Polymers as Versatile Players in the Stabilization, Capping, and Design of Inorganic Nanostructures

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ABSTRACT: The integration of simple components to generate sophisticated hybrid materials with fine-tuned properties represents a significant scientific challenge. Herein, we present recent advances in the use of polymers to control the synthesis and properties of three of the most relevant inorganic nanoparticles, namely, quantum dots (QDs), magnetic nanoparticles (MNPs), and noble metal nanoparticles (NMNPs). We show relevant examples of how polymeric structures synthesized by techniques such as ATRP, RAFT, and living cationic polymerization are used to aid in the synthesis and stabilization of the nanostructures to generate nanocomposites with outstanding capabilities. Special emphasis is placed on describing how some of the exceptional physicochemical properties of polymers are used as nanoreactors to facilitate the synthesis of the nanostructure by providing an adequate chemical environment. Additionally, we also describe how polymers are utilized to protect the integrity of the nanostructure from chemical degradation. The integration of polymeric structures and the nanostructures has a strong impact on the dispersion and morphology of the latter and, consequently, endow them with novel and promising features. The advances described here, particularly the use of polymers to modulate and provide new properties to nanoparticles, exemplify the great versatility of polymers and how these may expand the capabilities of inorganic nanostructures that can be used to generate novel and sophisticated hybrid materials.

1. INTRODUCTION
Polymers have been the most widely used material for the past few decades and it is expected that their applications will continue to increase in the future mainly due to the variety of properties they display, including insulating, conductive, hydrophilic, hydrophobic, and biodegradable or biocompatible properties. Even biopolymers—macromolecules obtained from natural sources—have attracted much attention for the design of novel materials due to their environmentally friendly features and mild methods for synthesizing and functionalizing nanoparticles.

The development of synthesis methods permits broad polymer versatility, allowing the combination of chemically different monomers to form macromolecules with different degrees of polymerization and monomer distributions capable of generating linear, branched, or 3D network structures arrangements and even nanoscopic or microscopic structures. In particular, block copolymers—polymers with two or more chemically different segments—possess unique features due to their self-assembly capabilities in solution, thin films, or bulk, which can be used to produce highly sophisticated materials.1

Recently, a substantial body of work has shown that polymers, both biopolymers and synthetic polymers, can play an active role in the synthesis and surface modification of nanostructured materials, functioning as templates, nanoreactors, stabilizers, coating agents, or a combination of those. Indeed, nanoparticle surface functionalization is of great importance for the design of new materials, and it frequently requires diverse strategies where the simple one-step processes frequently provided by polymers are preferred.2 In addition, hierarchical arrangements of nanostructures via polymer-guided assembly are highly desirable and possible through the use of polymers during or after nanoparticle formation.

Polymers used as templates or nanoreactors during nanoparticle synthesis often form complexes with nanoparticle...
precursors mainly by electrostatic interactions. A subsequent reduction of such metal ions, which is in many cases done by the same polymer, leads to nanoparticle nucleation and growth processes. Thus, polymer conformation, macromolecular architecture, and polymer–solvent interactions can create important modifications in the growth environment of nanoparticles, aiding in the control of the shape, size, and dispersion of the nanoparticles.

The use of polymers as stabilizers or capping agents for nanoparticle functionalization and stabilization, on the other hand, is mostly based on weak noncovalent bonds between both materials. Additionally, the polymer structure and the polymer–solvent interactions affect important processes such as self-assembly, impacting on the final properties of these hybrid materials.

Due to the rapid and extensive progress in the scientific field of polymers and inorganic nanostructures, in this minireview we focus our attention on describing how synthetic polymers are used in new and novel ways during the synthesis of inorganic nanostructures, including quantum dots, magnetic nanoparticles, and noble metal-based nanostructures, that enable the modulation of the physicochemical properties of the nanomaterials.

