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Synthesis and Applications of ZnO/Polymer Nanohybrids

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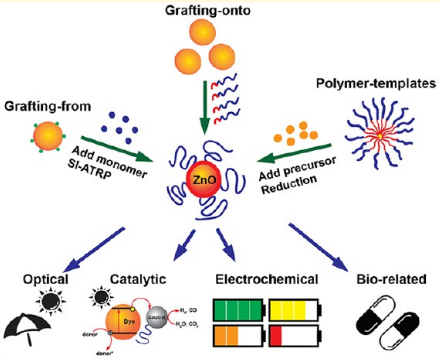
ABSTRACT: **Because of its distinctive combination of physical properties such as high thermal conductivity, ultraviolet (UV) absorbance, or catalytic behavior, zinc oxide-based nanoparticles have attracted interest for the use as fillers to augment a wide range of physicochemical properties of polymer materials, including their optical, dielectric, thermal, and catalytic characteristics. To accomplish the desired property enhancements, precise control of the microstructure of polymer/zinc nanoparticle blends is a prerequisite. This requires the ability to tailor and control the interactions between particle fillers and the polymer matrix. Much progress in the field of polymer/ZnO hybrids has been achieved through the development of surface-initiated controlled radical polymerization (CRP) methods that allow for the deliberate modification of zinc oxide surfaces with polymer chains. The ensuing enhancement in particle compatibility has enabled the design of novel multifunctional polymer/ZnO nanocomposite materials. This article surveys recent advances in the application of surface polymerization techniques to enable novel zinc oxide (ZnO)/polymer hybrids. The evolution of synthetic strategies from the pioneering work using "grafting-from" to recently developed "grafting-onto" and "templated synthesis" methods is presented. Subsequently, the opportunities for the design of functional nanocomposite materials based on ZnO hybrids with applications in optics, catalysis, energy, and biomedical areas are being presented. We conclude by highlighting current challenges and opportunities for research in this exciting area of polymer materials research.**



Because of their distinct thermal, mechanical, optical, magnetic, electronic, and catalytic properties, metal oxide nanocomposites are of particular interest. Among the different metal oxide semiconductors, zinc oxide (ZnO) has attracted particular interest, because of its outstanding properties, including high optical and thermal stability, low toxicity, excellent physical and chemical stability, and abundant availability.[1] Typically, ZnO is found in white color powder form as an inorganic material that is insoluble in water. It is applied as an additive in many materials and products, including lubricants, cosmetics, plastics, rubbers, ointments, food supplements, paper, pigments, batteries, ceramics, fire retardants, first-aid tapes, and cement.[2] ZnO is a wide bandgap (3.37 eV) binary compound of the II−VI semiconductor group.[3] ZnO crystallizes in wurtzite structure (*P*63*mc*); the absence of centrosymmetric gives rise to polar surfaces and renders ZnO a piezoelectric with potential applications in sensors or micromechanical systems.[4] Additional opportunities for modulation of physical properties are provided by spatial confinement in nanocrystal form. For example, size control of ZnO nanocrystals has been shown to enable tuning of the bandgap in the range of 3.1−3.37 eV,[5,6] along with a large exciton binding energy (60 meV),[7] and Hall mobility of 200 $cm^2\ V^{-1}\ S^{1-}$.[8,9] ZnO also exhibits a high dielectric constant ($\varepsilon_r \approx 8.5$) and refractive index ($n \approx 2$ at $\lambda = 580$ nm), as well as high thermal conductivity $k \approx 50\ W\ m^{-1}\ K^{-1}$.[10] The combination of physical properties along with chemical accessibility and robustness have motivated research in utilizing ZnO nanostructures as fillers for novel functional hybrid materials.[11−18]

Numerous synthetic methodologies for the preparation of ZnO with different nanostructures have been demonstrated, including "dry" methods and "wet" solution-phase methods.[19,20] Examples of synthetic methods encompass the sol−gel technique,[21,22] microemulsion synthesis,[23] mechanochemical processing,[24] spray pyrolysis,[25,26] organic precursor thermal decomposition,[27] plasma synthesis,[28] supercritical-water processing,[29] self-assembling,[30] hydrothermal processing,[31,32] vapor transport process,[33] microwave-assisted syntheses,[34] direct precipitation,[35] and homogeneous precipita-

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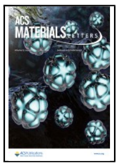

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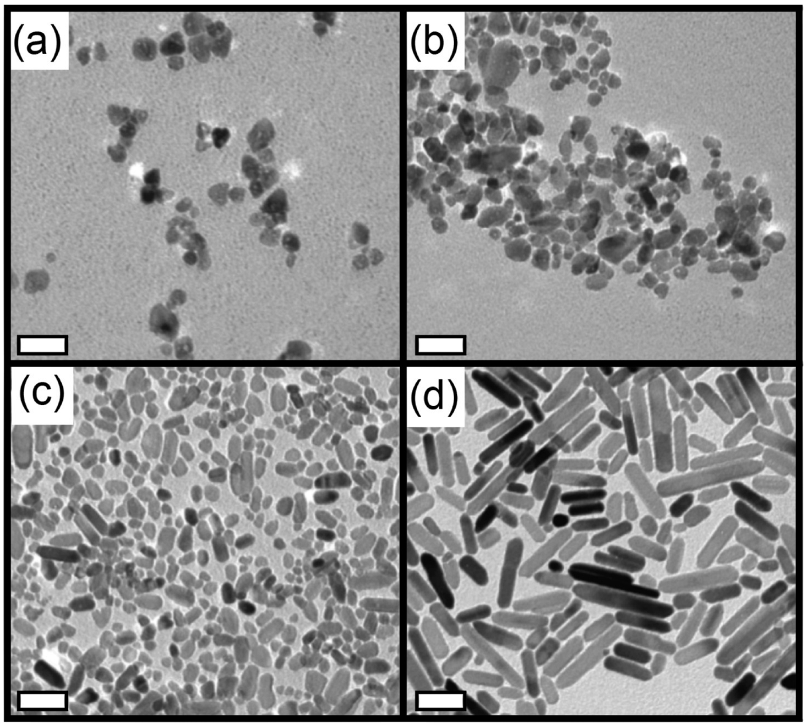
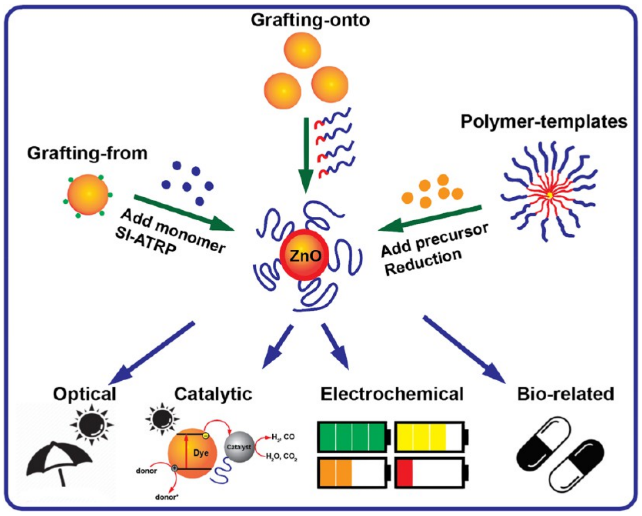


Figure 1. TEM images of the ZnO nanostructures prepared with different concentrations of Me_4NOH at low water content (0.06%): (A) 6% Me_4NOH (v/v), (B) 16% Me_4NOH (v/v), (C) 32% Me_4NOH (v/v), and (D) 66% Me_4NOH (v/v). The precursor Zn^{2+} concentration (0.16 mol/L), temperature (150 °C), and reaction time (24 h) were kept constant. Scale bars = 50 nm. [Reproduced with permission from ref 19. Copyright 2006, American Chemical Society, Washington, DC.]

tion.[36] Wet chemical methods enable control of size and shape of ZnO nanocrystals by variation of solvent, reactant concentration, and temperature.[37−40] For example, Figure 1 shows the evolution of different-aspect-ratio ZnO nanostructures (nanoparticles and nanorods) in water/alcohol solution with the organic base tetramethylammonium hydroxide.[19]

Because of the high surface-to-volume ratio, surface energy, and dielectric constant, ZnO nanoparticle dispersions are prone to aggregation; this is generally detrimental to performance characteristics and limits the application range of ZnO-based hybrids. To improve the dispersibility of ZnO nanoparticles in solution or composite matrix, surface modification is essential.[41] The modification of surfaces by tethering of polymeric chains has attracted particular interest as a strategy to stabilize particle-in-polymer dispersion, because of the more pronounced (enthalpy- and entropy-driven) compatibilization effect that is provided by polymeric ligands. With the advent of surface-initiated controlled radical polymerization (SI-CRP), also termed surface-initiated reversible deactivation radical polymerization (SI-RDRP), it has become possible to precisely control the molecular architecture of polymer canopy layers, thereby exerting a high level of control of particle−particle and particle−matrix interactions (Scheme 1). Atom transfer radical polymerization (ATRP) is the most widely employed CRP method. The typical ATRP process is modulated by a redox pair of transition-metal complexes (e.g., Cu^I/Cu^{II} species), the reaction relies on a dynamic equilibrium between propagating radicals and dormant alkyl halides. All of the polymer chains grow at the same rate, as the terminal radical on any single chain is only active for a very short period; thus, the well-controlled molar mass and narrow molecular weight distribution can be obtained. One feature of ATRP is its flexibility. This enables the realization of diverse polymer architectures and compositions that provide new opportunities for hybrid material design. For example, the synthesis of core−shell star polymer architectures has enabled new template-based synthetic approaches that provide polymer-modified ZnO nanoparticles with excellent size and property uniformity not previously attainable. This review focuses principally on the recent developments in the application of ATRP methods to facilitate polymer/ZnO hybrid materials with novel property combinations and their application in the areas of optical materials, catalysis, sensing, electrochemistry, and biomedical engineering.

Scheme 1. Synthesis and Application of ZnO/Polymer Hybrids



This review focuses principally on the recent developments in the application of ATRP methods to facilitate polymer/ZnO hybrid materials with novel property combinations and their application in the areas of optical materials, catalysis, sensing, electrochemistry, and biomedical engineering.

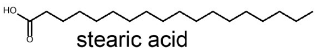
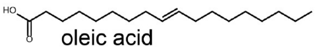
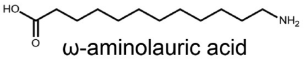
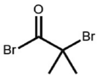
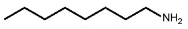
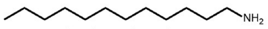
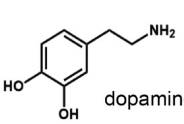
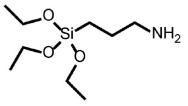
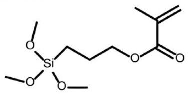
■ SURFACE MODIFICATION OF ZnO

A requisite for the fabrication of polymer–nanoparticle dispersions with uniform microstructure is the immobilization of polymer chains onto the surface of nanoparticle substrates, to afford compatibilization with the polymer matrix. The success of creating a stable bonding between the polymer ligands and inorganic constituents surface relies on the selection of appropriate and suitable anchor chemistries. Coupling agents are used to introduce specific surface functionalities. In the case of SI-ATRP, these functionalities serve as initiator moieties that induce surface polymerization. Depending on the availability of coupling chemistries, initiator groups can also be introduced via secondary coupling reactions with a primary functionalized surface. Surface functionalization of ZnO nanoparticles is well-explored; examples include the binding of thiols (−SH),[42−45] acids (−COOH)[46,47] and amines (−NH_2),[48,49] and silanes[50] was reported.[51] Table 1 illustrates several ubiquitous anchoring groups for applicable ZnO surfaces, which include acidic, basic, and silane coupling agents.

