Recent Advancement in Functional Core-Shell Nanoparticles of Polymers: Synthesis, Physical Properties, and Applications in Medical Biotechnology

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This paper covers the core-shell nanomaterials, mainly, polymer-core polymer shell, polymer-core metal shell, and polymer-core nonmetal shells. Herein, various synthesis techniques, properties, and applications of these materials have been discussed. The detailed discussion of the properties with experimental parameters has been carried out. The various characterization techniques for the core-shell nanostructure have also been discussed. Their physical and chemical properties have been addressed. The future aspects of such core-shell nanostructures for biomedical and various other applications have been discussed with a special emphasis on their properties.

1. Introduction

The core-shell nanomaterials and nanostructures (Figure 1) have become an important research area since few decades due to their potential applications in various fields like catalysts, industrial and biomedical applications, and so forth [1–12]. The core-shell nanocomposites and nanostructure may be with different sizes and different shapes of core and shell thickness with different surface morphology. They may be spherical, centric, eccentric, star-like, or tubular in shape. Depending on the size and shape, their properties tune from material to another. Individual core-shell nanoparticles have various applications in diverse fields of medical biotechnology, like molecular bioimaging, drug delivery, cancer therapy, and so forth. Whenever the surface of the nanoparticles is modified by functional groups or molecules or coated with a thin layer of other materials (with different constituents), they show enhanced properties compared to the nonfunctionalized uncoated particles. There are different types of core-shell structure, like (1) metal-core and different metal shell, (2) metal-core and nonmetal shell, (3) metal-core and polymer shell, (4) nonmetal-core and nonmetal shell, (5) polymer-core and nonmetal shell and (6) polymer-core and polymer shell where the two polymers are different. For these six categories, the core and the shell materials may be reversed. Below is the schematic of core-shell nanoparticles.

Recently, much attention has been focused on core-shell metal nanoparticles based on gold, platinum, and palladium because their properties markedly differ from their bulk [1]. These metal core-shell nanoparticles exhibit size-induced quantum-size effects (i.e., electron confinement and surface effect) [1, 2] and can be exploited for a number of advanced functional applications as sensors, electronics, optoelectronics and catalysis [3–5]. Polymer and semiconductor core-shell have attracted considerable interest as a class of new materials with applications in various electronics including organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), sensors, and organic field effect transistors (OFETs) due to their advantages, such as low cost and easy device fabrication abilities [6–9]. The design and
synthesis of novel core-shell nanomaterials/nanostructures with polymers, that possess high mobility, are one of the major challenges in polymer semiconductor research [10–12].

These core-shell nanoparticles are produced by various synthesis approaches like hydrothermal synthesis, solvothermal synthesis, emulsion polymerization, microemulsion polymerization, and so forth. On the basis of the core and shell of the materials, the synthesis techniques, their properties, and morphologies can be modified.

2. Synthesis and Characterization of Various Types of Core–Shell Nanomaterials

The synthesis, characteristics, and new properties of different core-shell nanomaterials with polymer as either core or shell are summarized in Table 1.

2.1. Polymer-Polymer Core-Shell Nanoparticles and Nanostructure

Functional core-shell polymer nanoparticles and nanocomposites have attracted a lot of attention due to the special thermal, mechanical, and electrical properties [33]. Significant improvement of properties can often be achieved at a very low nanoparticle volume fraction. A water-soluble fluorescent hyperbranched conjugated poly(9-carbazole) (HCP) with a unique double-layered architecture has been synthesized via the combination of alkyn poly-cyclooligomerization and alkyn-azide “click” reaction for live-cell imaging [54]. A number of important synthesis methods of core-shell nanoparticles/nanostructure have been discussed in the subsequent section. Han et al. have synthesized poly(NIPAAm-co-DMAAm) coated poly(butyl methacrylate) core-shell nanoparticles and formulated into electrically conductive colloidal inks appropriate for use in roll-to-roll printing (Figure 2).

