



Fine-tuning the assembly of highly stable oppositely charged cerium oxide nanoparticles in solution and at interfaces



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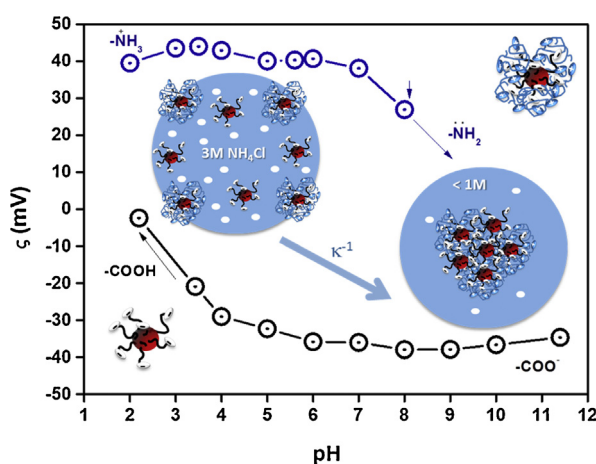
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HIGHLIGHTS

- Highly stable oppositely charged CeO₂ nanoparticles in saline environment up to 4M.
- Fine tuning the assembly/complexation of oppositely charged nanoparticles through a desalting route.
- All-nanoparticle CeO₂ functional layer grown directly in one step from a solid/liquid interface.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we have shown how to fine-tune the electrostatic assembly of oppositely charged cerium oxide nanoparticles (NPs) in a solution and at a solid/liquid interface. In a first stage, we have developed anionic and cationic CeO₂ NPs stable in a highly saline environment and a wide pH range via efficient electro-steric interactions. Anionic NPs were obtained by coating bare NPs with short polyacrylic acid (PAA) chains through a *Precipitation-Redispersion* method. Whereas cationic NPs were formulated by tethering branched polyethyleneimine (bPEI) chains onto PAA-coated ceria NPs through the formation of amide bonds with the help of imide cross-linkers. The covalent attachment of bPEI chains was evidenced through NMR characterizations while thermogravimetric (TGA), dynamic light scattering (DLS) and zeta potential measurements confirmed the successful encapsulation by both types of weak polyelectrolytes. In a second stage, the high stability of both NP dispersions toward high ionic strength (up to 4M NH₄Cl) enabled to generate *hybrid clusters* in a controlled way by fine tuning their co-assembly following a *desalting transition* route monitored by DLS. In a last part, we have extended our approach to surfaces and generated *all-nanoparticle* layer grown directly from a liquid/solid interface monitored by Quartz Crystal Microbalance (QCM). Such *thin nano-clustered* layer with tunable and relatively high volume fraction of

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ceria NPs represents a promising platform to impart functional coatings onto metal, ceramic and polymer substrates.

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1. Introduction

Electrostatic complexation [1] of oppositely charged macromolecules and colloids is a physico-chemical process ubiquitous in nature as the source of assembly in many biological processes ranging from protein & RNA folding to DNA segmentation [2,3], but also in many synthetic fields such as in the celebrated Layer-by-layer (LbL) approach [4] and more generally in the key domain of composite materials. Since the pioneering work of Bungenberg de Jong on the Arabic gum-gelatin system [5], a tremendous body of work has been devoted throughout the past three decades to the understanding of the complexation mechanisms and the development of versatile applications in many different fields such as water and protein purification, coatings, cosmetics, food & textile industries and in pH triggered drug delivery [6–9]. The formation and stability of the generated complexes depend on various experimental parameters such as the pH, the ionic strength and the molar charge ratio of the interacting species but also the way they are coming into intimate contact [1,10,11]. Under such strong attractive force, the direct mixing or titration of oppositely charged components results very often in the formation of thermodynamically out-of-equilibrium or “frozen” aggregates/clusters with a large polymorphism and polydispersity; likely a major drawback to the development of any functional materials and applications. In 2010, Chapel and co-workers showed that the competition between the *homogenization time* of the mixed solution and the *reaction time* of individual species play a significant role in controlling the electrostatic complexation between oppositely charged components [12–14]. The *homogenization time* depends on the order of addition and/or the mixing conditions. The *reaction time* depends on the initial concentration and the nature/strength of the different interactions at play. Electrostatic complexation can then be controlled/tuned either via the *mixing* or *interaction* pathway. Qi et al. studied the influence of the mixing pathway on a system comprising oppositely charged cerium oxide nanoparticles (CeO_2) and double hydrophilic block copolymers [12]. Whereas Berret and co-workers have adapted from molecular biology the desalting transition concept [15] to investigate the impact of the *interaction pathway*. In this method, two oppositely charged dispersions are mixed together at a sufficiently high ionic strength (I_s) to generate a so called *dormant dispersion* in which no interaction occurs due to charge screening. A further decrease of I_s by simple dilution (or dialysis) will trigger the electrostatic complexation featured by an abrupt transition from a non-clustered to a clustered state. Over the last few years, some key features of the desalting transition have been put forward by our group on either oppositely charged polyelectrolytes (PEs) or polyelectrolyte-nanoparticle pairs [13,15–18]. These results encouraged us to extend the desalting transition concept for the first time to oppositely charged nanoparticles (NPs). We believe that this approach would be a promising platform to generate novel clusters with controlled size and morphology possessing the specific attributes and characteristics of inorganic NP building-blocks.