Aliphatic acids and amines are broadly applied to stabilize ZnO nanoparticles in organic dispersion as surfactants or stabilizers. The coordination between carboxylates and amine functional groups with the metal elements in ZnO on the surface of nanoparticles is responsible for the binding of surfactants. For instance, ZnO nanoparticles with narrow size distribution were successfully synthesized by a one-step precipitation reaction in a basic aqueous solution (sodium hydroxide as the base) with zinc acetate as precursors and stearic acid (SA)[52] as the surfactant. With an acidic modifying agent, through *in situ* polymerization, hydrophilic poly(ethylene terephthalate) (PET)/ZnO and poly(ethylene glycol) (PEG)/ZnO nanocomposites were prepared. Monodisperse ZnO nanocrystals colloids with high crystallinity (wurtzite structure) were formed by capping the ZnO nanoparticles with alkylamines through organometallic synthesis.[65,66] Besides, tuning the size, shape, and luminescence intensities of the ZnO nanocrystals have been investigated by using dodecylamine and trioctylphosphine oxide modifying agents after various growth times.[49] Recent work has suggested the introduction of initiating moieties or even polymer ligands with a carboxylic acid or amino functional groups onto the surface of ZnO nanoparticles.[67] The initiator or polymer ligands containing carboxylate functional group was found to be effective for a wide variety of inorganic surfaces and many functionalization techniques. For example, the hydroxyl groups on the ZnO surface interact with carboxyl groups in the polymer chains to yield a poly(zinc methacrylate) complex.[68] Surface anchoring of poly(methacrylic) acid (PMAA) chains was found to promote the dispersion of ZnO nanoparticles in water.

In recent years, dopamine and polydopamine, both catechol derivatives, have attracted increasing attention in surface modification chemistry.[69] With a five-membered ring chelate structure, catechol is well-known to form stable noncovalent bonds to the surfaces of most inorganic and organic

Table 1. Surface Anchoring Reagents for ZnO Surface Modification[a]

Nature of the functionality	Examples of surfactants	Reference
Acidic anchors	 stearic acid  oleic acid	52, 53, 54
	 ω-aminolauric acid	55
	 α-bromoisobutyryl bromide	56, 57, 58
Basic anchors	 octylamine  dodecylamine	59, 60, 61
	 dopamine	62
Silane coupling agent	 (3-aminopropyl)triethoxysilane  3-methacryloxypropyltrimethoxysilane	63, 64

[a]Data obtained from refs 52−64.

constituents. Polydopamine, which has high amine and catechol contents, was used to functionalize various substrates, including metals, ceramics, semiconductors, and even some synthetic polymers, regardless of their size and shape. Besides, the coated polydopamine layer can further react with other reagents (such as thiol and amine functional groups) through secondary reaction. The composition and features of the secondary coating are remarkably tailorable.[69−71] Polydopamine was attached to the surface via in situ polymerization to assist the modification of ZnO nanorods with silver nanocrystals.[72,73]

In addition, another often used reagent for surface modification is the silane coupling agent. Many common functional silanes are commercially available from the silicone industry with a relatively low price, such as 3-aminopropyltriethyoxysilane, *n*-propyltriethoxysilane, and 3-methacryloxypropyltrimethoxysilane.[74−76] Organosilane reagents can possess one to three halide or alkoxy functionalities[67] and be covalently bonded with surfaces of ZnO nanoparticles to generate a stable shielding barrier of cross-linked polysiloxanes, which effectively changes the surface hydrophilicity and prevents the aggregation as well as the decomposition of the ZnO core.[77,78] It is reported that treatment of ZnO nanoparticles with a KH570 silane coupling agent improves their ability to form stable dispersions.[79] The effect of surface functionalization with silane coupling agents affected the antibacterial performance of ZnO nanoparticles, because of their dispersion state in a high-density polyethylene matrix. The KH560-modified nano-ZnO/high-density polyethylene films exhibited much better antibacterial properties than the unmodified ones.[80] Moreover, the organosilane coating can reduce the photocatalytic activities of the ZnO nanoparticle, since the coating serves as a barrier between the ZnO nanoparticle and the environment, thus preventing the formation of reactive oxygen species and improve their photostability as well as the UV-shielding effect.[77,81] On the other hand, similar to the surface modification of polydopamine, amino and hydroxyl groups are frequently incorporated after surface modification with silane coupling agents, which can subsequently yield diverse functionalities in secondary reactions, including ATRP initiator moieties or more-complicated functionalities through hydrosilylation.

■ PREPARATION OF ZnO/POLYMER HYBRIDS

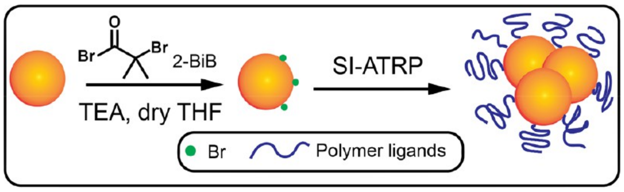
In the past decades, numerous synthetic techniques and procedures have been investigated to fabricate polymer−inorganic nanocomposites. The term "polymer−inorganic nanocomposite" refers to particle-in-polymer matrix dispersions, in which primary or strong secondary chemical bonds are being formed between the constituents. In this section, different approaches to prepare ZnO/polymer hybrid materials will be discussed, including "grafting-from", "grafting-onto", and "polymer template" methods.

"Grafting-from" Approach. Typically, the "grafting-from" of polymer ligands from ZnO nanoparticle surfaces involves two steps: the binding of initiating sites onto the surface of the particle and subsequent growth of macromolecular ligands through polymerization. Different functionalities introduced by various surface chemistry techniques allow the polymerization of numerous classic and novel monomers. Because of the even distribution of the attached initiating sites on the surface, as well as their low molar mass, the "grafting-from" process affords higher and more tunable grafting densities and, thus, better control of the physicochemical properties of particle brushes.[82] As the most commonly applied technique for the "grafting-from" method, CRP procedures cover a broad range of vinyl monomers' controlled polymerization under different reaction conditions.[83] SI-ATRP can serve as a powerful method in the synthesis process to modify the surface of the nanocomposite, because of its high tolerance to impurities and specific reaction requirement.[84]

Different functionalities introduced by various surface chemistry techniques allow the polymerization of numerous classic and novel monomers.

The most common method to functionalize ZnO nanoparticles involves the direct modification of the surface by ATRP initiator without prefunctionalized with anchoring agents and subsequent chain growth from the initiating sites (Scheme 2). For instance, functionalized ZnO nanoparticles having covalently bonded ATRP initiator moieties (α-bromoisobutyrate group) on the surfaces were synthesized by the sol−gel reaction with zinc acetate dihydrate as zinc precursors.[56] The introduction of the initiating sites on the surface was achieved through the condensation of 3-hydroxypropionic acid and α-bromoisobutyrate bromide (2-BiB) as well as the esterification of the −OH group on the ZnO surfaces. After functionalization, high-molar-mass poly(methyl methacrylate) (PMMA) and carbazole polymer (PCEM) with narrow-molecular-weight-distribution polymer ligands were grafted from ZnO nanoparticle surface by SI-ATRP (Figure 2a). The α-bromoisobutyrate initiating moiety was also attached to ZnO nanoparticles surface directly through the esterification between the hydroxyl groups and 2-BiB, poly(ethylene glycol) methacrylate (PEGMA) chains were subsequently prepared by SI-ATRP[57] (Figure 2b).

Scheme 2. Functionalization of ZnO Nanoparticle by ATRP Initiator and Synthesis of ZnO/Polymer Hybrid by SI-ATRP



Although direct functionalization with ATRP initiator can avoid the formation of an extra layer/interface between ZnO and polymers, it is difficult to achieve uniform/homogeneous surface modification through this approach, which will lead to agglomeration of the hybrid materials in the systems. To prevent the agglomeration of ZnO nanoparticles, one effective surface modification method is to use the (3-aminopropyl)-triethoxysilane (APTES) coupling agent (Scheme 3). The amine groups from coupling agents were then reacted with 2-BiB to form ATRP initiating sites on the surface of nanoparticles, and poly(*N*-isopropylacrylamide) (PNIPAM) was later grafted from the modified ZnO as a pH and thermally responsive polymer.[85] (Figure 3a). Similar silane coupling agents include aminopropyl silatrane (APS) and ATRP macroinitiator α-chlorophenyl acetyl chloride were used to

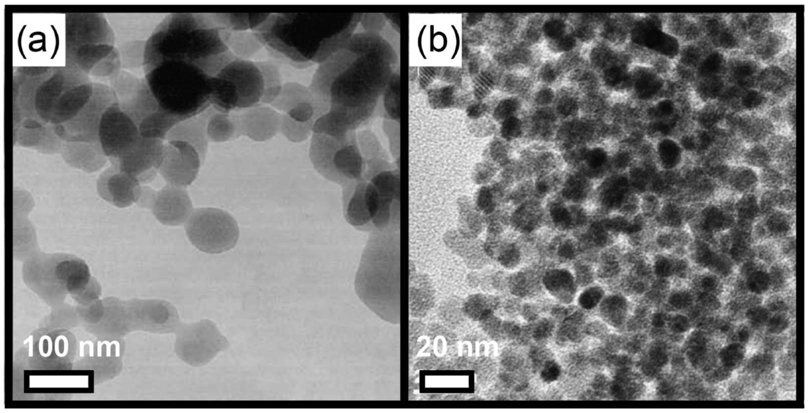
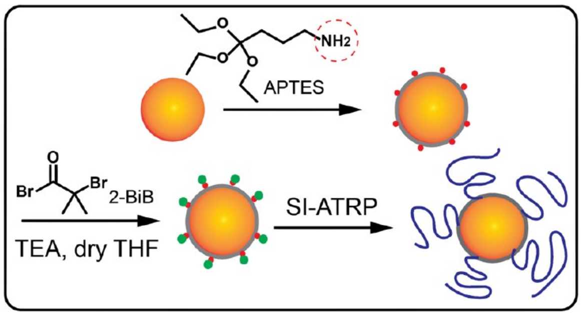


Figure 2. TEM images of (a) carbazole polymer (PCEM)/ZnO nanocomposite (scale bar = 100 nm). [Reproduced with permission from ref 56. Copyright 2008, Elsevier Science, Ltd.] (b) ZnO@poly(poly(ethylene glycol) methacrylate) (PPEGMA) nanoparticles after polymerization for 10 h (scale bar = 20 nm). [Reproduced with permission from ref 57. Copyright 2009, Elsevier Science, Ltd.]

