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Controlled heteroaggregation of two types of nanoparticles in an aqueous suspension

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ABSTRACT

Composite particles combining nanoparticles of different functional materials, as well as nanoclusters of nanoparticles of controlled size, can be synthesized by the assembly of nanoparticles in an aqueous suspension. Different interactions between the nanoparticles in the suspension can be applied for their heteroaggregation and controlled by engineering the surface properties of the nanoparticles. The heteroaggregation of nanoparticles in a suspension was studied on a model system composed of superparamagnetic carboxyl-functionalized silica-coated maghemite nanoparticles (cMNPs) (24 nm in size) and larger, amino-functionalized, silica nanoparticles (aSNPs) (92 nm). The heteroaggregates formed with electrostatic attractions between the nanoparticles displaying an opposite electrical surface charge, or with chemical interactions originating from covalent bonding between the molecules at their surfaces. The suspensions were characterized with measurements of the zeta-potential and dynamic light scattering (DLS). The heteroaggregates were analyzed by transmission (TEM) and scanning (SEM) electron microscopy. The kinetics of the heteroaggregation was followed by continuous monitoring of the changes in the average hydrodynamic size by DLS. The results show that covalent bonding is much more effective than attractive electrostatic interactions in terms of a much greater and more homogeneous coverage of the larger central aSNP by the smaller cMNPs in the outer layer.

1. Introduction

The use of magnetic nanoparticles dispersed in liquid media is normally based on the ability to manipulate them with an external magnetic field. Such magnetic nanoparticles have attracted a lot of attention in biomedicine, for example, in drug delivery or in the detection and targeting of specific (bio)molecules or cells [1–5]. They can also be used in technologies related to magnetic separation, particularly in environmental engineering [6,7], in chemical engineering [8,9], or in bioseparation processes [10–12]. Magnetic separation is a technique where magnetic carriers, i.e., small particles of a magnetic material, are dispersed into a liquid mixture containing specific targets, e.g., ions, such as toxic heavy metals, biomolecules, including proteins and enzymes, or cells and microorganisms [13,14]. After binding specific targets with magnetic carriers, the conjugates are separated with an external magnetic field [3,15]. The removal of the magnetic carriers from a liquid mixture using an external magnetic field is much more selective and effective than centrifugation or filtration [16–18].

When dispersing magnetic particles in a liquid medium it is beneficial if they are small enough to be in the superparamagnetic state. Superparamagnetism is a phenomenon related to ferro/ferrimagnetic particles when their size is reduced below a certain limit and thermal excitation induces rapid fluctuations, compared to the observation time, of the nanoparticles' magnetic moments. The superparamagnetic limit is at approximately 20 nm for soft-magnetic materials [19,20]. At this point these superparamagnetic nanoparticles no longer exhibit any spontaneous magnetic moments and, in contrast to larger ferromagnetic particles, they do not agglomerate in suspensions due to magnetic dipole–dipole interactions. However, the force acting on the magnetic particle in a magnetic field gradient is proportional to the particle's volume. It appears in practice, therefore, that individual superparamagnetic nanoparticles are just too small to be effectively separated [21]. This magnetic separation is much more effective if the superparamagnetic nanoparticles are assembled into nanoclusters, containing several superparamagnetic nanoparticles in a single nano-unit,

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but still retaining the relatively large surface area needed for bonding the targeted species [22]. For the magnetic separation of larger objects, such as cells and microorganisms, the individual superparamagnetic nanoparticles can be bonded onto their surfaces. Even if a relatively low surface concentration of the nanoparticles is bonded and the magnetization of the object is small, its magnetic moment in the magnetic field can be large enough for effective separation, because of its relatively large volume [23].

As the magnetic material for the carriers, simple magnetic iron oxides like maghemite (γ-Fe_2O_3) or magnetite (Fe_3O_4) are normally used in magnetic separation [24–26], because of their low cost and relatively simple synthesis. The nanoparticles of iron oxide are also considered to be nontoxic and were approved by the U.S. Food and Drug Administration (FDA) for *in vivo* medical applications [26].

Nowadays, micron-sized, superparamagnetic beads, i.e., spherical nanocomposite particles containing superparamagnetic nanoparticles dispersed in a solid matrix, usually a polymer, are the most frequently used materials as the magnetic carriers in bioseparation [26,27]. The superparamagnetic iron-oxide nanoparticles are usually synthesized within the pre-synthesized, micron-sized, porous polymer beads. The nanosized superparamagnetic nanocomposite particles can also be synthesized by different synthesis processes, such as mini-emulsion polymerization [28], in-situ polymerization [29], polymer coating [21], and emulsion solvent evaporation [5]. The disadvantages of the composite carriers are in the low magnetization related to the dilution of magnetic properties with the non-magnetic matrix and the low surface-to-volume ratio.

