

Nanoparticle Synthesis via Counterion-collapsed Polyelectrolyte Nanoreactors

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ABSTRACT

We report a facile method to synthesize a wide range of nanoparticles via polyelectrolyte nanoreactors. The nanoreactors are formed through ion-induced collapse of highly extended, high molecular weight anionic polyelectrolytes using metal salts. The formation of compact polyelectrolyte globular nanoreactors containing metal counterions is indirectly observed through viscosity measurements. The small size of the nanoreactors was measured by dynamic light scattering (DLS) as ~ 10 nm in diameter. By subjecting the nanoreactors to conditions that transform the counterions into inorganic nanoparticles, polyelectrolyte-encapsulated nanoparticles were formed. Depending on the metal salt used, this method can be used to produce a wide range of nanoparticles, including metals, metal oxides, complex semiconductors, and doped systems. As a case study, Ag and ZnO nanoparticles were synthesized using this method and characterization data is presented.

Keywords: nanoparticles, polyelectrolytes, nanoreactors, metals, metal oxides

1 INTRODUCTION

Polyelectrolytes are polymers having monomer units with ionizable groups such as amines, carboxylic acids, or sulfonic acids. They have been used as stabilizers and/or dispersing agents in water for nanoparticle powders [1], as complexing agents prior to nanoparticle synthesis [2], and in a tandem synthesis of both the polyelectrolyte and the nanoparticles [3]; however, there are no reports on exploiting a well-known property of polyelectrolytes, i.e. counterion-induced coil-to-globule collapse transition, to synthesize inorganic nanoparticles. We present here a versatile method to produce water dispersible nanoparticles using counterion-induced collapse of polyelectrolyte chains.

The conformation of polyelectrolytes in aqueous solution is governed by electrostatic interactions between the charged moieties in the chain. Under conditions of high ionization and low ionic strength, the individual chains assume a highly extended, swollen coil conformation arising from repulsive electrostatic interactions along the chain [4]. The addition of ionic species results in the screening of these repulsive interactions by counterions, causing the highly extended polyelectrolyte coils to collapse into globules [5]. These globules contain the

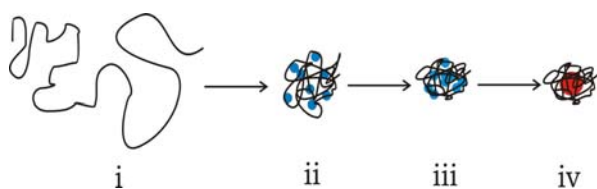
counterions used to induce collapse, and can range in size from ~ 1-50 nm [5,6], depending on the molecular weight of the polymer and the type of counterions used.

In this paper, we will demonstrate how these counterion-containing globules can be utilized as “nanoreactors” for the synthesis of silver and zinc (II) oxide nanoparticles in water. Both nanoparticles are made by exploiting the same basic principle of counterion-induced coil-to-globule collapse of polyacrylic acid (PAA) by silver and zinc (II) nitrate salts.

2 RESULTS AND DISCUSSION

2.1 Polymer collapse and the formation of nanoreactors

The basic premise of our process is illustrated in Scheme 1, and can be summarized as follows. An aqueous solution of a high molecular weight polyelectrolyte is treated with a solution of water-soluble inorganic salts resulting in collapse from an extended chain (i) to a compact globule (ii). The collapse process is accompanied by a decrease in the viscosity of the solution as reported previously [4, 7-8]. At this point, the interior of the collapsed polyelectrolyte chains contain tightly bound counterions in close proximity to each other, likening the whole system to a nanoreactor with the starting materials already inside. The whole system is exposed to radiation (iii) that stabilizes the structure of the collapsed polymer chain via intramolecular crosslinks and prevents its unraveling. The increased structural stability is demonstrated by dialyzing against deionized water. During dialysis, the viscosity of a solution of poly(acrylic acid) (PAA) collapsed with Ag(NO₃) gradually increases indicating that the chains are unraveling, while that of the same solution that has been exposed to radiation stays the same. The final step is to subject the whole system to suitable reaction conditions (iv) such as oxidation, reduction or controlled precipitation that will result in the formation of the inorganic nanoparticle from the counterions inside the globule. Note that these last two steps, (iii) and (iv), can be interchanged depending on the reaction conditions. The final product of the whole process is an inorganic nanoparticle encapsulated in, and therefore stabilized and dispersed in aqueous solution by, the polyelectrolyte nanoreactor.