Scheme 3. Functionalization of ZnO Nanoparticles by Silane Coupling Agents and Synthesis of ZnO/Polymer Hybrid by SI-ATRP



prepare PMMA-grafted ZnO nanocomposites.[82] (Figure 3b). Various polymers, such as polystyrene,[86,87] poly(hydroxyethyl acrylate) (PHEA),[88] PNIPAM,[89] and hyperbranched polymers[90] were grown this fashion from functionalized ZnO (nanoparticles, nanorods, and nanowires) surfaces.[91,92]

In addition to the silane coupling agent, one universal tetherable initiator, derived from the aliphatic amino acids, was reported.[55] This initiator, 12-(2-bromoisobutyramido)-dodecanoic acid (short for BiBADA), was prepared by a facile amidation between α-bromoisobutyryl bromide and ω-aminolauric acid. BiBADA was used in the surface modification for the broad spectrum of metal oxide nanoparticles. As an example, the modified-ZnO nanoparticles were linked to densely grafted PMMA or poly(n-butyl acrylate) (PBA) via SI-ATRP[55] (see Scheme 4 and Figure 4).

"Grafting-onto" Approach. Compared to the "grafting-from" strategy, an advantage of the "grafting-onto" method is the simplicity and scalability of the process. Presynthesized polymer ligands with at least one functional group/block that can facilitate coupling to the surface are tethered to the inorganic substrate surfaces. Because the appropriate coupling functional group can be designed for corresponding surfaces, minimal surface functionalization is required. However, despite the high viability, it is challenging to achieve high grafting densities through the "grafting-onto" approach, because of the steric repulsion between the grafted chains, especially for the high molar mass ligands. Unlike the "grafting-from" method, typically the "grafting-onto" yield dilute/semidilute grafting layers and collapsed "mushroom-like" structures, which correspond to grafting densities well below 1 chain/nm^2.

Conventionally, the reactive functionalities were attached to the polymer ligands' chain ends as end-groups or introduced by the comonomers during the polymerization. A limited selection of polymers was used directly for the "grafting-onto" process, such as poly(ethylene glycol) (PEG), and poly-

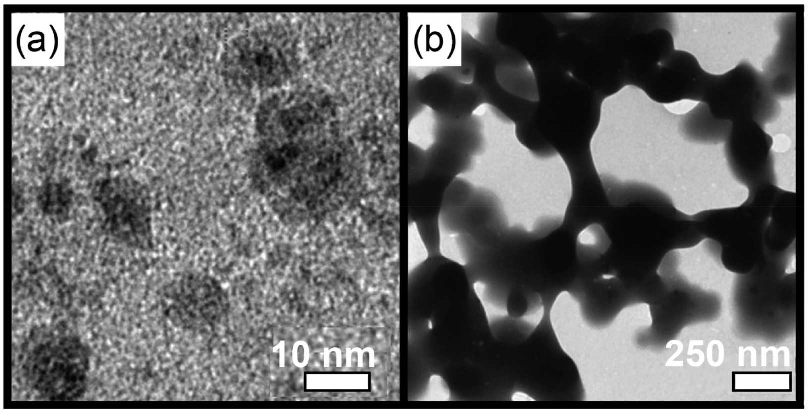
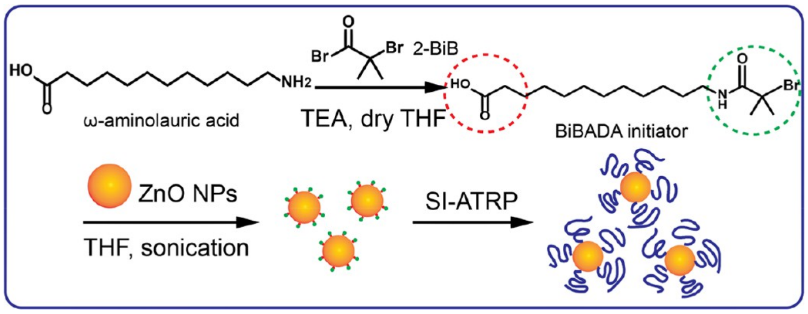


Figure 3. TEM images of (a) ZnO@PNIPAM and (b) PMMA-grafted ZnO. [Panel (a) was reproduced with permission from ref 85. Copyright 2014, Elsevier Science, Ltd. Panel (b) was reproduced with permission from ref 82. Copyright 2013, Taylor & Francis Group, LLC.]

Scheme 4. Functionalization of ZnO Nanoparticle by BiBADA Initiator and Synthesis of ZnO/Polymer Hybrid by SI-ATRP



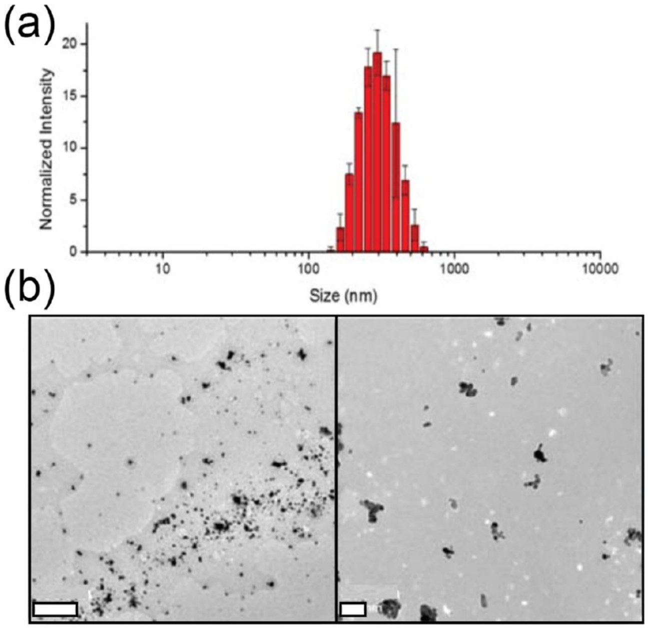


Figure 4. Characterization of PMMA-grafted ZnO_2 nanoparticles: (a) the intensity-weighted hydrodynamic size distribution of PMMA-grafted ZnO in THF and (b) TEM images. (In panel (b), the scale bars in the images are 500 nm (left) and 200 nm (right).) [Adapted with permission from ref 55. Copyright 2017, American Chemical Society, Washington, DC.]

(dimethylsiloxane) (PDMS), attributed to their intrinsic chain-end functionalities. Controlled radical polymerization affords versatile control over the synthesis of macromolecules with well-defined composition, architecture, and functionalities, which allows the preparation of polymer ligands with various specific functional groups. The synthesis of polymer ligands using controlled radical polymerization techniques is straightforward as the chain-end fidelity can be effectively preserved. For instance, the synthesis of monodisperse ZnO nanoparticles with narrow size distribution using poly(vinylpyrrolidone) (PVP) as the capping molecules was reported. The coating agent PVP served to stabilize the nanoparticles and passivate the ZnO surface to reduce the concentration of oxygen vacancy sites. The surface-modified ZnO nanoparticles were remarkably stable.[66] Another study used PMAA to decorate commercial ZnO nanoparticles in the aqueous solution. The hydroxyl groups on the surface reacted with carboxyl groups (COO−) of PMAA through esterification to form a poly(zinc methacrylate) complex.[68] Besides, water-soluble ZnO nanocrystals capped with poly(ethylene glycol) bis(carboxylate) ($PEG(COOH)_2$) were synthesized in ethanol/water mixtures, and the aspect ratio of the ZnO nanostructure was tuned by changing the water/ethanol content[93] (Figure 5a). 3-Hexylthiophene (3HT) was prepared via the Grignard metathesis method,[94] by introducing allyl magnesium bromide to harvest three allyl end-functional P3HTs (P3HT-allyl), which have well-preserved chain-end functionalities, high regioregularities, and narrow molecular weight distribution. A subsequent hydrosilylation was performed to covert the alkene

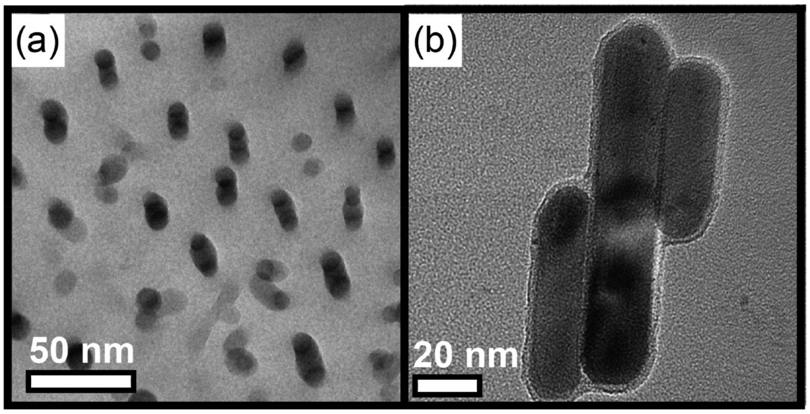
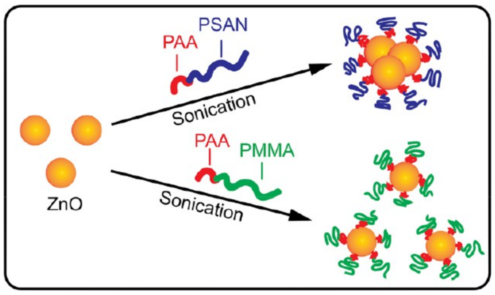


Figure 5. (a) TEM images of water-soluble ZnO nanoparticles coated with poly(ethylene glycol) bis(carboxylate) ($PEG(COOH)_2$) prepared in ethanol/water solutions. [Adapted with permission from ref 93. Copyright 2008, American Chemical Society, Washington, DC.] (b) TEM images of ZnO nanorods anchored with poly(3-hexylthiophene) (P3HT). [Reproduced with permission from ref 95. Copyright 2014, John Wiley & Sons. Inc.]

into triethoxysilane end groups. The pristine ZnO nanorods were dispersed in THF and stirred with an excess amount of silane-terminated polymer ligands to yield P3HT-grafted ZnO nanorods[95] (Figure 5b). These ZnO/P3HT core/shell hybrids materials are promising to design more-durable photovoltaic devices.

Other important functionalized ligands that are often used in the "grafting-onto" approach are block copolymers consisting of segments with featured surface affinities.[96,97] Grafting block copolymers with specific affinities to the targeted surface have been used to stabilize and disperse inorganic colloids in organic dispersions, including an organic solvent, polymer matrix, and some aqueous media. Generally, a weak interaction is sufficient to attach to the nanoparticle; thus, only a limited portion of the anchoring block was used to tether the polymer ligands to the surface. Controlled radical polymerization is widely utilized to prepare well-defined functional copolymers. Surface-active random copolymers (poly(lauryl methacrylate-*co*-dimethylaminoethyl methacrylate) (PLMA-*co*-PDMAEMA)) were synthesized to compatibilize hydrophobic ZnO nanoparticles in the polymer matrix.[98] Polymer ligands adsorbed on the particle surface enabled the successful integration of ZnO nanoparticles with the targeted polymer matrix. In block copolymers, the different affinity between each block was critical to prevent particle aggregation. For instance, poly(acrylic acid)-*block*-poly(methyl methacrylate) (PAA-*b*-PMMA) worked better as dispersant for ZnO nanoparticles than poly(acrylic acid)-*block*-poly(styrene-random-acrylonitrile) (PAA-*b*-PSAN) polymer ligands. Compared to methyl methacrylate, acrylonitrile units have higher polarity, leading to a competition between them and PAA block to be absorbed to the surface, causing particle bridgings[58] (Scheme 5).