2. QUANTUM DOTS AND POLYMERS

Quantum dots (QDs), also known as “artificial atoms”, are semiconductor particles with a size smaller than 10 nm, which confers them with size-dependent properties characteristic of the quantum confinement regime. This phenomenon allows highly tunable optical properties that, along with other features such as high photostability, broad absorption, and narrow emission spectra, make QDs valuable materials for different scientific fields, especially as excellent donors in Förster resonance energy transfer (FRET).

2.1. Polymers in the Synthesis of Quantum Dots. QDs are typically synthesized through the thermal or chemical decomposition of the precursors in solution. While the majority of syntheses are relatively simple and straightforward, most of them exhibit a common disadvantage related with the presence of some compounds typically used during the synthesis process, such as tri-n-octylphosphine oxide (TOPO) and trioctylphosphine (TOP). Previous research has shown that both TOPO and TOP, while essential in traditional QDs syntheses, can affect the quantum emission yield since they are prone to decomposition at high temperatures used during most syntheses. The resulting product exhibits luminescence that can be mistaken for the semiconductor’s emission. Additionally, the cytotoxicity exhibited by these ligands and the difficulty of removing them from the nanoparticle surface can impede their potential use in biomedical applications. Syntheses of polymer-based QDs, on the other hand, provide a good alternative to overcome some of these disadvantages faced by typical syntheses since polymers can not only aid in the nanoparticle synthesis but also yield nanoparticles with a variety of properties, including adequate biocompatibility and hydrophilicity. Besides, polymers can be used to enhance the QDs’ selectivity and sensitivity toward certain molecules and can also provide them with robust protection against oxidation and other physical phenomena that can suppress their photoluminescence, such as Auger recombination.

2.1.1. As Polymeric Templates and Nanoreactors. Highly sophisticated polymeric micelles formed by amphiphilic block copolymers can act as nanometer-sized reaction compartments (i.e., nanoreactors), which are able to assist in several NP syntheses. These micelles can be prepared by the self-assembly of block copolymer mixed micelles or by polymerization-induced self-assembly (PISA) approaches. The former approach is very straightforward and consists of a mixture of amphiphilic block copolymers in solution, which spontaneously self-assemble at concentrations above the critical micelle concentration (CMC) into micelles via interactions between the different block copolymers (e.g., hydrophobic interactions and stereocomplexation). On the other hand, in the PISA approach, the self-assembly occurs during the formation of the second block of the copolymer. Typically, the PISA method involves the use of a soluble precursor block that is immersed in a monomer solution with an initiator or activator, permitting the growth of a new block. Then, the newly synthesized block becomes insoluble in the reaction solution at a certain degree of polymerization, favoring the macromolecule’s self-assembly. This combination of polymerization and self-assembly yields different polymer morphologies such as spheres, worms, and vesicles that can be of utility in nanocrystal synthesis.

Coleman and Moffitt reported the design of nanostructures consisting of QD cores coated with polymer brushes that were prepared by the micelle mixed approach. Two types of block copolymers, polystyrene-\textit{block}-poly(acrylic acid) (PS-b-PAA) and poly(methyl methacrylate)-\textit{block}-poly(acrylic acid) (PMMA-b-PAA), were mixed to form reverse micelles and then left to interact with the QD precursors to provide a template for the nanocrystal growth. Once the nanocrystal formed, the polymer core was cross-linked to freeze the core structure. A final hydrolysis step was performed to obtain a mixed hydrophobic/hydrophilic polymer brush on the surface of the nanostructure. Interestingly, this mixed polymer brush provides the material with unique behavior; once the polarity of the solvent increases, centrosymmetric QDs@Polymers are obtained. However, in the presence of salts, the polymer brushes arrange in such a way that non-centrosymmetric Janus-like particles are produced. Those amphiphilic structures can be further self-assembled into QDs–polymeromes.

Liu et al., on the other hand, showed that some complex polymeric structures, such as amphiphilic graft star copolymers, can be used as nanoreactors for the synthesis of nanocrystals while also providing the nanoparticle with adequate protection (Figure 1). This highly complex polymeric structure was obtained by atom transfer radical polymerization (ATRP), a technique that allows not only control over the molecular weight but also the modulation of the structure of the polymer blocks, since the chains can be used as macroradicals due to their terminal functionality. The presence of these functional groups favors the permeation of the nanoparticle precursor into specific compartments, which facilitates the growth of the nanocrystals. Their approach yields nanocrystals with an outstanding stability against degradation due to the presence of the polymeric barriers that protect the surface of the nanocrystal against UV radiation, heat, and polar organic solvents.

