiated ATRP provides a “grafting-from” strategy to coat NCs, thus preventing their aggregation during the growth of polymer brushes. Second, ATRP allows the coating of NCs with shells of dense polymer brushes, so the stability and solubility of the resulting coated NCs should be dominanted by the polymer brushes rather than by the NCs themselves. Third, PDMA can be dissolved in common organic solvents (except alkanes), including methanol, ethanol, acetone, toluene, carbon tetrachloride, chloroform, dichloromethane, THF, and *N*,*N*-dimethylformamide (DMF). Because of its pK_a of 7.0 ± 0.5, PDMA can be partially protonated in water and is therefore water-soluble. The capped PDMA brushes render NCs soluble in both aqueous and organic phases, thus providing the freedom to disperse the coated NCs in either aqueous or organic solvents. This differs from traditional phase-transfer methods used to one-way direct NCs from the aqueous to the organic phase or vice versa with the aid of amphiphilic ligands. Fourth, PDMA chains are weak cationic polyelectrolytes that allow for the conjugatation of other functional materials, such as biomolecules, through electrostatic interactions. Scheme 1 depicts our method of generating amphibious NCs. First, ATRP initiators were capped on NCs by ligand exchange. Second, PDMA brushes were formed on NCs by surface-initiated ATRP.



Scheme 1. Generation of PDMA brushes on NCs by surface-initiated ATRP.

γ-Fe_2O_3 NCs of 4 nm were prepared in toluene by using a method based on that reported by Sun and Zeng.[4c] The surface stabilizers of the NCs were replaced with 2-bromo-2-methylpropionic acid (BMPA), as described by Yang and coworkers.[7a,8] In our work, little variation was observed by transmission electron microscopy (TEM) and UV/Vis absorption spectroscopy when γ-Fe_2O_3 NCs were compared before and after ligand exchange. Over a period of 2 h of BMPA-initiated ATRP, PDMA brushes were generated on γ-Fe_2O_3 NCs in toluene, marked as γ-Fe_2O_3@PDMA. The capped NCs could be isolated as a solid, which could be redispersed in either water or common organic solvents. A typical TEM image of γ-Fe_2O_3@PDMA nanoparticles reveals cores of γ-Fe_2O_3 of 4 nm (Figure 1 a). Figure 1 b shows typical absorption spectra of γ-Fe_2O_3@PDMA nanoparticles, dispersed in water (black), chloroform (red), and toluene (blue); there is little difference between the spectra and they are similar to that of the initial γ-Fe_2O_3 NCs (black dotted). The absorption spectra prove that the PDMA shell renders γ-Fe_2O_3 NCs soluble in both water and organic solvents. Our experiments indicate that γ-Fe_2O_3@PDMA nanoparticles can be well

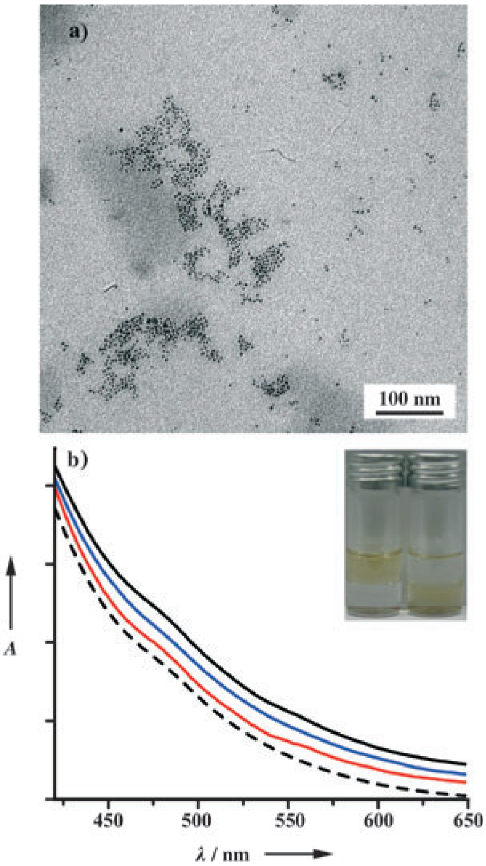


Figure 1. a) TEM image of γ-Fe_2O_3@PDMA nanoparticles consisting of 4 nm γ-Fe_2O_3 cores. b) UV/Vis absorption spectra of γ-Fe_2O_3@PDMA nanoparticles dispersed in water (black), toluene (blue), and chloroform (red) as well as of 4-nm γ-Fe_2O_3 NCs dispersed in toluene (black dashed). The inset shows photographs of an aqueous solution of pH 7 above chloroform. In the left sample the γ-Fe_2O_3@PDMA nanoparticles were initially dissolved in water and in the right sample in chloroform.