Scheme 5. Synthesis of ZnO/Polymer Hybrid through "Grafting-onto" Method with Presynthesized Diblock Copolymers



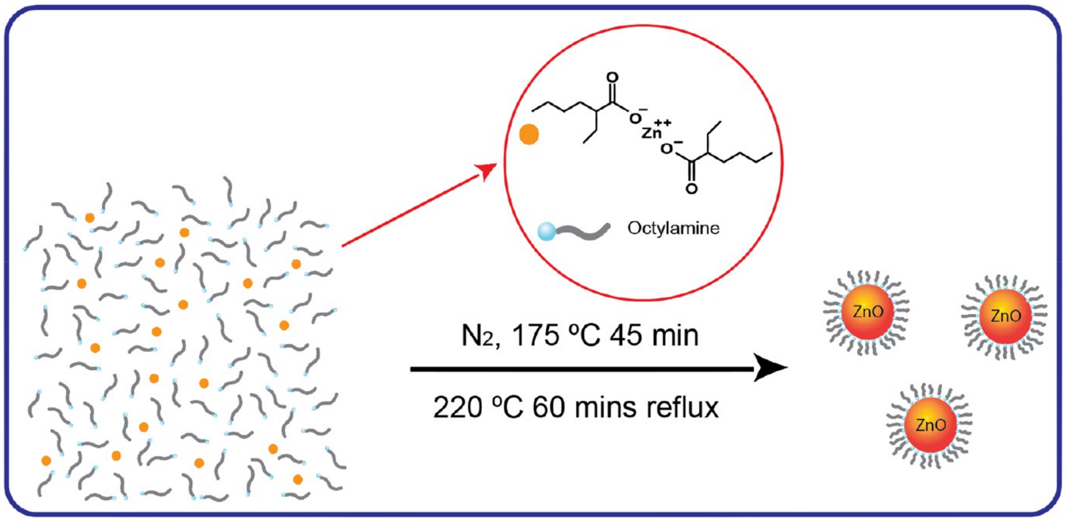
A special method to prepare inorganic nanoparticle/polymer hybrids that can be included in the "grafting-onto" approach is the "ligand exchange". In this case, instead of the corresponding functional groups, removable small-molecule ligands are present on the particle surface. The success of the exchange process requires either the long polymer ligands to possess a stronger affinity to the targeted surface than the small-molecule ligands or an external driving force to remove the small-molecular modifiers from the reaction environment. For instance, for noble-metal nanoparticles (e.g., gold), a single thiol functional group could be strong enough to substitute for other labile ligands.[99] Note that, for high-molar-mass polymer ligands with a single anchoring functionality, it is difficult to accomplish the desired ligand exchange, even with multiple repeats of the procedures and a large excess of polymer ligands. One possible way to solve this problem is adding a nonsolvent (for both polymer ligands and the small-molecule functionalized nanocomposites) into the dispersion to shift the equilibrium by increasing the local concentration of polymer ligands and nanoparticles, because the small-molecular ligands are more soluble in the mixed dispersions. Besides, unlike the classic "grafting-onto" approach, through the gradual substitution of densely coated small-molecule ligands, a high grafting density polymer nanocomposite was expected in the ligand exchange method.

To avoid the complexity of adding a certain amount of nonsolvent, the ligand exchange approach was simplified by applying detachable ligands. Thus, soluble ZnO nanocrystals were synthesized by using zinc 2-ethylhexanoate as a zinc precursor and the alkylamines (*n*-octylamine, *n*-dodecylamine) as surface capping agents[59,60] (see Scheme 6 and Figure 6a). The small-molecule capping agent, octylamine, has a fairly low boiling point of 175 °C. The ligand exchange of amino-group functionalized polymer ligands with octylamine was accelerated by continuously removing the volatile ligands from the reaction at high temperatures (>175 °C). High apparent grafting densities (up to 2.5 chains/nm^2) products were obtained with the usage of the polymeric ligand, PSAN-NH$_2$, which was presynthesized by ATRP. The PSAN coating permitted dispersion of the ZnO nanocrystals in acrylic glasses (PMMA matrix),[100] and it acted as the carbon source for ZnO-carbon hybrid materials[61,101] (see Scheme 7 and Figure 6b).

Templated Synthesis. The "grafting-from" and "grafting-onto" approaches discussed above are categorized as "inorganic-first" approaches. In contrast, the templated synthesis method is considered as a "polymer-first" approach, such as the synthesis of polymer grafted metal oxide nanoparticles from starlike polymer templates. Generally, in the template approach process, the polymer templates are presynthesized with precise control over the molar mass and architecture. Selected particle precursors are effectively loaded inside the polymer templated through coordination or electrostatic interaction between the precursors and functional groups in the templates.[102,103] Subsequently, the targeted inorganic nanoparticles are generated from the hydrolysis or redox process of the entrapped precursors within the core of the templates, while the remaining coronas serve as the coating layers.[104,105] Block copolymers with well-defined nanostructures and distributed functionalities have been comprehensively investigated as polymer templates for a variety of inorganic nanoparticle syntheses.[106−110]

Star Polymer Template. Starlike block copolymers are considered robust unimolecular templates for inorganic nanoparticle synthesis. Compared to linear block copolymers, the starlike templates have some advantages. Unimolecular micelles have a higher tolerance to external perturbation from the reaction environment, such as the temperature, pressure, pH values, and solvent polarity, hence affording easier control over the synthesis of inorganic nanoparticles. The well-defined and uniform spherical shapes of unimolecular starlike macromolecules ensure the formation of monodispersed nanoparticles with narrow size distribution during templating. Also, the starlike block copolymer templates allow precise control over the size and shape of the targeted nanoparticles. In the case of linear copolymers templating, the size of the inorganic nanoparticles corresponds to the micelle size, which is affected by several factors, such as the molar mass of each block, types of precursors, and reaction conditions. In contrast, the size of

Scheme 6. Synthesis of Octylamine (OA)-Capped ZnO Nanoparticles



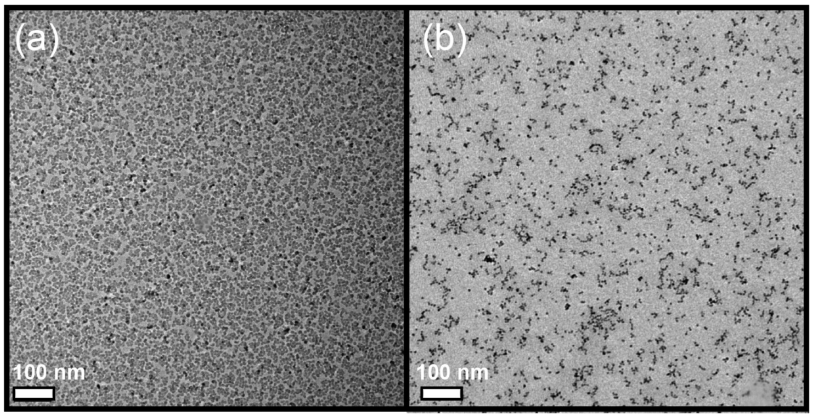
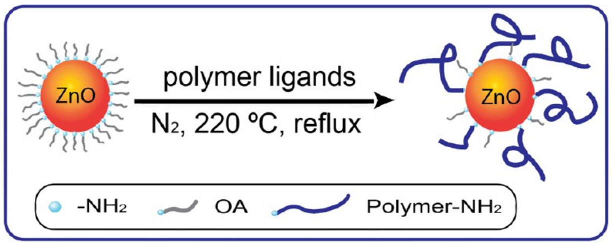


Figure 6. TEM images of (a) octylamine (OA)-capped ZnO nanoparticles and (b) poly(styrene-random-acrylonitrile) (PSAN)-capped ZnO NPs with PSAN-NH_2 polymer ligands. [Adapted with permission from ref 61. Copyright 2017, American Chemical Society, Washington, DC.]

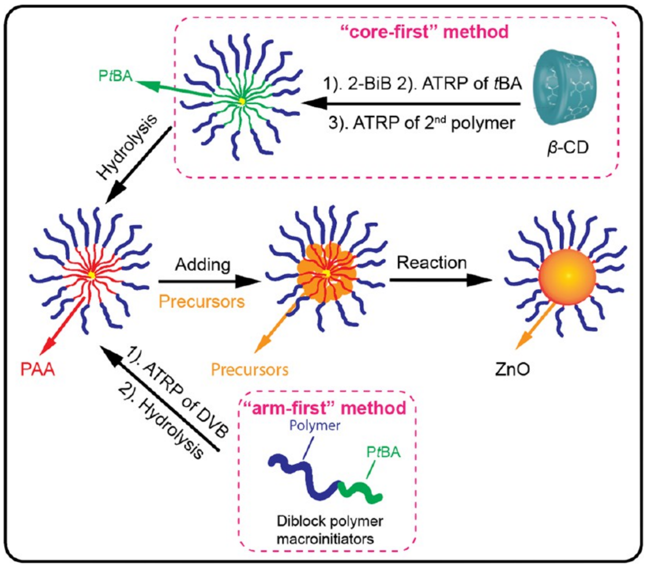
Scheme 7. Synthesis of Polymer-Capped ZnO Nanoparticles Using the "Ligand Exchange" Method



nanoparticles is directly and mainly determined by the molar mass of the functional blocks in starlike copolymer templating. There are two classic approaches to prepare starlike templates: the "core-first" approach and the "arm-first" approach.[111,112] In the case of the "core-first" approach, controlled polymerizations start straight from multifunctional initiator molecules, which can be synthesized from multifunctional molecules, including cyclodextrin (CD), silsesquioxane, or even a molecular wheel. If the starlike polymers are prepared by ATRP, no linear impurity is generated in the "core-first" process. However, the arm number in the star polymers is limited by the initiator's functionality and it is difficult to measure the molar mass of each arm. On the other hand, one convenient method to prepare starlike polymers is to cross-link the functional chain end of presynthesized polymer chains (also known as the arms) to form the core of the star, this method is called the "arm-first" approach. The "arm-first" approach enables higher arm numbers in starlike polymers and as a result higher grafting density of the hybrid nanoparticles. The characterization of the arms is easier and precise than it is before the cross-linking. However, because of the functionality of the polymer chains and the reaction conditions, there are certain amounts of linear impurities (uncross-linked arms) in the product that require further purification steps.[83,113−115]

Recent work established a universal approach to preparing polymer−inorganic hybrid nanoparticles utilizing starlike templates with block copolymer arms as nanoreactors.[116] This type of nanoreactors can be used to convert nanoparticle precursors into a wide range of hybrid nanocomposites. The starlike templates were prepared through a "core-first" approach, the inert outer block shell was polystyrene (PS), while the inner precursor anchoring block was poly(acrylic acid) (PAA), which was synthesized through hydrolysis of poly(*tert*-butyl acrylate) (P*t*BA) (Scheme 8). A large variety of nanoparticles included ZnO nanoparticles were prepared through the hydrolysis or redox process of the entrapped

Scheme 8. Synthesis of ZnO/Polymer Hybrids from Star Polymer Templates



precursors (Figure 7a). The starlike polymers with a high number of arms synthesized by the "arm-first" approach acted as nanoreactors for the preparation of ZnO hybrid nanoparticles[58] (Figure 7b). The size of ZnO nanoparticles could be tuned by altering the precursor loadings.[117] The developed precise control over the size of ZnO nanoparticles enabled a promising investigation toward their size-dependent features.