2.1.2. As Stabilizing and Capping Agents. Frequently, stabilization and protection of QDs are performed using polymers due to the high steric hindrance and great surface affinity they are able to provide. There are two main strategies to achieve this: (i) an encapsulation process, which involves
covering QDs and the original ligands from the synthesis within the polymeric structure, and (ii) the ligand exchange process, where the capping ligands from the synthesis process are replaced by polymer molecules.

2.1.2.1. Encapsulation Process. Complete coverage and good stability are some of the advantages that encapsulation techniques provide. Currently, most encapsulation methodologies are based on either hydrophobic—hydrophobic or electrostatic interactions between the polymer and the original ligands. Hydrophobic—hydrophobic interaction-based encapsulation can be done using amphiphilic copolymers by intercalating the hydrophobic blocks between the original nanoparticle capping ligands, which can render materials robust enough to be used in biological environments. Alternatively, encapsulation via electrostatic interactions is achieved through the interaction between charged polymers (polyelectrolytes) and the charged QD ligands, which can also be polyelectrolytes. Unlike the stability of covalent interactions, which depends on the bond strength, this encapsulation process allows for multiple anchoring points that can be easily functionalized, allowing the design of complex three-dimensional structures such as vesicles.

2.1.2.2. Ligand Exchange Process. Occasionally, it is necessary to remove the original capping ligands and exchange them for others that either guarantee the total coverage of the surface of the QDs and protection from physical phenomena or endow them with homogeneously distributed surface properties. Currently, one way to ensure complete QD surface coverage is to use molecules with amino or thiol functional groups on one or both ends of the polymer. This is possible through the interaction between charged polymers (polyelectrolytes) and the charged QD ligands, which can also act as reducing agents for the synthesis. Due to their responsiveness to external magnetic fields and small size, magnetic nanoparticles (MNPs) often exhibit superparamagnetism that makes them useful in different research areas, especially in the medical field such as T1 (i.e., negative) contrast agents in magnetic resonance imaging.

3. MAGNETIC NANOPARTICLES AND POLYMERS

Due to their responsiveness to external magnetic fields and small size, magnetic nanoparticles (MNPs) often exhibit superparamagnetism that makes them useful in different research areas, especially in the medical field such as T1 (i.e., negative) contrast agents in magnetic resonance imaging.
(MRI). In biological environments, MNPs interact with the protons of water molecules that disturb the nuclear relaxation environment, reflecting the loss of transverse magnetization (transverse relaxation) and increasing the signal contrast between the surroundings and the distal background.14

3.1. Polymers in the Synthesis of Magnetic Nanoparticles. Magnetic nanoparticles are commonly prepared by chemical methods such as coprecipitation, thermal decomposition, polyol, and solvo- or hydrothermal synthesis. The control of certain parameters in these reactions (temperature, pH, and the type of solvent, for example) has a profound impact on the morphology of the nanoparticles. However, these nanostructures, regardless of the synthesis used, tend to aggregate and even precipitate, affecting some of their potential applications. One of the most versatile strategies to improve the applications of magnetic nanoparticles is through the use of polymers during or after their synthesis. Polymers aid in minimizing the Gibbs free energy of MNPs in solution, avoiding the formation of large agglomerates.15 Likewise, a polymeric coating provides MNPs with a functionalized protective surface that allows them to have sensitivity to certain molecules, increases their biocompatibility, and in some cases makes them responsive to external stimuli, to name a few.

3.1.1. As Polymeric Templates and Nanoreactors. Polymers with high steric hindrances, such as hyperbranched copolymers, can be used as templates for the design of magnetic nanoparticles. The presence of functional groups along the complex ramifications of the polymers permits precursors to be fixed in specific locations by creating “complexes” inside the macromolecule that are subsequently chemically reduced by the reducing agent.16 It is at these same sites where both nucleation and the growth of MNPs take place.