The initial phase of the core-shell synthesis was the emulsion polymerization of poly(butyl ethacrylate) particles with a particle size between 100 and 300 nm [50]. The observed particle diameter from transmission electron microscopy (TEM) was 199 ± 4 nm. The observed Mw of the colloidal particles was 221 Dalton and the polydispersity index (PDI) was 2.08. The second step in the core-shell synthesis is to coat the PBMA particles with polyaniline. To protect the PBMA particles from flocculation in the low pH synthetic conditions, poly(N-vinylpyrrolidinone) (PVP, Mw = 360 000), a polymeric stabilizer, was dissolved into the suspension and allowed to be absorbed onto the particles. The resulting core-shell particles were purified by centrifugation. Zhang et al. have synthesized dextran grafted with Poly(N-isopropyl acrylamide-co- N,N-dimethyl acrylamide) (dextran-g-poly(NIPAam-co-DMAAm)) [51]. The first step was synthesis of the poly(NIPAam-co-DMAAm) with a methyl ester end group (STP-COOCH3). The polymerization reaction was carried out by free radical copolymerization. Then, Fe3O4 nanoparticles were encapsulated with this biodegradable thermosensitive polymer (Figure 3).

As Dextran-g-poly (NIPAam-co-DMAAm) thermosensitive polymer contains the active 4-nitrophenyl chloroformate groups, they can be cross-linked by 1,6-diaminohexane around the magnetic core to form the core-shell structure (Figure 3) [51]. On the basis of the behavior, the concept of synthesis and the schematic illustration of the experimental procedure of magnetic carrier coated with smart polymer are schematically depicted in Figure 4 [51].

Yuan and Wicks have prepared thermotropic color-changing core-shell nanoparticles through the polymerization technique [55]. Water-dispersed thermotropic nanoparticles with core-shell structures were synthesized by the in situ polymerization of a lightly cross-linked shell of poly(N-isopropyl acrylamide) (poly (NIPAM)) onto blue polystyrene cores. At room temperature poly(NIPAM) hydrophilic in nature and is in a fully swollen gel state. As the temperature is raised beyond 31°C, poly(NIPAM) becomes hydrophobic and eventually collapses as the temperature reaches the lower critical solution temperature (LCST) [55].

2.2. Polymer-Metal Core-Shell Nanoparticles/Nanostructure

Wang et al. synthesized Au-impregnated polyacrylonitrile (PAN)/polythiophene (PTH) core-shell nanofibers and showed improved semiconducting properties like mobility [38]. Tian et al. have designed the self-assembled colloidal core-shell nanoparticles with polystyrene as core and gold nanoparticles as shell [40]. The application of these core-shell-structured colloidal particles to protein separation is also investigated in this research work. Colloidal particles with polystyrene-(PS)-coated magnetic nanoparticles in the core were also prepared by this strategy [40]. Hydrophilic citrate-stabilized AuNPs were dispersed in water, and PS with thiol terminal groups (PS-SH) was dissolved in toluene. A stable emulsion was obtained by mixing two solutions via sonication. In the emulsion, AuNPs were located at a liquid-liquid interface. Colloidal particles with PS cores and AuNP coronae were prepared by adding the emulsion to excess methanol. The colloidal particles were stabilized by hydrophilic AuNPs in the coronae. Initially, PS-SH/PS-coated Fe3O4 NPs were dissolved (or dispersed) in toluene, and then colloidal particles with PS/Fe3O4 NPs in the cores and AuNPs in the coronae were prepared by a similar strategy (Figure 5).

The weight ratio of PS-SH to AuNP plays an important role in controlling of the morphology of colloidal particles.
Sodium dodecyl sulfate
Potassium persulfate
353 K
Monodisperse poly(butyl methyl acrylate) (PBMA) (diameter 200 nm)

Absorption of poly(vinyl pyrrolidone) (PVP)
Ammonium sulfate
300 K
Polymerization
Redisperse
Centrifuge
Core shell PANI-PBMA