dispersed in water and common organic solvents (except alkanes such as hexane). The inset in Figure 1b shows that γ-Fe_2O_3@PDMA nanoparticles prefer to reside in the bulk water of pH 7 (left) or chloroform phase (right) and no nanoparticles are observed at the water/chloroform interface, which demonstrates their amphibious nature. Because water solubility depends on the protonation of the ternary amine groups of the PDMA chains, the transfer from the aqueous phase to organic phase is expected to be slow in chloroform and deprotonation is expected to be slow in water. Hence, we do not observe phase transfer within a few days. This transfer is accelerated by reducing the pH and subjecting the sample to sonification. Even after sonification and a further wait of over two weeks, more than 90% of the particles remained in the phase in which they were initially dissolved, as determined by absorption spectroscopy (see the Supporting Information). As determined by dynamic light scattering (DLS), the hydrodynamic diameter of the resulting γ-Fe_2O_3@PDMA nanoparticles is approximately 8 nm, which suggests that the PDMA shell has a thickness of about 2 nm. Furthermore, DLS does not reveal any sign of aggregation. Due to the living character of ATRP, the thickness of the PDMA shell can be controlled by varying the polymerization time (see the Supporting Information).

The γ-Fe_2O_3@PDMA nanoparticles remain magnetic. In their aqueous or organic dispersions, we observe the accumulation of γ-Fe_2O_3@PDMA nanoparticles on the wall of a glass vial by applying an external magnetic field (see the Supporting Information). Our preliminary measurements with a superconducting quantum interference device (SQUID) indicate that these γ-Fe_2O_3@PDMA nanoparticles become superparamagnetic at about 20 K. The study of the magnetic property of γ-Fe_2O_3@PDMA nanoparticles as a function of their PDMA shell thickness is underway.

To generalize our method and to investigate the solvent effect on properties of NCs, we employed Au NCs as cores to grow PDMA brushes as their plasmon absorption band is sensitive to their environment.[9] Au NCs of 12 nm were synthesized by citrate reduction of chloroauric acid in the aqueous phase.[2a] To prevent Au NCs from aggregating during ligand exchange, 2,2′-dithiobis[1-(2-bromo-2-methylpropionyloxy)ethane] (DTBE) was synthesized as an ATRP initiator.[8] During DTBE-initiated aqueous ATRP, PDMA brushes were grown on Au NCs. PDMA-capped Au nanoparticles are denoted as Au@PDMA. DLS data reveal that the hydrodynamic diameter of Au@PDMA nanoparticles was about 32 nm, which corresponds to a PDMA shell of 10 nm in thickness. Figure 2a shows a typical TEM image of Au@PDMA nanoparticles in which individual nanoparticles with 12 nm Au cores are discernable. Due to the high electron density of the central Au core, it is not possible to detect the PDMA shell. During TEM measurement, drying may reduce the PDMA shell thickness considerably as the brushes collapse under vacuum.[7f] Thus, in some cases the core-to-core distance is smaller than the shell thickness in Figure 2a. As with the γ-Fe_2O_3@PDMA nanoparticles, those of Au@PDMA can be dispersed in both water and common organic solvents. The inset in Figure 2b demonstrates the amphibious nature of Au@PDMA nanoparticles. In comparison with that of Au NCs (520 nm, black dotted, Figure 2b), the plasmon absorbance band of Au@PDMA nanoparticles is red-shifted to 530 nm due to an increase of the refractive index of the surrounding of the Au cores,[9] which is induced by the PDMA brushes. Figure 2b verifies that the plasmon absorbance band of Au@PDMA nanoparticles has little dependence on the dispersion solvents (water black; methanol green; DMF brown; chloroform red; toluene blue). Turning neutral PDMA brushes into cationic brushes by quaternization, one observes a red-shift of the plasmon absorbance band (purple line, Figure 2). This shift suggests that the plasmon absorbance of Au cores is mainly determined by the capping PDMA brushes. Furthermore, we noted that an aqueous dispersion of Au@PDMA nanoparticles that contain 0.5 M NaCl remains stable for at least 3 months without any visible precipitation. The dotted line in Figure 2b indicates that the introduction of NaCl causes little change of the plasmon absorbance band of Au NCs. These data prove an absence of aggregates and a high colloidal stability of Au@PDMA nanoparticles in the aqueous phase.