As mentioned before, one of the most interesting advantages of using polymers during the synthesis of MNPs is the possibility to create “smart” materials built from smart polymers. Smart polymers are macromolecules that undergo physical or chemical changes in response to one or more external stimuli such as pH, temperature, and electromagnetic fields, to name a few. Kronenberg et al.17 demonstrated that smart diblock copolymers, where the two blocks respond to different stimuli, can be used to first control the nanoparticle synthesis and then to create switchable magnetic nanoparticle superstructures. The block copolymer, consisting of one block of poly[2-(2-ethoxy)ethoxyster vinyl ether] and a second block of poly(2-aminoethyl vinyl ether), was synthesized using living cationic polymerization. The polymer design allows the first block to modify its hydrophobic or hydrophilic behavior with temperature changes, permitting the final nanocomposite to be soluble in different solvents. The second block, attached to the MNP surface, displays a structural modification with pH, a very relevant feature in polymer-assisted nanoparticle synthesis.

3.1.2. As Stabilizing and Capping Agents. As previously discussed, polymers as capping and stabilizing agents in nanotechnology can help to protect the nanoparticles against harsh conditions or provide them with other properties. For this, the nature of the polymer is essential, since the nanoparticle protection depends on the affinity of the polymer for the nanostructure surface, and different types of interactions, including van der Waals forces, electrostatic interactions, and hydrogen bonds, become relevant for the stability of the nanocomposite. Also, properties such as chain functionality, size, and molecular weight affect the stability, dispersion, and interaction of nanoparticles with other molecules.

In this context, Xiao et al.18 investigated the role of the morphology of multidentate polymer ligands (i.e., linear versus brush) in the stabilization of ultrasmall superparamagnetic iron oxide nanoparticles (USPIOs). For that, they used two block copolymers. The first one is PEO-b-PMAA, which is composed of linear poly(ethylene glycol) (also known as poly(ethylene oxide) (PEO) depending on its molecular weight) and poly(methyl methacrylic acid) (PMAA). The second block copolymer is the branched POEOMA-b-PMAA, which is composed of a block of poly[oligo(ethylene oxide)-monomethyl ether methacrylate] (POEOMA) and PMAA. Both block copolymers, PEO-b-PMAA and POEOMA-b-PMAA, were synthesized by ATRP polymerization followed by partial hydrolysis. The results showed that nanocomposites made with both block copolymers have a strong stability under physiological conditions and that their size (9.9–14 nm) and surface charge prevent rapid blood clearance. However, the nanocomposites coated with the brushed copolymer showed greater interactions among the surface of blood vessels, blood cells, and plasma proteins, which were mainly attributed to the presence of a large number of reactive groups generating possible agglomerates. The nanostructures coated with the linear block copolymer showed high longitudinal relaxivities and an increased signal in T1-weighted imaging at low concentrations, making them more efficient as positive MRI contrast agents in T1-weighted MRI.

In the literature, there are also some examples where the presence of polymers conferred delicate features to the composite. Goyal et al.19 showed that polymer-encapsulated superparamagnetic nanoparticles can be used to selectively separate (S)-naproxen from a racemic mixture through molecularly imprinted technology (Figure 3). The presence of superparamagnetic cores helped to create selective active sites on the composite surface through accelerating the binding kinetics between the polymer and the (S)-naproxen molecule. For that, silica-coated Fe3O4 nanoparticles, prepared by coprecipitation, were surface-modified to later carry out a surface copolymerization process with ethylene glycol

![Figure 3. Design of imprinted nanomaterials for the separation of the (S)-naproxen molecule.](https://doi.org/10.1021/acsomega.1c05420)
dimethacrylate (EGDMA) and acrylamide (AM) monomers. Finally, [(S)-naproxen], the "template molecule", was added to the copolymerization reaction to create cavities with a specific size and shape, permitting enantiomer-specific fitting once the template was removed.