3. Polymer-Nonmetal Core-Shell Nanoparticles/Nanostructure. Rong et al. synthesized PSBM@silica core-shell NPs by emulsion polymerization method [15]. To achieve the core-shell, the surfaces of the silica particles were modified...
| Sl. no. | Materials | Synthesis method | Properties/uses | Average size of Core-shell particle | References |
|--------|-----------|-----------------|----------------|---------------------------------------|------------|
| 1      | Carbon black/polypyrrole | In situ chemical oxidative polymerization | Electrochemical energy storage | 50–100 nm | [13] |
| 2      | BaTiO$_3$/PMMA | In situ atom transfer radical polymerization (ARTP) | High dielectric constant materials with the inherent low loss of the base polymer | 150–200 nm | [14] |
| 3      | Polystyrene-n-butyl acrylate-methy methacrylate@silica | Emulsion polymerization | Dynamic modulus | 30–80 nm | [15] |
| 4      | Poly(vinyl amine)-silica | Wet chemical route | Silica precursor for composite materials formation | 200–250 nm | [16] |
| 5      | Silica@PMMA brush | Surface initiated photopolymerization | PMMA composite with enhanced thermal and mechanical properties | 100–150 nm | [17] |
| 6      | CdS@PMMA | Different physical and chemical routes | Electrical transport properties | 10–200 nm | [18] |
| 7      | Spiropyran-silica | Two-step sol-gel synthesis | Photochromic properties | 100–150 nm | [19] |
| 8      | (MMA@CuO) | Solution deposition method | — | 20–30 nm | [20] |
| 9      | Well-defined oxide (SiO$_2$ core-polymer (PMMA) shell | Chemical route | High mechanical strength | 20–90 nm | [21] |
| 10     | T-ZnO whiskers/Polyaniline | Graft polymerization | Electrical conductivity | 500 nm | [22] |
| 11     | PS cores and thermosensitive poly(N-isopropylacrylamide) (PNIPA) shells | Self-assembly encapsulation | Drug diffusion | Less than 100 nm | [23] |
| 12     | Silica-polymer (methyl methacrylate (MMA)) core-shell nanoparticles | Seed copolymerization | Excellent antimicrobial | 20–30 nm | [24] |
| 13     | PMMA@PCL | Coaxial electrospraying | — | 3–6 μm | [25] |
| 14     | PS@SiO$_2$ | Sol-gel synthesis | — | 200–250 nm | [26] |
| 15     | Fe$_3$O$_4$@styrene/butyl acrylate | Initiator free miniemulsion polymerization | Magnetite and their corresponding behavior | 150–200 nm | [27] |
| 16     | Polyaniline-polystyrene sulfonate@Fe$_3$O$_4$ | Surface-initiated polymerization | Conductive and magnetic properties | 60–200 nm | [28] |
| 17     | SiO$_2$@polypyrrole | In situ polymerization through electrostatic interaction | — | 200–300 nm | [29] |
| 18     | PMMA spheres with a core of Fe$_3$O$_4$ | Spontaneous Pickering emulsification | — | 50–80 nm | [30] |
| 19     | PS@SiO$_2$ | Alcoholic dispersion polymerization | Catalytic | 1000 nm | [31] |
| 20     | Poly(2-vinylpyridine) @silica | Emulsion polymerization | Cationic azo initiator | 200 nm | [32] |
| 21     | SiO$_2$@Poly(3-aminophenylboronic acid) (PABBA) | Ultrasonic irradiation method | Conductivity | 100–200 nm | [33] |
| 22     | Collagen-g-PMMA Ag@TiO$_2$ | Graft polymerization water in oil emulsion polymerization ultrasonic irradiation | Lower infrared emissivity | 60–100 nm | [34] |
| Sl. no. | Materials | Synthesis method | Properties/uses | Average size of Core-shell particle | References |
|---------|-----------|-----------------|----------------|-----------------------------------|------------|
| 23      | SiO₂@polyaniline | In situ polymerization | High electrical conductivity | 20–30 nm | [35] |
| 24      | PANI@Fe₃O₄ | Ultrasonic polymerization to assist chemical oxidative polymerization | Decreases its electrical conductivity | 20–25 nm | [36] |
| 25      | SiO₂@PAM | UV assisted in situ surface initiated free radical polymerization | Good dispersion stability | 50–200 nm | [37] |
|         | PAM: polyacrylamide | | | | |
| 26      | Au-impregnated polycrylonitrile (PAN)/polythiophene (PTH) core-shell nanofibers | Shadow mask | High-performance semiconducting properties | 30–50 nm | [38] |
| 27      | Smart core-shell hybrid nanogels with Ag nanoparticle core and poly(N-isopropylacrylamide-co-acrylic acid) shell | Copolymerization process | pH-Regulated drug delivery and for cancer cell imaging | 40–80 nm | [39] |
| 28      | PS cores and Au shell nanoparticle coronae | Self-assembly | Hydrophobic nanoparticles | 80 nm | [40] |
| 29      | Upconverting NaYF₄ nanoparticles with PEG-phosphate ligands | Water-dispersible | Biolabeling within the biological window | 30–40 nm | [41] |
| 30      | Au@PEG (polyethylene glycol) | Combined swelling heteroaggregation | Dielectric applications | 300 nm | [42] |
| 31      | Ag-polystyrene | Hydrothermal method | Characteristic plasmon resonance | 200 nm | [43] |
| 32      | Ag@poly(acrylic acid) | In situ immobilization | Tunable photoluminescence, act as multiple-sensitive hybrid microgels | 100 nm | [44] |
| 33      | Highly controlled core (Au/shell (PANI) structures | In situ polymerization, | Tunable conductive polymer | 61–92 nm | [45] |
| 34      | Au-PS hybrid colloidal particles | Precipitation polymerization method | Fabricating photonic devices via a self-assembly approach | 200–250 nm | [46] |
| 35      | Fe₃O₄@polyaniline@Au Nanocomposites | Solvothermal reaction | Catalytic activity | 70–80 nm | [47] |
| 36      | Luminescent silver@phenol formaldehyde resin core-hell nanospheres | Facile one-step hydrothermal approach | In vivo bioimaging | 180–1000 nm | [48] |
| 37      | Poly(butylene adipate) on the surface of SiO₂ | Chemical route | Improve the toughness and stiffness | 100–1000 nm | [49] |
| 38      | Polyaniline-coated poly(butyl methacrylate) | Chemical route | Printing technology | 100 nm | [50] |