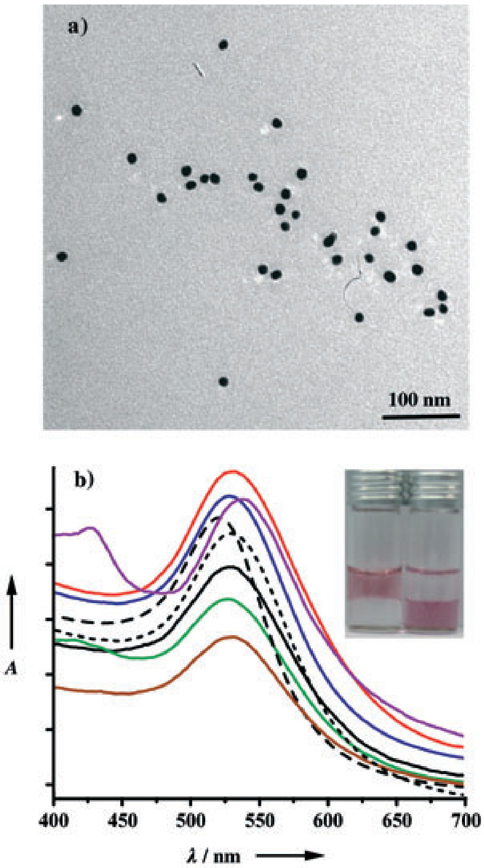


Figure 2. a) TEM image of Au@PDMA nanoparticles consisting of 12 nm Au cores. b) UV/Vis absorption spectra of Au@PDMA nanoparticles dispersed in water (black), methanol (green), DMF (brown), toluene (blue), chloroform (red), and 0.5 M NaCl aqueous solution (black dotted), and of quaternized Au@PDMA nanoparticles (purple) as well as of 12-nm Au NCs dispersed in water (black dashed). The inset in (b) shows photographs of a water solution of pH 7 above chloroform. In the left sample the Au@PDMA nanoparticles were initially dissolved in water and in the right sample in chloroform.

In summary, we have demonstrated a new and efficient approach—coating with PDMA brushes—to pull both hydrophobic and hydrophilic NCs into specific media without detectable aggregation, while their intrinsic magnetic and optical properties are maintained. PDMA brushes have been formed on hydrophobic γ-Fe$_2$O$_3$ and hydrophilic Au NCs by surface initiated ATRP. The capping PDMA brushes render NCs an amphibious character; the coated NCs can be dispersed in both aqueous and common organic solvents except alkanes without sticking to the aqueous/oil interfaces. The PDMA-capped NCs exibit long-term colloidal stability in aqueous and organic media. Our approach provides interesting opportunities for the exploitation of different NCs in aqueous media for biological applications. Our preliminary results demonstrate the potential of forming NC bioconjugates through electrostatic interactions between proteins and PDMA brushes (see the Supporting Information). Clearly, our approach can be extended to other NCs, such as CdTe and CoPt, which is ongoing research in our laboratory. Moreover, such amphibious NCs provide functional building blocks for other existing assembly strategies.

Experimental Section

The toluene dispersion of 4 nm γ-Fe$_2$O$_3$ NCs was prepared based on the method of Sun and Zeng.[4c] The aqueous dispersion of citrate-stabilized Au NCs of 12 nm was synthesized as described elsewhere.[2a] BMPA was purchased from Aldrich. DTBE was obtained by acrylation of bis-(2-hydroxyethyl) disulfide with 2-bromoisobutyryl bromide in the presence of triethylamine by using a procedure described elsewhere.[10] The γ-Fe$_2$O$_3$@BMPA and Au@DTBE NCs were prepared as described previously.[8] ATRP of DMA on γ-Fe$_2$O$_3$@BMPA nanoparticles was carried out in toluene at 40 °C, triggered by adding CuBr/(−)-sparteine (SP) complex. Aqueous ATRP of DMA on Au@DTBE nanoparticles was started by adding the CuBr/2,2′-bipyridine (BPy) catalyst at room temperature. The initial DMA concentration based on toluene or water was 50 vol %; the molar ratio of initiator/CuBr/SP or BPy was 1:1:2. After 2 h ATRP under Ar, the PDMA-capped NCs were collected by repeating the cycle of centrifugation/THF wash/redispersion for three times.

UV/Vis absorption spectra were recorded by using a Cary 50 UV/Vis spectrophotometer. TEM images were obtained by a Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV. DLS measurements were implemented by a Malvern HPPS 500.

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