Molecular Bottlebrushes Templates. Molecular bottlebrushes are macromolecules with an elongated chain-extended structure.[118] They are comblike copolymers with densely grafted side chains. Because of the strong steric hindrance between the side chains, as the backbone length is sufficiently longer than the side chains, the extended, cylindrical conformation is adopted by the bottlebrushes. Polymer-inorganic hybrid nanocomposites prepared using the molecular bottlebrushes inherit the template's morphology, becoming one-dimensional. This enables molecular bottlebrushes to be employed as unimolecular templates for making one-dimensional nanomaterials, which were difficult to prepare by conventional processes, including nanotubes, nanorods, and nanowires.[119−133]

This enables molecular bottlebrushes to be employed as unimolecular templates for making one-dimensional nanomaterials, which were difficult to prepare by conventional processes, including nanotubes, nanorods, and nanowires.

A generic synthetic route to prepare anisotropic polymer brush-grafted nanoparticles was developed (Scheme 9). Typically, a series of detailed procedures started with precursor poly(2-trimethylsiloxyethyl methacrylate) (PHEMA-TMS). Later, it was converted to the ATRP initiator-containing backbone poly(α-bromoisobutyryloxy)ethyl methacrylate) (PBiBEM). The precursor anchoring block was subsequently grafted. Finally, the outer block was grafted from the inner block to prevent aggregation. The anisotropic hybrid nanocomposites were formed by the reduction/decomposition of precursors loaded in the anchoring block. The outer block prevented the aggregation of nanoparticles, and the inner block defined the shape and size of the final nano-object. The wormlike morphology of molecular bottlebrushes templates was reported to fabricate anisotropic one-dimensional (1D) nanomaterials with various inorganic contents including TiO_2,[134,135] Fe_2O_3,[136] ZnO,[58] Au,[137] Pt,[127] silica,[138] and CdS.[139]

Recently, well-defined branched molecular bottlebrushes were prepared and applied as templates to make inorganic nanoparticles tunable anisotropy and complex topologies, such as TiO_2−polymer hybrids (Figure 8b).[140] ZnO nanoparticles with narrow size distribution were fabricated using brushlike templates ($PBiBEM_{372}$-g-(PAA_{47}-b-PS_{92})) with poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS) side chains..[58] Wormlike nanostructured ZnO nanoparticles were confirmed in the TEM images (Figure 8a). The number-average length of the nano-objects was 75 nm with dispersity (L_w/L_n) = 1.08, as demonstrated through the statistical analysis of the images.

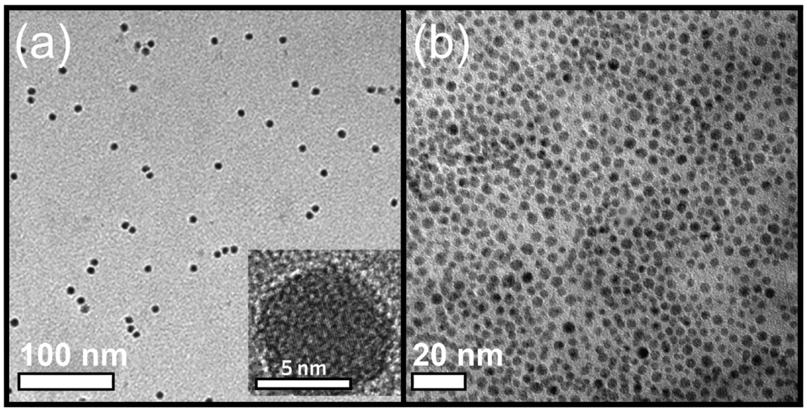
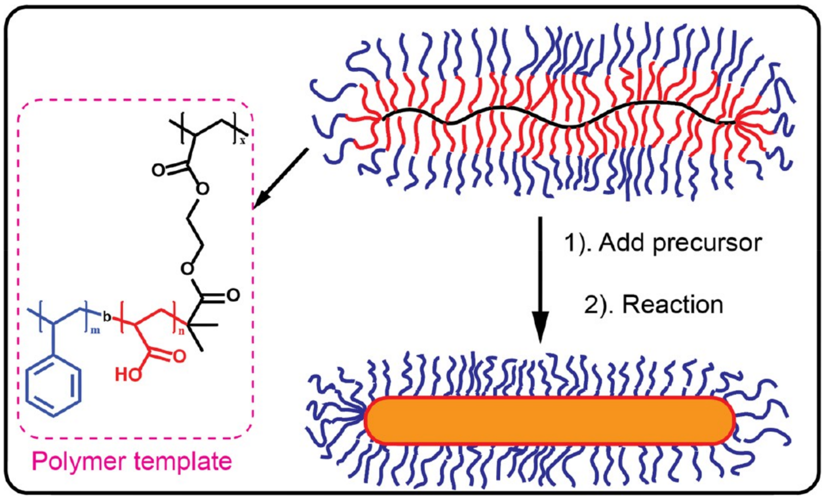


Figure 7. (a) TEM images of ZnO nanoparticles synthesized using starlike poly(acrylic acid)-*block*-poly(styrene) (PAA-*b*-PS) templates (D_{ZnO} = 6.3 nm). Inset shows that the crystalline lattice of ZnO nanoparticles is clearly evident in HRTEM images. [Adapted with permission from ref 116. Copyright 2013, Springer Nature.] (b) TEM image of poly(styrene-random-acrylonitrile) (PSAN)-capped ZnO synthesized by poly(styrene-*random*-acrylonitrile)-*block*-poly(acrylic acid)-poly(divinylbenzene) PSAN-*b*−PAA-PDVB star copolymer templates. [Adapted with permission from ref 58. Copyright 2016, Elsevier Science, Ltd.]

Scheme 9. Synthesis of Metal Oxide/Polymer Hybrids from Bottlebrush Polymer Templates



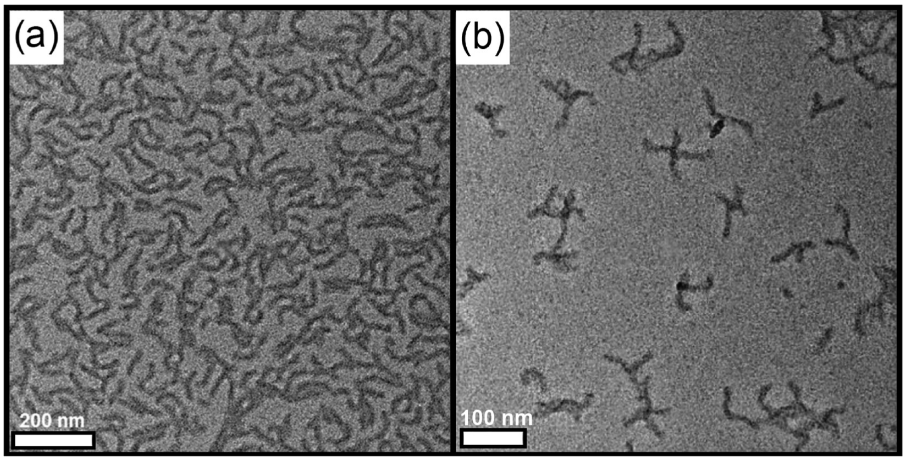


Figure 8. (a) TEM images of ZnO nanoparticles by brushlike templates. [Reproduced with permission from ref 58. Copyright 2016, Elsevier Science, Ltd.] (b) TEM images of TiO_2−polymer hybrids prepared from the branched brush template Backbone (DP = 205)−poly(acrylic acid) (DP = 53)−polystyrene (DP = 73). [Reproduced with permission from ref 140. Copyright 2016, Elsevier Science, Ltd.]

PISA Polymer Templates. Polymerization-induced self-assembly (PISA) is a well-developed strategy that yields a wide range of nano-objects *in situ* in the reaction dispersion, including spheres, worms, lamellae, and vesicles.[141−144] Unlike the conventional self-assembly in dilute solution, PISA occurs during the polymerization over various reagents' concentrations, even up to 50 wt % solids content. This process requires the in situ synthesis of well-defined amphiphilic block copolymers, which is fulfilled by controlled radical polymerization techniques. Through variation of reaction conditions, different nanostructured block copolymers with tunable sizes and morphologies were formed in the concentrated reaction mixtures. Complex nanostructures including wormlike and vesicle morphologies were prepared by tuning the further chain extension conditions.[145] PISA presents a facile approach to preparing precisely controlled self-assembled amphiphilic block copolymers and the extensively diverse nano-objects potentially broadens the number of applications of self-assembled block copolymers, such as the synthesis of templating nanocomposites.[146−149]

Both PISA and conventional self-assembly form nanostructured block copolymers with selective segment aggregation. After loading the precursors into targeted segments and immobilizing the inorganic constituents, hybrid nanocomposites were generated within the PISA nano-objects. The self-assembled diblock copolymer poly(styrene)-*block*-poly(methyl methacrylate/methacrylic acid) (PS-*b*-PMMA/PMAA) was synthesized via ATRP in two steps, as the poly(methacrylic acid) served as the hydrophilic segment. Incomplete hydrolysis of the methyl ester of the PMMA block was performed subsequently under acidic conditions. These block copolymers were used as nanoreactors for inorganic nanoparticles (such as ZnO) preparation.[150] Recently, a soluble poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) chain transfer agent (PDMAEMA-CTA) was used as the surfactant in PISA to prepare stable phase-separated spherical block copolymers poly(2-(dimethylamino)ethyl methacrylate)-*block*-polystyrene (PDMAEMA-*b*-PS). These polymeric nanospherical templates are suitable and effective for nanoparticle synthesis, specifically gold, SiO_2, Fe_3O_4, and TiO_2 nanoparticles, directly by loading the corresponded precursors into the anchoring amine groups distributed among the nanosphere shells.[151−153]

Summary of Preparative Methods for ZnO/Polymer Hybrids. Procedures were developed to prepare ZnO/polymer hybrid materials. With the direct surface functionalization step,

