



Review Articles

Layer-by-layer assembled iron oxide based polymeric nanocomposites

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ARTICLE INFO

Keywords:

Magnetic nanocomposites
Iron oxide nanoparticle
Polymers
Layer-by-layer assembly
Dipolar interactions
Ferrites

ABSTRACT

Hybrid nanocomposites are nowadays the focus of intensive scientific and industrial research motivated by expectations from fields as diverse as microelectronics and medicine. One of the challenges faced by these materials, before getting into applications, is the development of methodologies capable of processing them in the form of thin planar nanostructures. To achieve this, bottom-up manipulation, such as the layer-by-layer approach capable of growing nano-objects while controlling position and inter-particle distances, has made possible the construction of assemblies with properties tailored on the nanoscale level. This review will summarize the new initiatives taken in the area of colloidal iron oxide nanoparticles and their arrays in polymeric matrix employing the layer-by-layer technique related research. Aiming to understand fundamental issues such as the effect of nanocomposite morphology on the collective magnetic properties, experiments and simulations performed to assess both the nanocomposite's morphology and the corresponding magnetic signatures, will be discussed. Applications leading to future developments related with these nanostructures, as for instance chemical sensors and storage devices, will also be highlighted.

1. Introduction

The assembly of molecular and nano objects – to build multifunctional materials, provides exciting opportunities for technologies at the interfaces between chemistry, physics, biology and nanomedicine – has been attracting significant interest in recent years [1–4]. The nanoparticles which possess unique geometrical shapes and media responsive optical, electronic and magnetic properties, have been employed as inorganic counterparts in nanocomposite assemblies [5–8]. In addition, recent development of colloidal synthesis methods and bottom-up approaches, enabled the production of organized 2- and 3-D nanostructures from DNA, enzymes, proteins, peptides, polymers, metallic and iron oxide nanoparticles, magnetic nanoparticles, graphene, carbon nanotubes, quantum dots, etc [9–15]. For most applications, ultrathin layers are required for the devices active layers [16–18]. Among bottom-up approaches, the layer-by-layer (LbL) assembly [19–20], consisting of sequential adsorption of different molecules and nano objects, has been successfully employed. In this technique, different components are transferred and held together at the surface of a solid support by different types of intermolecular forces. This approach allows the design of all-organic and organic-inorganic multilayers with molecular-level control over the composition, morphology, thickness, and architecture. The LbL nanocomposites can be engineered on the surface of any type of solid support, ranging from smooth to rough, in any shape such as flat slides, rods, beads and in any size, of solid

support from macro to nanoscale. In addition, LbL approach ensures efficient scale-up, cost effectiveness, and automation facilities [21–23]. The assembled nanostructures not only combine attractive functionalities of each component but also show synergetic characteristics, enabling them for multiple applications such as coatings, capacitors electrodes, storage energy, chemical sensors, and drug delivery systems [24–26].

Regarding magnetic nanomaterials, the LbL technique can be employed to assemble several types of superparamagnetic iron oxide nanoparticles (IONP) with common polyelectrolytes, resulting in nanocomposites with a synergistic combination of properties from both components [27]. Polyelectrolytes are essential in these types of nanocomposites, since they not only hinder nanocrystal agglomeration but also provide the mechanical and chemical stability of the nanomaterial. In addition, some types of polyelectrolytes may present electrical conductivity or response to temperature gradients, which thus turn films smart materials [28]. As inorganic magnetic components, IONPs, with small size (3–20 nm), exhibit novel size- and shape-dependent magnetic, electric, chemical, optical and thermal properties in comparison to their bulk counterparts. They are usually elaborated as stable colloidal dispersions, also known as magnetic fluids (MF), nanofluids or ferrofluids [29–32]. In particular, IONPs exhibit superparamagnetism [33,34] biocompatibility, and surface functionalities, making them very attractive for fundamental studies and a variety of potential applications [35,36], such as biomolecular separation [37],

E-mail address: soler@unb.br.<https://doi.org/10.1016/j.jmmm.2018.07.035>

Received 1 March 2018; Received in revised form 2 June 2018; Accepted 10 July 2018

Available online 18 July 2018

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nanocatalysis [38], rotating seals and magnetorheological vibration dampers [39], magnetic recording media [40], SERS probe [41], insulating oil for improvement of transformer's cooling efficiency [42], sensors [17,25,43–44], and biomedical applications [45–48]. Interesting, under external magnetic field, colloidal suspensions of IONPs exhibit reversible physical properties. For instance, the thermal conductivity of colloidal magnetite suspensions can be increased by changing the linear aggregation length from nano- to micron scales [32]. Systematic studies about the effect of applied magnetic field on the tunability of the thermal conductivity and viscosity of colloidal IONPs has demonstrate that magnetically controllable colloidal IONPs can behave like a multifunctional “smart” material that can remove heat and also arrest vibrations acting as a damper, opening an opportunity for applications in microfluidic devices [32,49].

IONPs can also be encapsulated inside the oil droplet during the emulsification process, using an anionic surfactant of sodium dodecyl sulphate as a stabilizer. It allows to one produce oil-in-water (O/W) ferrofluid emulsions [50]. These magnetic responsive nanoemulsions have been employed as non-enzymatic approach for glucose [51], and urea detection [52]. In another approach, magnetic emulsion stabilized with poly(N-isopropylacrylamide) (PNIPAM) were employed to prepare thermally tunable grating [53]. The temperature responsive conformational changes of PNIPAM, at the O/W interface, enables the inter-particle periodicity control. These thermo-magnetic multi-stimuli nanoemulsions are promising candidates for applications in visual and calorimetric sensors, temperature tunable grating, photonic materials, optical devices, and drug delivery systems [53].

