



Colloidal assembly of magnetic nanoparticles and polyelectrolytes by arrested electrostatic interaction



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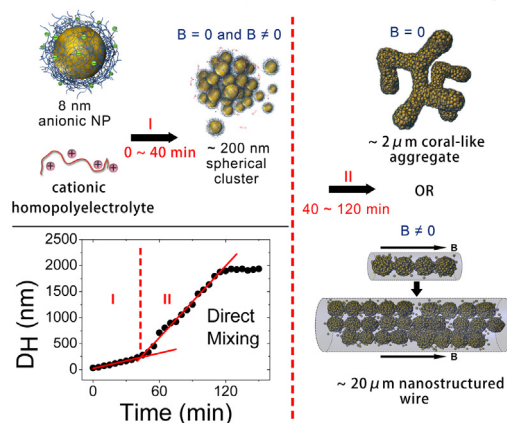
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HIGHLIGHTS

- Direct mixing of oppositely charged nanoparticles and polymers in solutions.
- Kinetics of self-assembly is decreased and controlled aggregates are generated.
- Simple assembly route can be generally extended for practical applications.

GRAPHICAL ABSTRACT

Controlled electrostatic complexation at critical ionic strength



This work presents a simple approach which can efficiently moderate the wild electrostatic attractions between anionic nanoparticles and cationic homopolyelectrolytes. Sizes and morphologies of the synthesized aggregates do not show any dependency on the formulation in terms of charges ratios or on the chemical nature of the polycations. This simple direct mixing process does not require a specific manipulation device which is of great interest for potential applications.

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ABSTRACT

Electrostatic interaction of charged colloids and polyelectrolytes is a useful method to assemble matter into hybrid nanostructures with numerous examples in materials science as well as in biology. However, the colloidal electrostatic interaction is rapid and uncontrolled, the strong interaction usually leads to large and irregular aggregates. Therefore, control of the electrostatic interaction in order to resulting well-defined nanostructures remains a challenge. Here we report on a general and simple method to moderate the wild electrostatic interaction. Direct mixing of stock solutions containing anionic superparamagnetic nanoparticles and widespread cationic homopolyelectrolytes at an appropriate ionic strength

Polyelectrolytes
Electrostatic interaction
Controllable assembly
Nanostructured wires

generates aggregates with controlled shape and morphology. The simple and versatile methodology not only efficiently moderates electrostatic interactions but also enables the corresponding growth mechanism to be revealed by light scattering and electron microscopy as aggregation occurs at much slower timescales. The present results carry important implications for both practical applications and understanding on nanoscale electrostatic interaction between colloids.

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1. Introduction

Although the synthesis of various inorganic nanoparticles (NPs) has been well-established, their controlled assembly into larger superstructures [1–7] remains an ongoing challenge [8,9], en route to applications ranging from medical therapeutics [10,11] and diagnostics [11–14] to photonics [15] and photovoltaics [16,17]. For instance, the establishment of a useful and controllable methodology for the assembly of NPs into well-defined rods or arrays is particularly important because it offers immense opportunities for applications in optoelectronics [18–20] and sensing [21,22]. During the last decade several research groups have reported on the assembly of colloidal particles [23–29]. In spite of the development based on these advanced approaches, the establishment of simple and cost-efficient methodologies for the controllable assembly of NPs into well-defined rods or wires remains a challenge.

Recently electrostatic interactions have been increasingly exploited as a simple and versatile route to assemble NPs into well-defined superstructures with oppositely charged polyelectrolytes (PEs) [30,31]. The process performed at room temperature and atmospheric pressure displays much higher yield than the “grafting-from” or “grafting-to” covalent reactions allowing scaling up any process to large quantities and workloads, as required by industry. The electrostatically driven assembly between PEs and oppositely charged colloids is spontaneous and the direct mixing of their solutions can result in phase separation. This is the case for PEs and surfactants for which micellar coacervates and liquid crystalline phases have been observed [32–34]. Interaction is favored by the electroneutrality of the PE/micelle complex and can be enhanced or suppressed by changing salt concentration as it increases or decreases the binding affinity of micelles to polyelectrolytes [35,36].