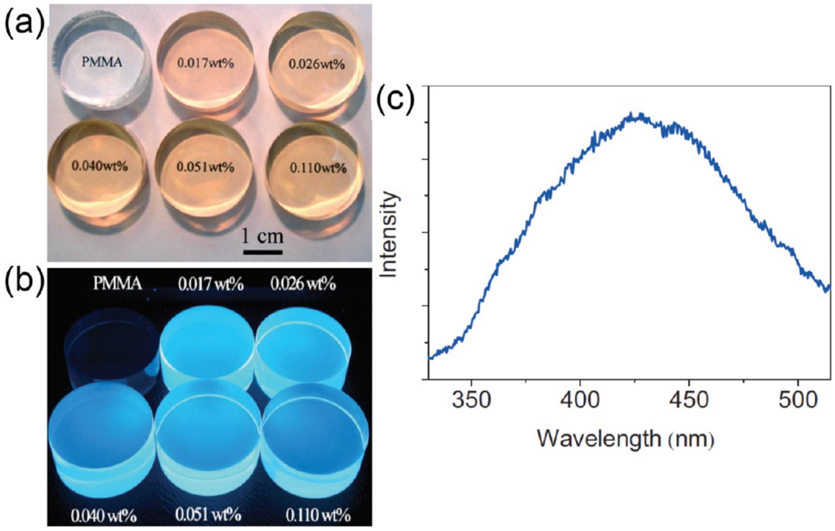


Figure 9. (a) Digital photographs of the bulk transparent PMMA−ZnO hybrid materials under visible light with a thickness of 1 cm; (b) PMMA-ZnO hybrid materials containing various concentrations of ZnO quantum dots under a low-intensity UV light (λ = 362 nm) show significant blue emission from the ZnO quantum dots in the PMMA matrix; (c) photoluminescence emission spectrum of PMMA-ZnO hybrid materials (0.026 wt %) under a UV light (λ = 280 nm). The dimension of the bulk specimens is ~1 cm thick with a diameter of 2.5 cm. [Reproduced with permission from ref 172. Copyright 2007, John Wiley & Sons, Inc.]

the "grafting-from" approach afforded higher and tunable grafting densities and precise control of the structures over the ZnO/polymer nanocomposites without linear homopolymer impurities. On the other hand, the "grafting-onto" approach is more economical and scalable by applying presynthesized polymer ligands with functional groups/blocks to attach onto the ZnO surfaces. However, generally, the "grafting-onto" approach yields dilute/semidilute grafting layers and often introduces linear polymer ligand impurities in the product. As a special case in the "grafting-onto" approach, the "ligand exchange" method enables high grafting density through the gradual removal of the small-molecule ligands on the particle surfaces, although this method requires specific solvent and ligand combinations (e.g., low-boiling-point small-molecule ligands versus high-boiling-point solvent). At last, recent progress in synthetic polymer chemistry, especially the controlled radical polymerization technique, has facilitated access to polymer nano-objects of well-defined structures. Starlike polymers, molecular bottlebrushes, and PISA polymer templates were used to prepare ZnO/polymer hybrids with different morphologies, including nanoparticles, nanowires, and hollow nanostructures. The next section will discuss some specific applications of ZnO/polymer hybrids.

■ APPLICATIONS OF ZnO/POLYMER HYBRID MATERIALS

Nanosized ZnO, as one of the important semiconductors, has a large family of morphological structures, a high redox potential, superior physicochemical stability, high electron mobility, nontoxicity, and *n*-type carrier defects.[154−156] It is suitable for making optoelectronic devices, such as light-emitting diodes (LEDs),[157,158] ultraviolet (UV) photodetectors,[159,160] and electronic devices, such as varistors[161−163] and transistors.[164] Its piezoelectric properties[165,166] make it a promising candidate for piezoelectric transducers[167,168] and mechanical actuators.[169] ZnO nanoparticles have also improved the thermal behavior of polymers.[170,171] Besides, it is also widely used in catalysis, energy storage, and biomedical fields. This section summarizes recent developments in the applications of ZnO/polymer hybrid materials.

Optical Properties and Applications. Because of their wide bandgap and large exciton binding energy at ambient temperature, nanosized ZnO (i.e., nanoparticles with at least one dimension between 1 nm and 100 nm) has prominent UV-shielding property, which makes it an efficient UV absorber.[3,172] Hence, they have various applications in coating sealants,[173] sunscreens,[174] and photocatalysts.[175−177] Research also has reported optically pumped lasing and strong photoluminescence in ZnO nanoparticles, making it a promising material for stable, room-temperature luminescent, and lasing devices.[178−181]

Despite the high transparency, conventional polymers usually have a low refractive index and low UV-shielding efficiency. Numerous studies have demonstrated that the incorporation of inorganic fillers into the polymer matrix is an effective method to overcome these drawbacks.[182−184] To prepare polymer nanocomposites with desirable properties, it is crucial to enhance the interfacial adhesion between fillers and polymer matrix, thus achieving a good dispersion of the fillers.[185] Because of its outstanding integrated properties, ZnO is considered a suitable material for developing polymer nanocomposites for optoelectronic devices. The successful fabrication of bulk highly transparent ZnO/PMMA hybrid films through the in situ sol−gel polymerization techniques was reported.[172] The ZnO/PMMA hybrid materials exhibited outstanding UV-shielding performance over the full UV range, even under the lowest ZnO contents (0.017 wt %) (Figure 9). This work has directed the application of transparent UV-protective materials, as well as an optical sensor or optical fibers in a certain wavelength range. A series of amphiphilic polyurethane modified ZnO nanoparticles were prepared by an inverse mini-emulsion process.[186] The size of ZnO nanoparticles was ~48 nm. The polymer ligands were poly(tetramethylene glycol) (PTMG)-based amphiphilic polyurethane, end-terminated by different hydroxyl-containing reagents, such as butyl alcohol (BA), hydroxyethyl meth-

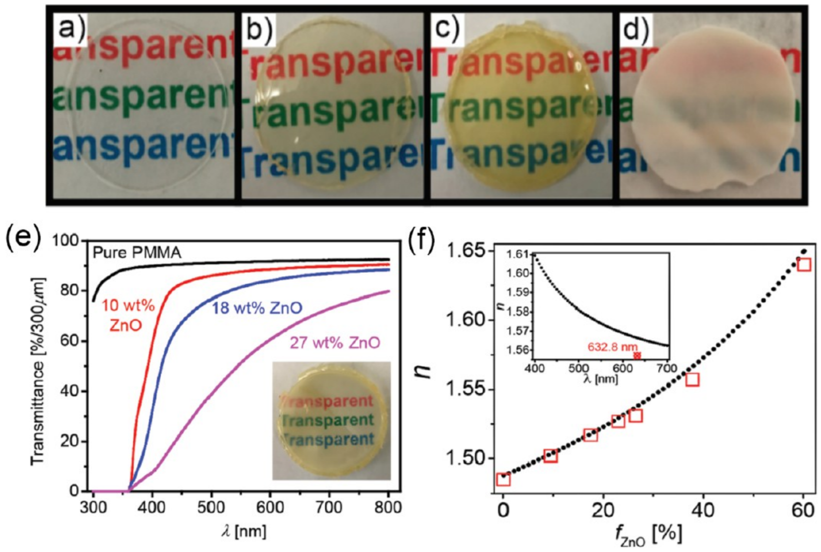


Figure 10. Photographs of pure PMMA, PSAN-capped ZnO/PMMA, and OA-capped ZnO/PMMA hybrid bulk films: (a) pure PMMA (thickness: 666 μm), (b) PSAN-capped ZnO/PMMA-1 (10 wt % ZnO, 570 μm), (c) PSAN-capped ZnO/PMMA-2 (18 wt % ZnO, 646 μm), and (d) OA-capped ZnO/PMMA (10 wt % ZnO, 590 μm). The image area is 9 cm^2. (e) Normalized ultraviolet-visibble light (UV−vis) transmittance spectra of the pure PMMA and the PSAN-capped ZnO in the PMMA matrix. The normalized transmittance corresponds to films with a thickness of 300 μm. Inset shows a photograph of PSAN-capped ZnO/PMMA bulk films with 27 wt % ZnO (370 μm). (f) Dependence of refractive index on ZnO content in hybrid thin films. Dashed line represents the theoretical trend line calculated using the Maxwell−Garnett theory, and red squares indicate the measured refractive index at 632.8 nm. Inset shows the refractive index of ZnO/PMMA hybrid bulk film (38 wt % ZnO content) at a different wavelength. [Adapted with permission from ref 100. Copyright 2017, American Chemical Society, Washington, DC.]

acrylate, and pentaerythritol triacrylate (PETA). After attaching polymer ligands onto ZnO surfaces, the nanocomposites were successfully dispersed in acrylic monomers and organic solvents. With only 0.3 wt % ZnO incorporating into polyurethane, there are significant enhancements in Young's modulus, fragile toughness, tensile strength, and UV-blocking properties without diminishing the transparency of the nanocomposites. Moreover, through the further hydrogen bonding interactions between carboxyl and urethane groups in the amphiphilic polyurethane with other polyurethane, acrylic copolymers, nylon, polyester, and other polar molecules, the polyurethane-functionalized ZnO was used as a multifunctional filler to fabricate various polymer nanocomposites.

The incorporation of ZnO nanoparticles into the PMMA matrix can significantly improve the optical performance of the polymer, including high refractive index and UV-shielding properties.[187] However, the large difference in refractive index between ZnO and PMMA can trigger severe optical scattering, diminishing the transparency of the blended composites. The effect of refractive index mismatch is negligible only when the particles are monodispersed into domains with a particle size much smaller than the wavelength of the incident light.[188−190] In particular, the transparency of nanocomposites has a tendency to decrease with larger scattering center dimensions and shorter scattering mean free paths. Moreover, since nanofillers are generally easy to aggregate, which causes the increase of effective scattering center size, even at a low inorganic loading concentration, the aggregation of fillers could result in poor transparency.[191] A recent work presented a facile route to fabricate PMMA/ZnO films with high optical transparency and refractive index exceeding 1.6 in the visible range[100] (Figure 10). The method relies on the utilization of PSAN polymer ligands, which have an enthalpically favorable interaction with PMMA, enabling the uniform distribution of ZnO in the matrix. PSAN-capped ZnO nanoparticles were prepared through a ligand exchange approach. ZnO nanoparticles were readily dispersed in PMMA with fractions up to 35 wt %. The considerable increase in the refractive index of the PMMA matrix could encourage the development of ZnO to more optical devices.

On the other hand, although ZnO particles effectively block the UV radiation, they can act as light-induced sensitizers, because of their special electronic structure (a filled valence band and an empty conduction band). Hence, ZnO nanoparticles are actively involved as photocatalysts in the UV curing process.[192,193] Various ZnO/polymer nanocomposites have been prepared by modifying the pristine ZnO particles with small organic or large polymeric molecules.[190,194,195] A special type of polymer functionalized ZnO nanobelt-based device has been fabricated, and its ultraviolet features were characterized to study the electric transport under UV radiation.[196] Poly(diallyldimethylammonium chloride) (PDADMAC), as a positively charged polymer, was chosen to endorse the adsorption of negatively charged polymers onto the surface of bare ZnO nanobelts as well as the electrostatic-induced assembly process. Polystyrene sulfonate (PSS), poly(styrene-co-maleic acid) (PS-*co*-MAc), negatively charged PNIPAM, and carboxymethylcellulose (CMC) were tested in the experiment with different wavelengths to evaluate their performance on enhancing UV response; the UV triggered photoconductance increases by 5 orders of magnitude with the UV-sensitive polymer coatings.