In this work, we have generated in a first stage highly stable anionic and cationic cerium oxide NPs. These rare-earth oxides NPs are indeed drawing a lot of attention [19] and are key actors of the nanotech developments [20,21] ranging from material science [21,22] to biomedical [23] applications. Anionic

polyacrylic acid (PAA) coated NPs ($\text{CeO}_2\text{-PAA}_{2k}$) were obtained through a Precipitation-Redispersion approach [24] whereas cationic polyethyleneimine (bPEI) coated NPs ($\text{CeO}_2\text{-cbPEI}_{25k}$) were formulated from the anionic NPs. The polyelectrolytes used to formulate our NPs are weak PEs and interact not only through electrostatic interactions but also through different secondary forces (H-bonding, acid-base and hydrophobic with nanoceria surface). The presence of these secondary forces increases the critical bulk ionic strength corresponding to desalting transition from about 1 M (typical for purely electrostatic forces) to 4 M. The main features of both types of formulated NPs were further characterized by NMR, DLS and zeta potential measurements. Their good stability in a high saline environment enabled in a second stage the fine control of their bulk complexation/assembly following a *desalting* transition route. We have finally extended our approach to surfaces by generating *all-nanoparticle layers* grown in one shot directly from a liquid/solid interface.

2. Experimental

2.1. Materials

Polyacrylic acid (PAA) of $M_w \sim 2000 \text{ g mol}^{-1}$ (PAA_{2k}), branched polyethyleneimine (bPEI) of $M_w \sim 25,000 \text{ g mol}^{-1}$ (bPEI_{25k}), cross linkers such as 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC-HCl) and *N*-hydroxysuccinimide (NHS), polystyrene (PS) of $M_w 250,000 \text{ g mol}^{-1}$ and octadecyltrimethoxysilane (TMOS) were purchased from Sigma Aldrich. Cerium oxide (ceria) nanoparticle dispersions were kindly supplied by the Rhodia-Solvay chemical company. Other chemicals such as HNO_3 , NH_4OH , HCl, NaOH, NH_4Cl and NaNO_3 were used as such without further purification. MilliQ water ($18\text{M}\Omega/\text{cm}$) was used for all experiments.

2.2. Methods

2.2.1. Formulation of anionic ceria ($\text{CeO}_2\text{-PAA}_{2k}$)

Dynamic light scattering was performed on an ALV set-up ($\lambda = 632 \text{ nm}$) for measurements of the collective diffusion constant $D(c)$. The autocorrelation functions were interpreted using both the method of cumulants and the CONTIN fitting procedure. Bare CeO_2 NPs of average hydrodynamic radius $R_H = 4.3 \pm 0.35 \text{ nm}$ (polydispersity index of 0.12) were coated with PAA_{2k} chains following a Precipitation-Redispersion route based on a direct mixing protocol [24]. In short, mixed solutions of bare ceria NPs (pH ~ 1.5) and PAA_{2k} (pH ~ 3.5) were prepared by simple mixing of equal volumes (volume ratio $X = \text{volume of NPs solution } (V_{\text{NP}}) / \text{volume of polymer solution } (V_{\text{pol}} = 1)$) of dilute solutions prepared at the same weight concentration c (1 wt%). The most efficient and reproducible formulation pathway to generate singlet PAA_{2k} -coated CeO_2 NPs uses the quick injection of the NPs into the PAA_{2k} solution in one shot using a syringe. After homogenization of the solution under stirring for one hour at room temperature (RT), the pH of the solution was gradually increased by a drop by drop addition of NH_4OH (0.1 M). Above pH 8, the solution turned transparent due to the electro-steric repulsion between charged polymer coronas. The size ($D_H = 9.3 \pm 0.5 \text{ nm}$), the molecular weight ($\sim 282,000 \text{ g mol}^{-1}$) and the number of PAA chains per NP (~ 40) were figured out with

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