As an alternative, the superparamagnetic nanoclusters can be synthesized by assembling individual superparamagnetic nanoparticles into nanoclusters in their aqueous suspension. The assembling can also be used to combine nanoparticles of different functional materials into multifunctional composite nanoparticles, for example, by combining magnetic nanoparticles with catalytic, photocatalytic, fluorescent, plasmonic, etc., nanoparticles [30–32]. Heteroaggregation, i.e., the process of aggregation between nanoparticles of different types (composition, charge, or size) has been shown to be important in many areas, such as waste-water treatment [33–35], catalytic materials [36], and in biotechnology, for example, in cell recovery [37–39]. The key to the synthesis of nanoclusters or composite nanoparticles is in controlling the interactions between the nanoparticles in the suspension. Understanding the interactions between the nanoparticles in the suspension is also of crucial importance for bonding a high surface concentration of superparamagnetic nanoparticles onto large targets, such as microorganisms, in the process of their magnetic separation.

Generally, the interactions can be divided into electrostatic attractions, acting between nanoparticles displaying opposite surface charges, and chemical interactions, originating from chemical reactions between different molecules at the nanoparticles' surfaces. The electrostatic heteroaggregation is based on electrostatic interactions in the suspension [40]. Unlike van der Waals interactions, which are primarily attractive in nature, electrostatic interactions can be either attractive (between oppositely charged particles) or repulsive (between like-charged particles) and even directional (in the case of particles with asymmetric surface-charge distributions) [41]. While van der Waals attractions will result in nonspecific spontaneous agglomeration, electrostatic forces can be applied to control the aggregation. The heteroaggregates formed by electrostatic interactions between oppositely charged nanoparticles were synthesized by the attachment of smaller nanoparticles, e.g., gold or maghemite, to the functionalized surfaces of larger nanoparticles, e.g., silica or polystyrene [42–45]. Another possibility for synthesizing heteroaggregates by electrostatic interactions is by using layer-by-layer (LbL) techniques, where a multilayer of smaller nanoparticles is attached onto larger templates [46–49].

Even better control over the process of heteroaggregation in suspensions can be achieved by using the chemically-directed assembly of nanoparticles in suspensions [50,51]. The nanoparticles will assemble into clusters as a result of chemical interactions originating from covalent bonding, hydrogen bonding, or donor–acceptor interactions. To control the surface chemistry of the nanoparticles, they are usually functionalized, i.e., appropriate organic molecules are grafted onto the nanoparticles' surfaces in order to provide reacting terminal functional groups. For instance, heteroaggregates were formed by the hydrogen bonding between amino-functionalized gold nanoparticles and crown-ether-decorated superparamagnetic iron-oxide nanoparticles [52] or by grafting gold nanoparticles onto thiol-functionalized magnetic nanoparticles [53]. Hetero-aggregates were also formed by using the assembly of amino-functionalized magnetite nanoparticles and NiO nanoparticles [54]. Usually, the formation of heteroaggregates is studied using larger silica spheres, e.g., thiol- or amino-functionalized, and smaller functionalized nanoparticles, such us palladium [55], or magnetite [56]. Specific biomolecular cross-linking interactions originating from DNA duplexes [57,58], biotin–avidin interactions [59], antigen–antibody recognition [60], or low-affinity immune-system carbohydrate-selectin interactions [51] can also be applied for improved selectivity of the interactions between nanoparticles. In addition, the nanoparticles can be assembled by using crosslinker molecules [61,62]. These crosslinkers are chemical reagents used to bind molecules together with a covalent bond and are applied in protein-crosslinking applications, e.g., in the immobilization of proteins on solid supports for affinity purification [63,64].

In this work the formation of heteroaggregates by the controlled heteroaggregation of two different types of nanoparticles in their aqueous suspensions has been studied. The carboxyl-functionalized, silica-coated, maghemite nanoparticles (cMNPs) and the amino-functionalized silica nanoparticles (aSNPs) were assembled into heteroaggregates in an aqueous suspension applying electrostatic interactions and chemical interactions between the nanoparticles. For the synthesis of the superparamagnetic clusters for applications in magnetic separation the two types of superparamagnetic nanoparticles, i.e., amino-functionalized and carboxyl-functionalized, would be assembled in the suspensions. The same approach can also be used in the synthesis of multifunctional nanocomposite particles, combining nanoparticles of different materials. On the other hand, the bonding of the smaller maghemite nanoparticles onto larger silica nanoparticles represents a model for bonding individual superparamagnetic nanoparticles onto larger objects, for example, microorganisms, which is a crucial part in the process of their magnetic separation.

The work represents a rare direct comparison between the heteroaggregation controlled by the two types of interactions in the same system of the two types of functionalized-nanoparticles. Up to now, mainly the heteroaggregation of larger micron- or sub-micron-sized particles has been studied [65–67].

2. Materials and methods

2.1. Materials

Silica nanoparticles (SNPs) were synthesized using a modified Stöber process by Dr. Marjan Bele from the National Institute of Chemistry, Ljubljana, Slovenia [68]. For the amino-functionalization of the silica nanoparticles (aSNPs) 3-(2-aminoethylamino) propylmethyldimethoxysilane (APMS) was grafted onto their surfaces, as described elsewhere [69].