In order to control the electrostatic interaction and to preserve the colloidal stability with desired size and shape, a novel mixing protocol for assembling anionic poly(acrylic acid) coated maghemite (γ -Fe₂O₃-PAA) NPs and cationic PEs was recently reported [37–40]. This protocol denoted “desalting kinetic” was inspired by molecular biology techniques developed for the *in vitro* reconstitution of chromatin [41]. Using NPs (γ -Fe₂O₃-PAA) and oppositely charged homopolyelectrolytes (homoPEs) such as poly(diallyldimethylammonium chloride) (PDADMAC) or poly(ethyleneimine) (PEI), this method generates rod-like clusters with regular cylindrical form, but only when one of the oppositely charged species is introduced in large excess [37,39]. The “desalting kinetic” method applied to a mixture of NPs and homoPEs at the isoelectric point (IP)—where the amount of negative charges brought by the NPs equals the amount of positive charges brought by the PEs chains—fails to form regular rod-like clusters but rather creates large and irregular aggregates with macroscopic phase separation [37,39]. Consequently, a general and simpler method that overcomes the restrictive assembly conditions is required.

In this work, we present a useful approach which can efficiently moderate electrostatic attraction during the entire self-assembly. Stock solutions of NPs (γ -Fe₂O₃-PAA) and homoPEs (PDADMAC or PEI) are directly mixed at an appropriate ionic strength I_s of the

aqueous medium. In this case, the interaction process is slowed down to the timescale of hours rather than the quasi-spontaneous assembly of existing methods. The increased time of reaction allows aggregation of reactive species into well-defined colloids and also enables the corresponding growth mechanism to be revealed. Using this approach the conditions of assembly, namely the chemical nature of building blocks and assembly protocols are subject to the minimum restrictions.

2. Experimental section

2.1. Materials

The following chemicals were used for synthesis of polymer-coated NPs: FeCl₂, H₂O; FeCl₃ 27 wt.% in water, hydrochloric acid, sodium hydroxide, ammonia at 20 wt.% in water, nitric acid at 52 wt.% in water, Fe(NO₃)₃, acetone, diethyl ether, poly(acrylic acid) (Mw = 2000 g mol⁻¹, polydispersity = 1.7).

Cationic homoPEs included poly(diallyldimethylammonium chloride) (PDADMAC), Mw < 100,000, 35 wt.% in H₂O and poly(ethyleneimine) (PEI), Mw = 2000, 50 wt.% in H₂O. The molecular structures of the cationic homoPEs are shown in Scheme 1.

All chemicals were obtained from Sigma Aldrich and used as received. All the water used in the study was MilliQ quality water (Millipore®).

2.2. Poly(acrylic acid) coated maghemite NPs

2.2.1. Synthesis

Poly(acrylic acid) coated iron oxide NPs were prepared following reported protocols. First, maghemite (γ -Fe₂O₃) nanocrystals were synthesized by the Massart method [42]. Briefly, iron (II) and iron (III) salts are co-precipitated in an alkaline medium at room temperature. The obtained magnetite (Fe₃O₄) nanocrystals were then transferred in nitric acid and oxidized into maghemite by the addition of Fe(NO₃)₃ at boiling temperature for 30 min. Their color progressively changed from black to orange-red. Polydispersity of the sample was reduced by size sorting. After two successive liquid-liquid phase separations induced by the addition of large amount of nitric acid [43], γ -Fe₂O₃ nanocrystals of a median diameter of 9.3 nm and a narrow polydispersity of 0.18 were obtained. The bare γ -Fe₂O₃ NPs are positively charged with zeta potential of +30 mV at pH = 2 and T = 25 °C. In these conditions, the net positive charge around the particle surface ensures their reliable colloidal stability [44]. Second, the bare NPs were coated in acidic condition with poly(acrylic acid) oligomers with a molecular weight of 2000 g mol⁻¹ using the precipitation-redispersion process [45]. The drop-by-drop addition of a solution of poly(acrylic acid) (PAA_{2K}) at pH = 2 (HNO₃) to a dispersion of bare NPs at pH = 2 (HNO₃) leads to precipitation of the nanocrystals and their adsorbed PAA_{2K} chains. Single particles are then recovered by redispersion at pH = 12 (NH₄OH). The dispersion of PAA_{2K} coated NPs (γ -Fe₂O₃-PAA_{2K}) is finally purified by dialysis in deionized water.

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