with oleic acid. The addition of silica NPs inhibit the chain movement and increased the moduli, which are strongly dependent on the extent and distribution of silica NPs in PSBM. Annenkov and coworkers found that the degree of polymerization and the pH of organic polymer decide the morphology of the end product (i.e., core-shell nanoparticles (CSNPs)) [16]. In the synthesis of poly(vinyl amide@silica), it is observed that only high molecular weight polymer with longer chain length (i.e., degree of polymerization is high) helps to form the core-shell structure. When the degree of polymerization is less than 1000, then the associates of polymer silica core shell form nanostructure. The cooperative interactions of the silica with polymer chains tune the size of the particles with the degree of polymerization and pH. Chen et al. synthesized silica@PMMA core-shell nanoparticles with light-initiated polymerization method [17]. The thickness of
Table 2: Comparison of infrared emissivity values of various samples.

| Samples                          | Infrared emissivity (ETIR at 8–14 𝜇m) |
|---------------------------------|---------------------------------------|
| Collagen                        | 0.851                                 |
| Collagen-g-PMMA                 | 0.896                                 |
| Ag@TiO₂                         | 0.514                                 |
| Collagen-g-PMMA/Ag@TiO₂         | 0.496                                 |

Figure 3: (a) TEM micrograph and (b) selected electron diffraction pattern (SAED) [51].

the PMMA shell can be tuned by UV irradiation (Figure 11) without altering the main chemical structures and bondings of the composite systems [12]. The SiO₂ particles impregnated in the PMMA help to enhance the overall mechanical and thermal properties of the core shell.

Chen and coworkers have also synthesized well-defined PMMA brush on silica particles by surface-initiated photopolymerization (SIPP) [17]. The photochemical method is a convenient and simple route to achieve polymer brush on the surface of a nanoparticle. They synthesized PMMA brush on silica particles (SPs) through nucleophilic addition between amine and epoxy groups and then initiated photopolymerization of MMA to generate PMMA brush on SPs at room temperature (Figures 12 and 13).

Synthesis of polymer brush on particles by photochemical approach has potential application as a printing ink and is little challenging because of the excellent UV absorbance hypoxanthine [60]. Thioxanthone can absorb UV light (250 nm–350 nm) with a large extent even in the case of pigment particles’ shield and is consequently widely used in photocuring systems containing pigment particles such as coating and printing ink [61].