Catalysis. ZnO is widely used as an activator in global rubber commercial manufacturing to accelerate the vulcanization process. Among all different organic and inorganic activators, ZnO is recognized to be the most efficient.[197] ZnO plays an important role in promoting the formation of sulfide cross-links and improving the kinetics of the curing process,

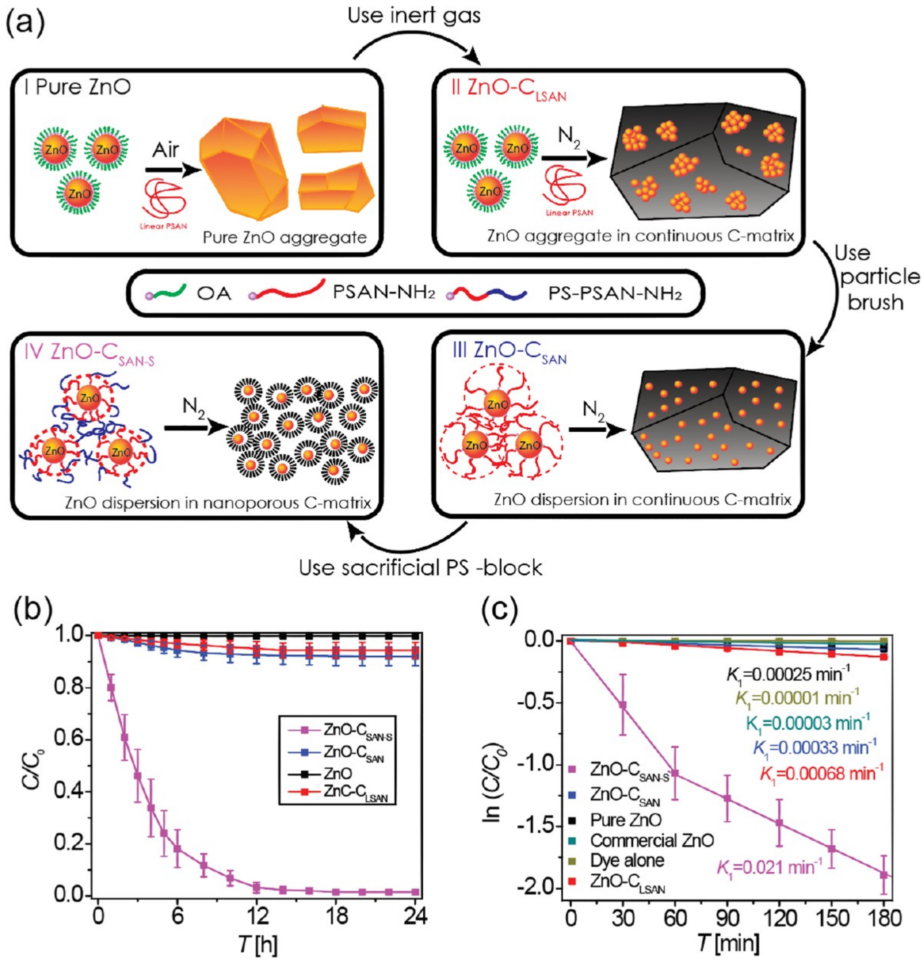


Figure 11. (a) Comparison of the synthetic routes I−IV toward ZnO/C hybrid materials and resulting morphology of ZnO/C hybrid materials. (b) Effect of contacting time on MB dye adsorption for pure ZnO (system I, black), ZnO−CLSAN (system II, red), ZnO−CSAN (system III, blue), and ZnO−CSAN-S (system IV, magenta). (c) Methylene Blue dye degradation for different sample materials (pure ZnO (system I, black); ZnO-CLSAN (system II, red); ZnO−CSAN (system III, blue); ZnO−CSAN-S (system IV, magenta); commercial ZnO (dark cyan); and pure dye (dark yellow)). [Adapted with permission from ref 101. Copyright 2017, American Chemical Society, Washington, DC.]

thus achieving higher cross-linking densities in rubbers.[198] A recent research demonstrated the usage of 5-nm OA-capped ZnO nanoparticles in the vulcanization of natural rubbers.[199] Compared to commercialized ZnO, OA-capped nanosized ZnO exhibited significantly better dispersion in a rubber matrix and effectively improved the curing efficiency of natural rubber, which potentially could have a great impact on reducing ZnO loadings in commercial rubber manufacturing.

Also, ZnO has been increasingly applied in the area of photocatalysis, because of its prominent photocatalytic activity.[200] Photocatalysis is a widely utilized technique for water purification, as well as the destruction of organic pollutants.[201,202] The desired photocatalyst is described as biologically/chemically/optically stable, is able to utilize visible and/or near UV light, has low cost, and is nontoxic.[203] Semiconductor photocatalysis is a rapid oxidation process, which can effectively degrade pigment contaminants and pollutants.[204] Among many oxygen-deficient metal oxides, ZnO photocatalytically degrades complex organic molecules under UV illumination.[205−207] The synthesis of novel nanocomposites photocatalysts (PNIPAM/ZnO hybrid nanoparticles) via SI-ATRP was reported.[89] By controlling the grafting density of thermoresponsive PNIPAM ligands on the surfaces of ZnO nanoparticles, the nanocomposites could retain sufficiently active sites on the ZnO surface and maintain the efficiency of photocatalysis. Meanwhile, the photocatalytic activity test of Rhodamine B degradation illustrated that the grafted polymer ligands could endow ZnO nanoparticles with temperature-controlled switching behaviors by altering the environmental temperatures. Another special material that has attracted much interest in ZnO-based photocatalysts is the ZnO/carbon composite. Depending on the special structure, the carbon components in the hybrid system can perform as a photoelectron reservoir. Besides, the presence of carbon materials can increase the adsorption capacity of the hybrid materials, which results in photoactivity enhancement.[208] Polyacrylonitrile is a common carbon source for the preparation of ZnO/carbon hybrids through the pyrolysis process. A series of well-defined PS-*b*-PSAN-NH_2 diblock copolymer ligands were synthesized by ATRP to graft onto the surface of 5-nm ZnO nanocrystals by the "ligand exchange" method.[101] The PS-*b*-PSAN capped ZnO nanoparticles served as precursors to prepare ZnO/carbon hybrids. The outer PS blocks were designed as sacrificial blocks to prevent cross-linking of carbon shells. The results showed ZnO/carbon hybrids with a specific surface area of 170 m^2/g and a 0.021

min^{-1} rate constant for Methylene Blue degradation under visible-light illumination. This approach provided a synthetic strategy to prepare ZnO/carbon hybrids that disperse fine ZnO nanoparticles within a highly porous carbon matrix (Figure 11).

Electrochemical Properties and Applications. ZnO is used not only for traditional rubber vulcanization activators and inorganic UV-shielding materials but also for optoelectronic materials, including nanogenerators, solar cells, supercapacitors, and light-emitting diodes (LEDs).[56] ZnO-based nanomaterials have become one of the most promising electrode materials, because of their remarkable features such as high reversible capacity, low cost, and good physical/chemical stability.[52] The particle sizes strongly affect the optoelectronic properties of ZnO nanoparticles.[209] It is important to tune the particle size during their preparation process and control their aggregation state by attachment of organic/polymeric ligands onto the surfaces.[66]

> ZnO-based nanomaterials have become one of the most promising electrode materials, because of their remarkable features such as high reversible capacity, low cost, and good physical/chemical stability.

The optimal spatial arrangement of nanostructures and mechanical design are essential factors in the hybridization of piezoelectric materials. A recent study reported the power enhancements in a hybrid nanogenerator; the piezoelectric structure was comprised of ZnO nanowires array and poly(vinylidene fluoride) (PVDF) polymer.[210] Compared to the "PVDF-only" nanogenerator, the device with the hybrid structures exhibited superior electrical power outputs in the electrical properties characterization. Under mechanical deformation, the ZnO nanowires transported a larger range of strains to the PVDF and enhanced the power generation of the hybrid nanogenerator.

The effectiveness of using a combination of organic and inorganic materials for photovoltaic applications has been well-illustrated. ZnO, in particular, has previously been proven as a good candidate for hybrid solar cells,[211−215] mainly attributed to its high electron mobility, low-temperature processability, and ease of synthesis.[216,217] For instance, ZnO nanoparticles can be dispersed in relatively nonpolar solvent mixtures and can further be mixed with poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-vinylene] (MDMO-PPV). An extremely fast charge transfer occurred upon excitation. This application is suggested to be used to produce high-filling-factor hybrid photovoltaic cells with open-circuit voltage.[218] A novel inverted polymer solar cell was fabricated by employing a ZnO nanoparticle and poly[(9,9-bis(3′-(*N*, *N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) bilayer structure as the electron-collecting layer.[219] ZnO nanoparticles served as an efficient electron transport and buffer layer to reduce the series resistance; meanwhile, through the formation of an interfacial dipole, the PFN interlayer in the devices can be used to improve the energy level alignment.

As mentioned above, ZnO has drawn interest as semiconductors for the fabrication of pseudocapacitors.[220−222] Incorporation of ZnO with other pseudocapacitive materials, such as amorphous carbon, resulted in a substantial enhancement of capacitance performance. A facile synthetic route to prepare ZnO/carbon hybrids via the pyrolysis of uniformly structured ZnO/polymer nanocomposites was demonstrated recently.[223] A series of PSAN polymers were synthesized by ATRP as the matrix and carbon precursors. ZnO/PSAN hybrid composites were cast from tetrahydrofuran (THF) solutions. The final ZnO/carbon nanocomposites with uniform microstructure were obtained after subsequent pyrolysis. The electrochemical performance of ZnO/carbon hybrid electrodes was evaluated by the specific capacitance and cycling stability tests, the gravimetric capacitance of $145\ \mathrm{F\ g^{-1}}$ was accomplished and 91% of the initial capacitance was maintained after 10 000 charge−discharge cycles. It is suggested that this new material holds great potential for electrochemical applications.

Biomedical Applications. Because of their special physical/chemical features, semiconductor nanoparticles have particular advantages in biomedical applications, including sensors, bioimaging, and drug delivery.[224−226] For instance, quantum-dot (QD)-tagged polymer beads with encoded fluorescence can theoretically recognize millions of biological targets.[227] However, most semiconductors suffer from drawbacks such as poor biocompatibility and high toxicity to humans and animals, which strongly limit their applications.[228,229] ZnO, as a new type of low-cost and benign material, has no cellular toxicity, which makes it ideal for biomedical applications. It has been demonstrated that ZnO nanoparticles have been utilized as antibacterial agents and anticancer drugs.[230−233] The unique properties of nanosized ZnO are attributed to their abundant functionality with large specific surface areas, their similar size with biomolecules, and the quantum size effects.

