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Controlled accommodation of metal nanostructures within the matrices of polymer architectures through solution-based synthetic strategies

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ABSTRACT

Controlled accommodation of metal nanostructures (MNSs) into the matrix of a well-defined polymer architecture offers an effective approach to achieve hierarchically structured nanocomposites with tunable synergistic properties to broaden application potentials in the emerging fields of energy, environmental science, and medicine. This review focuses on the recently developed zero-dimensional and one-dimensional MNSs@polymer hybrid nanostructures obtained by solution-based synthetic strategies. Progress in the controlled synthesis of those hybrid nanostructures in terms of the number (e.g., monomer, dimer and trimer), organization manner (e.g., linear alignment or confined assembly in certain domains), and spatial arrangement (e.g., in the core and shell) of the MNSs within the distinct polymer matrices are detailed. The synergistic properties and potential applications of those MNSs@polymer hybrids associated with their compositions and morphologies are also reviewed.

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Abbreviations: 1D, one-dimensional; 2D, two-dimensional; ATRP, atom transfer radical polymerization; CS, chitosan; CT, X-ray computed tomography; CTAB, trimethylammonium bromide; DMAP, 4-dimethylaminopyridine; DMF, dimethylformamide; DNA, deoxyribonucleic acid; DT, dodecanethiol; FITC, fluorescein isothiocyanate; GG, guger gum; HMT, hexamethylenetetramine; LBL, layer-by-layer; LCST, lower critical solution temperature; LSPR, localized surface plasmon resonance; MNS, metal nanostructures; MNS@polymer, MNS accommodated polymer architectures; MOF, metal organic framework; MPA, 3-mercaptopropionic acid; mPThP, monopyrene-terminated hyperbranched polyglycidol; MUL, 11-mercapto-1-undecanol; NIR, near infrared; NP, nanoparticle; NSi8, octa(3-aminopropyl)silsesquioxane; P2VP, poly(2-vinyl pyridine); P4VP, poly(4-vinyl pyridine); PAA, poly(acrylic acid); PAH, poly(allylamine hydrochloride); PAM, polyacrylamide; PANI, polyaniline; PBzMA, poly(benzyl methacrylate); PDDA, poly(diallyldimethylammonium chloride); PDMA, poly(2-(dimethylamino)ethyl methacrylate); PDP, pentadecylphenol; PEI, polyethyleneimine; PEO, poly(ethylene oxide); PFR, phenol formaldehyde resin; PFS, polyferrocenylsilane; PFVBT, Poly[9,9-bis(6'-N,N,N-trimethylammonium) hexyl]fluorenyldivinylene-*alt*-4,7-(2,1,3-benzothiadiazole) dibromide; PI, polyisoprene; PLGA, poly(lactide-*co*-glycolide); PMMA, poly(methylmethacrylate); PMPD, poly(*m*-phenylenediamine); PMPS, poly(methylphenylsilane); PMVS, polymethylvinylsiloxane; PNIPAM, poly(*N*-isopropylacrylamide); poly(OEG-*A-co*-DEG-*A*), poly(oligoethylene glycol methacrylate)-*co*-poly(di(ethylene glycol) methyl ether methacrylate); PoPD, poly(*o*-phenylenediamine); Ppy, polypyrrole; PS, polystyrene; PS-*b*-PVP, polystyrene-*b*-poly(4-vinylpyridine); PS-*co*-DVB, poly(styrene-*co*-(divinyl benzene)); PS-*co*-PGMA-IDA, polystyrene-*co*-poly[2-methacrylic acid 3-bis-(carboxymethylamino)-2-hydroxypropyl ester]; PSS, poly(styrene sulfonate); PSVPh, poly(styrene-*ran*-vinyl phenol); PTh, polythiophene; PVA, poly(vinyl alcohol); PVP, poly(vinyl pyrrolidone); RAFT, reversible addition-fragmentation chain-transfer polymerization; SDS, sodium dodecylsulfate; SEM, scanning electron microscopy; SERS, surface enhancement Raman scattering; TEM, transmission electron microscopy; THF, tetrahydrofuran; VLS, vapor-liquid-solid.

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1. Introduction

In recent decades, the synthesis of well-defined polymer architectures has attracted great attention because of their potential use in various nanosystems and nanodevices. Through a variety of synthetic strategies, such as self-assembly and templating approaches [1], a large number of polymer nanostructures have been constructed and featured in flexible chemical compositions, tunable morphologies, abundant surface functionalities, and responsive features depending on external stimuli. Importantly, these polymer architectures offer flexible platforms to host additional guest materials to generate novel hybrid nanostructures.

As an important type of guest materials, MNSs, especially those composed of the noble Au, Ag, Pt, and Pd metals, have emerged as fundamental tools for a number of fast growing applications in optoelectronic, biomedical, and catalytic fields, because of the unique optical, electronic, and catalytic properties associated with their particular compositions, sizes, morphologies, crystal structures, and surface features [2–7]. In many cases, the surface of MNSs needs to be passivated by organic materials, such as synthetic polymers, small molecules, and biomacromolecules to prevent their aggregation [8–15]. Mediated by these functional passivation layers, a variety of MNSs can be engineered into the matrices of different host polymeric architectures to produce novel MNS@polymer hybrid nanomaterials. These nanomaterials tend to exhibit synergistic properties that are different from those of the individual building blocks due to coupling and exchange phenomena [16]. These collective properties greatly broaden their potential applications in the emerging fields of energy, environmental science, and medicine [17–20].

In addition, polymers as host materials for accommodating MNSs have a number of outstanding advantages over conventional small organic molecules and inorganic

oxides: (1) they provide convenient dielectric media for the encapsulation of MNSs and endow them with high density of surface-coating so as to their enhanced long-term stability even under the chemically aggressive conditions, adjustable solubility and amphiphilicity, and abundant surface functionalities which facilitate further tailoring of their surface properties through diverse chemical schemes; (2) they render the corresponding MNSs@polymer hybrids with additional features and functions by taking advantage of their intrinsic and synergistic physicochemical properties; (3) they provide flexible handles to manipulate the organization of MNSs within the polymer matrix and direct the shape of the hybrid materials via varied techniques such as self-assembly; (4) hybrid materials may be manufactured on a large scale through different polymeric processing techniques, such as extrusion, molding, and thin-film casting.

It is recognized that the synergistic properties of MNS@polymer hybrids greatly depend on not only the chemical composition, size, and shape of the encapsulated MNSs, but also the volume fraction, spatial distribution and organization of the MNSs within the polymer matrix. For example, localized surface plasmon resonance (LSPR) derived from the collective excitation of conduction electrons is one of the most distinguishing features of MNSs [21]. The LSPR wavelength of MNSs (Au or Ag) can be readily tuned via the polymer coating as a result of the change in the local refractive index of their surrounding environments [22]. In particular, this wavelength shift can be controlled upon the variations of the utilized polymer types, the shell thickness of polymer passivation layers, as well as the interparticle spacings of MNSs and the size of MNS clusters [23–28]. Therefore, it is of significance to precisely assemble MNSs into the polymer matrix in a controlled manner. Sustained exploration of this controlled synthesis is believed to be a fundamental step toward the construction of functional nanodevices using MNS@polymer hybrids as building blocks.

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