Allouche et al. synthesized hybrid spiropyran-silica nanoparticles with a core-shell structure by sol-gel synthesis having good photochromic properties [19]. Photochromic hybrid spiropyran-silica nanoparticles with a core-shell structure were synthesized via a two-step sol-gel procedure using tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) as silica precursors. The chemical nature and porosity of the materials were modified by the precursor ratio, and the silylated spiropyran derivative chromophore was grafted and confined inside the nanoporous shell producing photoresponsive nanomaterials with a tunable dye photochromic response [19].

Polymer nanoparticles can be coated with silica by the Stober method [62, 63]. In this method, the reaction rates depended on the pH. At low pH the reaction rate is very low. That means there is very thin coating or almost no coating of silica on polymer beads at low pH. But at high pH, thick silica coating with heterogeneous nucleation is observed. Chen et al. have found out that the surface modification of the core material plays an important role in the synthesis of core-shell structures [22]. It also provides enhancement of properties of CSNPs (core-shell nanoparticles). In the synthesis of tetra-needle-like ZnO whiskers (T-ZnOw)@polyaniline core-shell composites, surface modification of T-ZnOw with ATPS amino propyl triethoxysilane results in intactness of the morphology structure of T-ZnOw and provides a surface site for in situ polymerization of the T-ZnOw. These CSNCs showed a higher electrical conductivity than that of the pure T-ZnO.

Polystyrene particles with hollow structure can also be coated with SiO₂ through sol-gel method. Initially, polystyrene latex particles can be synthesized using 4-VP (4-vinylpyridine) as functional comonomer and PVP as surfactant (Figure 14) [26]. The morphology depends on the initial feeding rate of the precursors like 4-VP and PVP.

Core-shell magnetic colloidal particles have potential demand in the fields of nano technology. Fe₃O₄@PS core-shell magnetite nanoparticles can be modified by styrene and butyl acrylate through miniemulsion polymerization [27]. Mahdavian et al. have prepared surface-modified Fe₃O₄ (m-Fe₃O₄) through ultrasonication and polymerization methods [27]. A synthesis method for core shell has been introduced by Lee et al. to achieve PANI-polyaniline-polystyrene sulfonate@Fe₃O₄ (conducting magnetic) core-shell nanoparticles [28]. Each core-shell particle has single Fe3O4 (magnetic) particle and the polymer shell evenly encapsulated the core (Figure 15).
Lee et al. synthesized poly(aniline)-poly(styrenesulfonate)@Fe$_3$O$_4$ core-shell nanoparticles using aqueous solution that contained PSS@Fe$_3$O$_4$ and was added to freshly distilled aniline and APS. The yielded PANI-PSS@Fe$_3$O$_4$ core-shell nanoparticles are dark-green solids [28]. Liu et al. have synthesized SiO$_2$@polypyrrole conductive core-shell nanoparticles [29]. In situ polymerization of pyrrole monomers leads to these structures. Through this approach, the core-shell nanoparticles as well as hollow pyrrole nanoparticles are obtained. For hollow nanoparticles the core is etched off by HF. The shell thickness could be controlled by adjusting the monomer concentration and hydrothermal temperature (Figure 16). Through this method large quantities of core-shell conductive and hollow nanoparticles could be obtained via in situ polymerization under hydrothermal conditions.

3. Properties

Controlling the size of the core and thickness of the shell are of paramount significance in tailoring the properties of core-shell nanomaterials. Core-shell structure has attracted much attention as the extra dimension of control over the core NPs. For optimal control of the properties, an ideal sample of core/shell nanoparticles (NPs) should form a stable structure. It has different physical, chemical, and biological properties on the basis of tenability of the composition, surface morphology and structural order of NPs.

3.1. Physical Properties. The core-shell nanostructure and surface functionalization of core-shell nanomaterials have a wide range of advancement of properties. The most important properties like upconversion, electrical conductivity, and dielectric properties have been discussed below.