Scheme 1: Polymer collapse to make nanoparticles

2.2 Synthesis and characterization of nanoparticles – Ag and ZnO

Following our general process, we used $\text{Ag}(\text{NO}_3)$ to produce collapsed PAA containing ~ 31 mol% Ag^+ with respect to monomers of acrylic acid. The resulting collapsed PAA nanoreactors containing Ag^+ was subjected to crosslinking radiation and then the Ag^+ ions were reduced using NaBH_4 . Figure 1 shows the UV-visible absorbance spectrum and the transmission electron microscopy (TEM) image of the synthesized Ag-PAA nanoparticles. The absorbance spectrum of the final solution showed a single peak at ~ 420 nm corresponding to the known plasmon band of Ag nanoparticles [9]. The size of the nanoparticles was determined by TEM to be ~ 3 -12 nm. Figure 2 shows a typical volume size distribution of the Ag nanoparticles in 0.1M NaNO_3 as measured by DLS. On average, we measured a hydrodynamic radius of ~ 8 -10 nm. We observe the characteristic diffraction peaks for metallic silver by powder x-ray diffraction (PXRD; not shown).

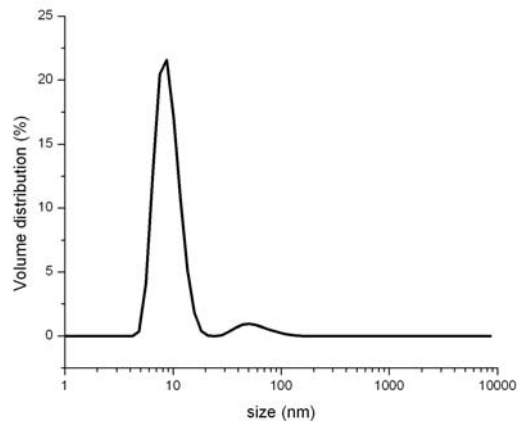


Figure 2. Typical volume size distribution of Ag nanoparticles measured by DLS.

To synthesize zinc oxide nanoparticles, we used $\text{Zn}(\text{NO}_3)_2$ as the counterion to produce collapsed, PAA containing ~ 17 mol% Zn^{+2} with respect to monomers of acrylic acid. The system was then subjected to ionizing radiation followed by adjusting the pH to 9 and heating to 80°C for 30 minutes. The final solution showed particles that are ~ 5 -10 nm in diameter as characterized by TEM (figure 3). DLS measurements (figure 4) gave a hydrodynamic radius of ~ 8 nm in 0.1M NaNO_3 . Figure 3 also shows the UV absorbance characteristic of ZnO nanoparticles. The pXRD (not shown) pattern of the synthesized nanoparticles confirms the formation of ZnO.

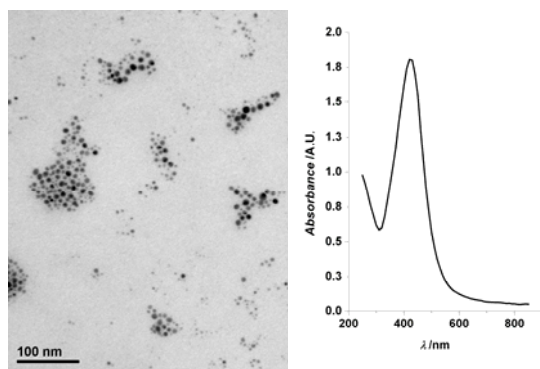


Figure 1. TEM image and UV-visible spectra of Ag nanoparticles.