4. NOBLE METAL-BASED NANOPARTICLES AND POLYMERS

Noble metal-based nanoparticles (NMNPs) are often called plasmonic nanoparticles due to their ability to couple their electron density with electromagnetic radiation, causing coherent oscillations of free electrons (conduction band electrons) on the nanoparticle surface. The oscillation is extremely sensitive to morphology, size, dispersion, and the environment that surrounds the nanostructures; thus, their intense colors, remarkable absorption and scattering are affected. Indeed, their remarkable optical and electromagnetic properties can be used to enhance the surface Raman scattering and create "hot spots", which are favored by agglomerations of the nanoparticles. Therefore, when they are combined with other materials to design hybrid materials, especially with polymers, agglomerations must be controlled.

NMNPs also show important antimicrobial properties through diverse mechanisms that include the generation of reactive oxygen species (ROS), interactions with the cell wall, and their absorption into the cell, which have detrimental effects on bacterial metabolism.21

4.1. Polymers in the Synthesis of Noble Metal-Based Nanoparticles. NMNP colloids are usually prepared by reducing dissolved metal precursors in solution to generate atoms that will nucleate and grow. However, during synthesis the presence of molecules to modulate the nanostructures' size and also to prevent their agglomeration is often necessary. Polymers are often used to achieve the aforementioned goal and also work as templates during nanoparticle synthesis. In fact, some macromolecules can act as reducing agents, templates, and stabilizers at the same time, simplifying the synthesis process and yielding nanocomposites with different interesting capabilities.

4.1.1. As Polymeric Templates and NanoReactors. Polymers can be so versatile that they can assist in the synthesis of nanostructures with unique morphologies and compositions, such as metal heterodimers. For instance, Qiu et al.22 showed that polymers can be used to partially protect gold seeds that allow the subsequent generation of Janus-like nanoheterodimers composed of a gold nanoparticle and another noble metal-based nanoparticle (Ag, Pd, or Pt). This partial protection improves nanoparticle dispersion and, through the high affinity between the metallic species, favors the nucleation and growth of the second metallic nanostructures. For that, a surface poly styrene polymerization in the seed of the gold nanoparticles was first carried out, yielding a PS/Au structure (Figure 4). Then, after the removal of the PS component, highly tunable heterodimers of metal nanoparticles were obtained. This process avoids the use of "linkers", which are difficult to remove and whose presence compromises some important properties, and an asymmetric modification to obtain Janus-like particles, which depends on a considerable number of parameters.23

4.1.2. As Stabilizing and Capping Agents. The self-segregation capabilities that block the display of copolymers can be used to obtain anisotropic forms with controlled morphologies. Along these lines, Song et al.24 utilized surface ligands of different chain lengths to control the variation of polymer shell localization on both isotropic (gold spheres) and anisotropic (tellurium nanowires) particles after an annealing process.

To study the surface ligand–polymeric shell interactions, two types of surface ligands were used: a nepheline thiol ligand (i.e., a short ligand) and a polystyrene thiol ligand (PS-SH, i.e., a long surf ace ligand). In both cases, an amphiphilic block copolymer, polystyrene-b-poly(acrylic acid) (PS-b-PAA), was used as the polymeric shell. Once isotropic and anisotropic particles were encapsulated with PS-b-PAA, they were subjected to a post-heating treatment, allowing the polymer shell to adapt to the morphology with the lowest overall surface energy. AuNPs@PS-b-PAA with PS-SH adopt a centrosymmetric structure due to strong hydrophobic–hydrophobic interactions between the polymer shell and the PS surface ligand. Janus-like particles were obtained in AuNPs@PS-b-PAA with the nepheline thiol ligand because the polymer shell and the surface ligand interactions are weak; therefore, nanostructures cannot be covered completely, allowing subsequent superficial modifications.