3.1.1. Upconversion Properties. The upconversion (UC) refers to nonlinear optical processes characterized by the successive absorption of two or more pump photons via the intermediate long-lived energy states followed by the emission of the output radiation at a shorter wavelength than the
Figure 5: Schemes for the preparation of (a) colloidal particles with PS cores and gold nanoparticle (AuNP) coronae and (b) colloidal particles with PS/Fe₃O₄NP core and AuNP coronae [40].

Figure 6: TEM images of colloidal particles prepared at different weight ratios of PS-SH to AuNP—(a) 1:17, (b) 1:4, (c) 1:2, and (d) 3:1. (e) Magnified TEM image of a colloidal particle showing the details of the structure. (f) TEM image of colloidal particles after changing the solvent from methanol to water [40].
Liu et al. synthesized a new type of bifunctional nanocomposites with upconversion nanoparticles and SiO$_2$ for biomedical applications. The NaYF$_4$:Yb$^{3+}$, Tm$^{3+}$ was coated with Ru(II) complex doped SiO$_2$ by combining the upconversion and oxygen sensing properties of individual components (Figure 17) [63]. The upconversion properties and the intensity of the emission and its color from the NaYF$_4$:Yb$^{3+}$, Tm$^{3+}$ predominantly depends on the concentration of Yb$^{3+}$ and Tm$^{3+}$ in NaYF$_4$ matrix system, the nature of shell, and shell thickness (either it is inorganic or polymer shell), as well as on the liquid dispersion medium (Figures 18 and 19). These bifunctional nanocomposites have potential applications in biochemical and biomedical fields, such as biolabels and optical oxygen sensors, which can measure the oxygen concentrations in biofluids.

Li et al. have worked on the influence of the TGA (Thioglycolic acid) modification on upconversion luminescence of hexagonal-phase NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ Nanoparticles [56]. The possible conjugation and mechanism of TGA with NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ nanoparticles is shown in Figure 20 where it is clear that the linking occurred through the–COOH ends. Oleylamine formed a layer on the NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ nanoparticles and formed a successful stable dispersion.

Fluorescent nanoparticles used for biomedical applications should be small with narrow-size distribution and water-soluble with high luminescent efficiency (Figure 21). First, the Er$^{3+}$ ion is excited from the ground state 4I15/2 level to the excited state 4I11/2 via ET of neighboring Yb$^{3+}$ and Er$^{3+}$. Subsequent nonradiative relaxations of 4I11/2-4I13/2 populate the 4I13/2 level. In the second-step excitation, the same laser pumps the excited state atoms from the 4I11/2 to the 4F7/2 level via ET, or from the 4F9/2 to 4F9/2 state via phonon-assisted ET. Chen et al. have found that the nY$_2$O$_3$/Yb$^{3+}$/Er$^{3+}$ nanocrystals were enhanced by up to half of the bulk counterpart by tri-doping with Li$^+$ ions, which can be contrasted to the usually 2 orders of magnitude higher UC radiations of the bulk compared to Li$^+$-free nanocrystals [64]. Additionally, a remarkable enhancement of emission by three times in ceramic bulk Y$_2$O$_3$ suggests the effectiveness of the Li$^+$ ions for bulk materials, which, however, requires an appropriate technique to dope large concentrations of Li$^+$ ion into the host lattice for higher enhancement times [64].

3.1.2. Conductivity and Dielectric Properties. Nanoparticles can be easily coated with polymeric shells by electrostatic layer-by-layer assembly of certain polyelectrolytes. The colloidal dispersion stability can be enhanced with polyelectrolyte concentration, contour length of polyelectrolyte chain, and the ionic strength. Core-shell nanocomposites show good conductivity at moderate temperature (283 K to 423 K). According to Yang et al., these properties are prominent for carbon and conductive polymer-(polypyrrol-) based core-shell nanocomposites (C@polypyrrole) (Figure 22) [13]. They also observed the high discharge capacity when they used these composites as electrode materials in supercapacitors in 1.0 M NaNO$_3$ electrolyte solution. The temperature dependence of conductivity of the CB/PPy nanocomposites is represented in Figures 23 and 24. As the temperature increased,
the conductivity increased in the range of 283–423 K. The temperature dependence of conductivity indicated that all the samples showed the semiconducting characteristics [13].