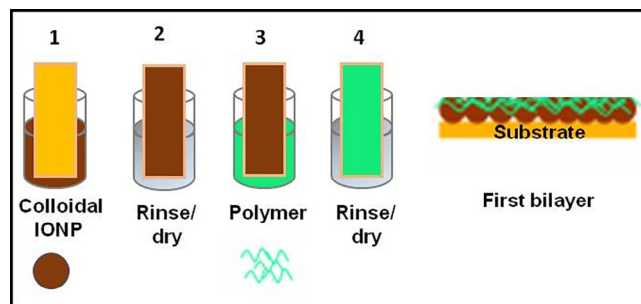
The LbL technique has also been successfully employed for the preparation of magnetic nanocomposites, incorporating nanosized magnetite, maghemite, and cobalt ferrite, with different polyelectrolytes, including conducting polymers [24,25,27,54–76]. The magnetic nanoparticles, provided as aqueous colloidal dispersions, behave as electrolyte species. Thus they can be assembled through electrostatic interactions with oppositely charged polyelectrolytes. The inter-particle distances within the multilayered film can be finely tuned by varying physicochemical conditions of deposition dispersions; as well as by the number of deposited layers [62,69,70,72], or by manipulating the nanocomposite architecture [57,68,74]. Therefore, the LbL approach creates a unique window of opportunity to investigate morphological effects on magnetic nanocomposite properties, and in particular superparamagnetic behavior in quasi-bidimensional (2D) or 3D structures.

Through the years, LbL IONP/polymer nanocomposites have been investigated through both experiments and simulation of IONP adsorption kinetic, NP oxidation, morphology, structure, optical, dielectric, electrochemical and magnetic properties [24,25,54–76]. Furthermore, LbL-IONP/polymer structures present potential applications beyond the superparamagnetic behavior. The existence of Fe^{2+} and Fe^{3+} ions makes the iron oxide nanoparticles very useful for a variety of electrochemical devices, including electrodes for supercapacitors [24,76] and chemical sensors [17,25].

In this review, we shall focus mainly on recent progress in LbL nanocomposites comprising IONPs and polymers. Details of LbL assembly, and physicochemical aspects of mono and multilayer formation, nanocomposite morphology, and magnetic properties, as well as emerging applications, will also be discussed.

2. LbL assembly of nanocomposites

The LbL approach consists of the sequential dipping of a solid functionalized substrate into colloidal suspensions or polymer solutions of different species producing mono or multilayered assemblies held together by a wide range of intermolecular forces, including ionic interaction, hydrogen bonding, complexation, biospecific recognition, hybridization, hydrophobic interaction, and covalent attachment [9,21]. Furthermore, the LbL technique is quite inexpensive since it



Scheme 1. Illustration of the LbL assembly of IONP/polymer nanocomposite and the first deposited bilayer.

does not require clean rooms or sophisticated glassware, and is conducted at room temperature. Despite its simplicity, LbL provides an unprecedented control of film thickness and internal structure.

Under electrostatic approach, the nanocomposite deposition starts with a functionalized substrate, comprising charged surface groups, being immersed into an oppositely-charged polyion solution, or NP dispersion. Because the charge balance between substrate surface and polyelectrolyte (or IONP) ionized groups, after a short period of time (order of few minutes) an ultrathin polyelectrolyte or NP monolayer is attached to the substrate and, the process proceeds and ends at its own. In fact, in the electrostatic LbL, the net charge of the substrate is overcompensated by the upcoming polyelectrolyte (or IONP) layer and the initial substrate charge is reversed [77]. When this condition is reached, the process ends and no more additional polyelectrolyte (or IONP) are adsorbed due to inherent electrostatic repulsions. Because of this character, the LbL is classified as a self-assembly method. During the deposition, the IONP/polymer bilayer is formed first, acting as the elementary repeating unit (see Scheme 1), the nanocomposite thickness can thus be increased by simply adding more IONP/polymer bilayers provided that anionic and cationic layers are adsorbed alternately.

Nanosized iron based cubic ferrites have been employed as inorganic counterparts in the LbL nanocomposite assembly. The chemical composition of cubic ferrites is MFe_2O_4 , where M denotes a divalent transition-metal as Fe, Co, Ni, Mn, Cu, Zn, and Cd, which present ferromagnetism magnetic ordering. Cubic iron oxide ferrites possess the spinel structure formed by a nearly close-packed face-centered cubic array of oxygen anions with interstices partly filled by metallic cations [29,78]. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is an iron-deficient cubic ferrite [79], which is one of the most investigated iron oxides besides. In addition, magnetite has a half-metallic character with a large spin polarization at the Fermi level, presenting a high Curie temperature (850 K) and electrical resistivity of the same order of magnitude as a semiconductor. Hence it is a promising candidate for spintronic applications [80,81].

Bulk magnetic materials have a multi-domain structure, comprising regions of uniform magnetization surrounded by a domain wall (DW) structure. As the dimension of the magnetically-ordered material decreases towards the nanoscale, the typical domain-size and the DW-width decrease modifying its inner structure. Therefore, the orientation of the magnetization no longer splits into smaller domains, but instead maintains the magnetic structure of a single-domain. The magnetic behavior of a single-domain particle is described as a single “giant” spin, because of the atomic moments being aligned along the easy axis direction, which results in a big magnetic moment, called superparamagnetism. In the superparamagnetic regime, the orientation of the nanoparticle magnetic moment thermally fluctuates around the easy axis direction. The simplest picture describing the magnetic moment dynamics within the superparamagnetic particle is the one-dimensional symmetric double-well potential stemmed from the magnetocrystalline anisotropy. It lines up the magnetic moment in a particular crystallographic direction, as for instance the [111] direction in magnetite. However, thermal energy induces re-orientation of the magnetic

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