ZnO nanomaterials (e.g., nanocrystals, nanowires, nanorods) have been utilized for fluorescence imaging of cells.[234−237] Besides, ZnO QDs, as a type of economic and safe luminescent label, have promising prospects in biological imaging applications, such as dual-modality magnetic resonance imaging/fluorescence imaging.[238,239] Researchers in this field have reported the synthesis of water-soluble ZnO/(poly(ethylene glycol) methyl ether methacrylate) (PEGMEMA) core−shell nanoparticles through a sol−gel method.[235] The resulted functionalized ZnO QDs with tunable photoluminescence emission are almost nontoxic for the human cells. Water-soluble polymer-modified ZnO QDs were fabricated by coating the surface of ZnO with PDMAEMA.[240] These polycation-functionalized ZnO QDs combined functions of gene delivery and bioimaging, as they can condense plasmid DNA into transferable nanocomplexes loaded with ZnO, which emit yellow luminescence under UV radiation with a high quantum yield. With low cytotoxicity, this material is a promising candidate for the development of the novel transgenic vector.

Because of its low cost and high production safety, besides bioimaging,[241,242] ZnO also has gained many practical applications in protein enrichment[243] and drug delivery[244] areas. Compared to many other reported drug carriers, one of the most important features of ZnO is its lower cytotoxicity and biodegradable properties. The surface of ZnO can be readily modified by various anchoring molecules.[45,245,246] If the surface is in direct contact with the solution, ZnO can slowly dissolve under both acidic and strong basic conditions and work as a pH-sensitive carrier.[247,248] On the other hand,

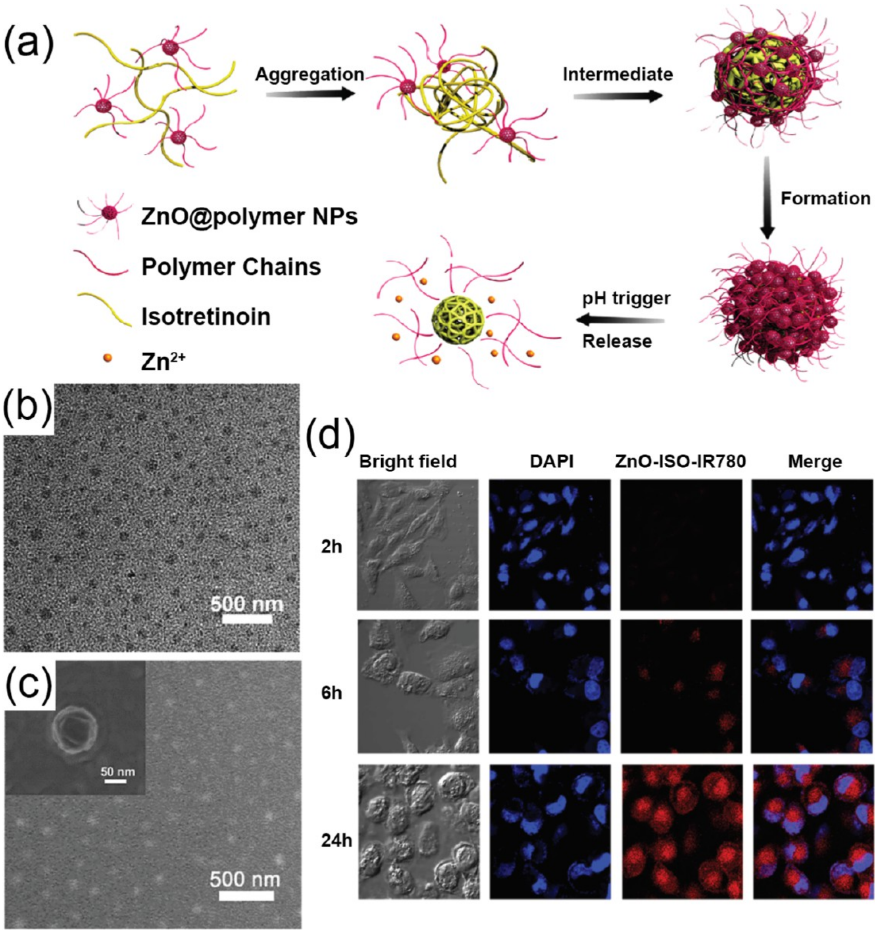


Figure 12. (a) Scheme for the formation and decomposition of ZnO−isotretinoin. (b) TEM image and (c) low-magnification SEM image (with an inset showing a high-magnification SEM image of the ZnO-isotretinoin composites) (the weight ratio for the preparation is 1:0.5). (d) CLSM images of A549 cells treated with DAPI (blue) and ZnO−isotretinoin-IR780 (red) for 2, 6, and 24 h, respectively. These images were taken using a 63× objective lens. [Adapted with permission from ref 250. Copyright 2017, American Chemical Society, Washington, DC.]

although drug-delivery systems based on ZnO nanomaterials have shown promising therapeutic efficacy, it is a real challenge to maintain a good dispersibility and long-term stability of the drug-delivery systems in water, since ZnO nanoparticles are prone to aggregate during storage and many drugs are not soluble in water. These limitations can be overcome after a suitable design and facile controlled synthesis.[249] For example, the surface modification of ZnO with biocompatible polymers can significantly reduce its cytotoxicity. Polydopamine-functionalized ZnO nanoparticles were grafted with biocompatible polymers (gelatin) to form ZnO/gelatin hybrids via a mussel-inspired method.[62] With the incorporation of gelatin, the hybrid composites not only exhibited enhancement of biocompatibility but also showed good antibacterial properties. Also, the water-soluble ZnO/PEGMEMA core−shell nanoparticles were synthesized through radical polymerization and dispersed in aqueous solutions.[250] Although the anticancer drug isotretinoin is not soluble in water, it can be loaded into the 100-nm novel capsules with 34.6 wt %, which were self-assembled by the ZnO/polymer nanoparticles in an aqueous solution. On one hand, the loading capacity of the capsule is higher than that on nanoparticle surfaces, which resulted in lower cytotoxicity as well as stronger anticancer activity. On the other hand, through the ZnO decomposition under low pH conditions, the release of isotretinoin was complete (Figure 12). This self-assembled hybrid capsule may provide a general procedure for the controlled release of hydrophobic drugs. Besides, reversible thermal- and pH-responsive properties of the drug delivery system can be achieved with PNIPAM grafted on ZnO nanoparticles via SI-ATRP.[85]

As a high bandgap semiconducting metal oxide, ZnO nanomaterials possess distinct properties and have wide applications in many fields. ZnO/polymer hybrid materials incorporate the unique properties of ZnO with the superior processability of polymers. One of the major problems in the utilization of ZnO nanomaterials is the aggregation of nanofillers, which can tremendously impact the performance of the nanocomposite, such as the mechanical strength, transparency, and catalytic efficacy, as well as electron and heat transfer. As discussed above, the polymer ligands attached to the surface of ZnO nanostructures serve the role of preventing the aggregation and improving the dispersion of nanofillers in the nanocomposites and polymer matrix, thus enhancing the performance of the final products. Recent advances in controlled radical polymerization have promoted the synthesis of well-defined polymer nanocomposites, such as block copolymer particle brushes,[251] polymer nanocapsules,[252−254] and vesicles,[149,255,256] etc. On the other hand, the study on the self-assembly behaviors of polymer nanocomposites facilitates the fabrication of hybrid materials with different microstructures and particular properties on a large scale, which brings more opportunities in developing novel and multifunctional ZnO/polymer hybrid materials.

OVERALL SUMMARY AND OUTLOOK

ZnO-based nanocomposites have attracted increasing interest as novel materials with unique properties. This Review has covered recent studies on fundamental synthetic strategies and application-driven discussions about ZnO/polymer hybrids in the past decades. The synthetic strategy can be divided into two aspects: one is ZnO surface functionalization, and the other is the preparation of ZnO/polymer hybrids. As a binary compound, ZnO can slowly dissolve in both acidic and strong basic conditions, which makes the surface of ZnO readily modified by various anchoring molecules, including polydopamine, aliphatic acid/amines, carboxylates, silane coupling agents, and functionalized polymer ligands. Future work should endeavor to develop more efficient and stable anchors. The review of the preparation of ZnO/polymer hybrids mainly focused on the controlled radical polymerization techniques, especially atom transfer radical polymerization. Three approaches were applied: "grafting-from", "grafting-onto", and "templated synthesis". The "grafting-from" approach relies on the attachment of initiating sites onto the surface of ZnO through the surface modification step. Another important advantage of the "grafting-from" approach is that polymer nanocomposites prepared using this method can get high and tunable grafting densities. However, very limited tethered initiators are commercially available at a reasonable price. In contrast, the "grafting-onto" approach requires the formation of stable covalent/coordinating bonds between pristine ZnO and presynthesized polymer ligands. However, with the surface treatment of the inorganic compounds, the achievable grafting density in the "grafting-onto" approach is limited. Moreover, further purification steps are needed to remove linear polymers with certain choices of ligands. The more recent derived approach, "ligand exchange", can obtain higher grafting densities with the cost of a limited selection of high boiling point solvents and interchangeable small-molecular ligands. The last synthetic technique covered is the "templated synthesis" approach, which was employed to prepare ZnO/polymer hybrids materials with defined and challenging morphologies, such as some anisotropic structures. The major challenges that limited the application of this method include the nanoreactor synthesis, the selection of appropriate precursors, and the loading efficiency of the precursor into the anchoring blocks. Although there is no single approach that can fulfill all the requirements of ZnO-based materials for different purposes, the "grafting-from" and "templated synthesis" are generally recognized as promising and favorable. The last section of this Review provides an extensive analysis centered on the recent advances in the applications based on ZnO/polymer hybrid materials because of their special properties, which include optical, catalytic, electrochemical, and biomedical areas.

Polymer−inorganic hybrids combine the advantages of inorganic and polymeric materials. The versatile and unique properties of ZnO make it a hot topic in the field of hybrid materials. Recent progress in controlled radical polymerization has encouraged many researchers to develop novel synthetic methods to achieve precisely defined polymer nanocomposites; more existing polymer architectures will be applied to ZnO nanoparticle surfaces or used as polymer templates for ZnO nanostructures synthesis, such as block/gradient copolymer particle brushes, polymer nanocapsules, and polymer vesicles. On the other hand, the study on the self-assembly behaviors of polymer nanocomposites facilitates the fabrication of hybrid materials with different microstructures and particular properties on a large scale, which brings more opportunities in developing novel and multifunctional ZnO/polymer hybrid materials, as well as further understanding the structure−property correlations. Further investigation with synthetic methodologies and fabrication techniques should help to accomplish these goals.

> Recent progress in controlled radical polymerization has encouraged many researchers to develop novel synthetic methods to achieve precisely defined polymer nanocomposites; more existing polymer architectures will be applied to ZnO nanoparticle surfaces or used as polymer templates for ZnO nanostructures synthesis

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M.B. and K.M. conceived and organized the project, and all three authors wrote the manuscript.

Notes

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