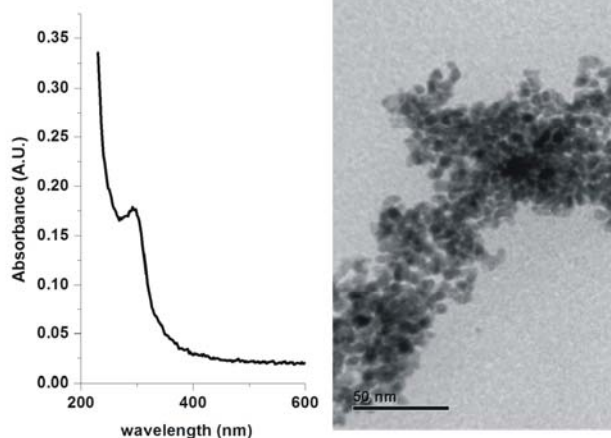


Figure 3. UV-visible spectra and TEM of synthesized ZnO nanoparticles.

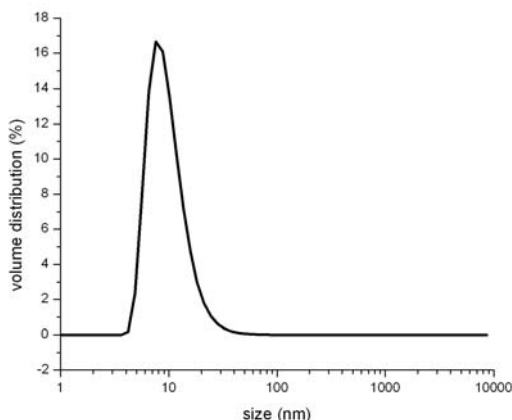


Figure 4. Typical volume size distribution of ZnO nanoparticles measured by DLS.

There are a number of advantages to synthesizing the nanoparticles inside the polyelectrolyte nanoreactor. The charged, polymeric nanoreactor provides both steric and electrostatic stabilization in aqueous solution – all nanoparticles synthesized showed no visible signs of aggregation after storage for 6 months. The nanoreactor also helps to control the size of the nanoparticles, which can be in the ultrasmall (< 10 nm) regime. Unlike other solution-phase methods to make nanoparticles, which require careful control of nucleation and growth processes, this nanoreactors act as templates that govern the growth kinetics of the nanoparticles. The easily scalable synthesis is done in one-pot, without organic solvents, and using inexpensive reagents.

More importantly, the use of collapsed polyelectrolytes as nano-reactors allows us to produce a variety of nanoparticles. We have illustrated here that by collapsing with metal counterions and using reduction or oxidation chemistry, extremely small metal (Ag) and metal oxide (ZnO) nanoparticles can be produced. Using appropriate collapsing counterions and reaction conditions, this approach can easily be extended to other systems such as quantum dots, mixed metal nanoparticles, more complex oxides, and other multi component systems. Furthermore, the presence of reactive carboxylates or other charged groups allows further conjugation or functionalization to enhance the utility of the nanoparticles. This method can also be extended to positive polyelectrolytes to synthesize cationic nanoparticles.

While the process is quite versatile, it does have certain limitations. In particular, the inorganic salts as well as the polyelectrolytes have to be water soluble, and the reaction conditions for forming the nanoparticles have to be compatible with aqueous chemistry. This method also does not allow the formation of water-reactive substances such as metal hydrides or species that do not have stable oxidation states in water under ambient conditions. But even with these limitations, the range of potential

nanoparticles that can be produced covers most commercially relevant materials.

3 CONCLUSION

In summary, we have demonstrated that collapsed polyelectrolytes can be used as nanoreactors to form inorganic nanoparticles. The process is simple, cost-effective, amenable to scale-up and water-based. The resulting polyelectrolyte-encapsulated nanoparticles are small, stable, and can be further modified to incorporate them into composites. Most importantly, we have shown that collapsed polyelectrolyte nanoreactors can be used to produce metal and metal oxide nanoparticles, and proposed that they can be used to produce a wider range of materials.

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