Amphiphilic polymers and nanostructures are widely used in the design of supramolecular hybrid ensembles (i.e., "host–guest" system), which are built by noncovalent interactions between the components. This method constitutes a novel way to create sophisticated materials with varied morphologies. Fan et al.25 exemplify this by using β-cyclodextrin (β-CD) attached to the amphiphilic block copolymer and gold nanoparticles to prepare spherical, worm-like, and vesicular host–guest systems (Figure 5). The "host" part was an amphiphilic block copolymer containing β-cyclodextrin-polyethylene glycol)methyl ether methacrylate and poly(hydroxypropyl methacrylate)-4-cyano-4(((dodecylthio)-carbonothioyl)thio) pentanoic acid, β-CD-POEGMA-b-PHPMA-CDPA, was synthesized through RAFT and PISA methodologies. The morphological variations for this "host" structure into spheres, worms, and vesicles were achieved by varying the degree of polymerization (DP) and therefore the molecular weight (Mw) of the HPMA block. This confirms that the relative volume fraction of the hydrophilic block, as well as the Mw dictates the evolution of the morphology and the aggregation dimensions.
of the nanostructures (Figure 5). For the “guest” component, AuNPs coated with thiol-modified poly(N,N-dimethylacrylamide) (PDMA) containing adamantane (Ada) moieties (AuNPs@SH-PDMA-Ada) were used because the Ada fragments fit perfectly into the hydrophobic conical cavity of β-CD ($K_a \approx 10^4$ M$^{-1}$). Again, RAFT polymerization of N,N-dimethylacrylamide (DMA) was used to obtain the guest component, where 1-adamantanemethylamine coupled with CDPA acted as the RAFT agent, and a final modification yielded the thiol group, which allows a strong interaction with the surface of the AuNPs. Lastly, β-CD-POEGMA-b-HPMA-CDPA and the AuNPs@SH-PDMA-Ada were mixed to generate the “host–guest” system.

Yan et al.$^{26}$ showed how an amphiphilic block copolymer (polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP)) can be used as a scaffold to design systematic arrangements of nanoparticles through flat-emulsion-droplet confined assembly (FEDCA). This technique allows the block copolymers to gradually assemble into flat emulsion droplets as the organic solvent evaporates, causing the copolymer to precipitate into 2D arrangements with active sites for the subsequent growth of nanostructures. The synthesis procedure required the block copolymer to be dissolved in an organic solvent and then mixed with an aqueous solution of cetyltrimethylammonium bromide (CTAB). Later, the organic solvent was slowly evaporated so that the emulsion droplets collapsed to form a flat droplet with a low interfacial tension. Then, the glassy PS-b-P4VP particles were centrifuged and dispersed in deionized water, resulting in a PS sheet with a hexagonal arrangement of P4VP cylinders on the surface. Once the scaffolds were prepared, gold nanoparticle precursors were added. Due to the strong electrostatic interaction between the P4VP block and the metallic precursors, AuNPs nucleate and grow only in the hexagons, generating a uniform periodic arrangement of nanostructures.

5. CONCLUSIONS

The positive impact that nanostructures have in different fields due to their outstanding properties motivates those interested in materials science to explore innovative ways of synthesizing them and designing sophisticated structures in combination with other materials. This minireview addresses recent contributions on the use of polymers as nanoreactors, stabilizers, and capping agents for three of the most relevant inorganic nanoparticles, namely QDs, magnetic nanoparticles, and noble metal-based nanostructures. Polymers, as discussed above, influence the shape, size, and dispersion of these nanoparticles, impacting on their possible applications. Therefore, interesting biosensors, enantiomeric separators, and hybrid structures with hard-to-achieve morphologies such as nanoheterodimers and host–guest complexes can be made. There are still many new possibilities and challenges to explore, such as the use of computational tools (i.e., modeling and simulations) to delve into each of the complex processes that occur when combining polymers and nanostructures (e.g., nucleation and growth of nanostructures within polymeric nanoreactors, self-assembly of block copolymers decorated with nanostructures to design various molecular architectures, etc.). In addition, polymers obtained through other sources, such as biopolymers, can enrich the possibilities presented in this review for designing new composite materials. It is our hope that the condensed information described here will provide ideas and tools to continue expanding this scientific field and its applications.

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