Core-shell nanocomposites also show high dielectric constant over a wide range of frequencies. The in situ atom transfer radical polymerization of MMA produces BaTiO$_3$@PMMA core-shell nanoparticles, which shows high dielectric constant over a range of 0.1 Hz to 1 MHz frequencies [14]. The high dielectric loss can be observed only at low frequencies/high temperatures. They also showed low loss of base polymer MMA over a wide range of frequencies. The effective dielectric constant of CSNP hybrids can be tailored by simply changing PMMA shell thickness.

Core-shell nanoparticles possess multiple functional properties. for example, PANI@Fe$_3$O$_4$ core-shell nanocomposite exhibits both magnetic and conducting properties [65]. To get PANI@Fe$_3$O$_4$ core-shell nanocomposite, the Fe$_3$O$_4$ nanoparticles are encapsulated by PANI and dispersed in PANI. In another study, it was found that the more amount of Fe$_3$O$_4$ content decreases the crystallinity of the PANI and increases the doping level. As the content of Fe$_3$O$_4$ increases, the magnetization of PANI/Fe$_3$O$_4$ composite increases simultaneously but conductivity decreases [36]. Li et al. found that the moderate permittivity of the Al$_2$O$_3$ layer greatly suppresses the leakage currents and dielectric loss in these nanocomposite materials. Such nanocomposites, with high permittivity, small dielectric loss, and small dependence of permittivity and dielectric loss on temperature, are attractive for physically small capacitors with large energy storage capacities and high rating voltages [65].

### 3.2. Physicochemical Properties (Magnetic Resonance Imaging, Catalytic Behavior, etc.)

Imaging (MRI) experiments with polysiloxane-containing diblock copolymer-coated IONPs showed excellent T(2)-weighted contrast effect from coated IONPs with a transverse relaxivity $r(2) = 98.6 \text{ mM}^{-1} \text{s}^{-1}$ (at 1.5 T) [57]. Such thin coating layer has little effect on the relaxivity when compared to that of IONPs coated with conventional amphiphilic copolymer. The surface modification of magnetic nanoparticles with thermo-responsive hydroxypropyl cellulose resulting core-shell nanostructure is the excellent candidate for fabricating biocompatible stimuli-responsive magnetic nanoparticles.

Long et al. have synthesized the Pt-Pd core-shell nanoparticles [66]. They studied the comparison of electrocatalytic properties of Pd-Pt bimetallic nanoparticles to confirm their highest catalytic performance. They have noted that catalytic activity of Pt-Pd alloy and core-shell nanoparticles was investigated to develop novel electrocatalysts in direct methanol fuel cells (DMFCs). According to the data analysis, core-shell nanoparticles with the thin nanoshells as monolayers exhibit better nanocatalysts.
Figure 9: AFM surface images (top) of a PS bead covered with AuNPs—(a) single bead \((10 \times 10 \ \mu m^2)\), (b) boxed area of bead in (a) \((2 \times 2 \ \mu m^2)\) [42].

Figure 10: Schematic diagram of preparation process of \(Fe_3O_4/PPy/Au\) nanocomposites [52].

Alonso et al. also worked on the development of environmentally safe polymer-metal nanocomposite materials containing polymer-stabilized metal nanoparticles (PSMNPs) [67]. These materials can be developed by a functional polymer with immobilized Pd@Co core-shell PSMNPs distributed mainly near the surface of the polymer which makes PSMNPs maximally accessible for reagents in catalytic applications. All PSMNPs nanocomposites were used to check the effective catalytic behaviors in Suzuki cross-coupling reactions between arylboronic acids and aryl halides to produce biphenyls as a reference reaction [67]. The BaTiO\(_3\) and ZrO\(_2\) core-shell nanoparticles having variable Al\(_2\)O\(_3\) shell thicknesses can be prepared via a layer-by-layer deposition of methylaluminoxane. With increasing or
3.3. Biological Properties

3.3.1. Surface Modification and Biocompatibility Properties. Hydroxypol cellulose is a biocompatibility as well as biodegradable polymer. Polysiloxane-containing diblock copolymer-coated IONPs are stable without aggregation or binding to proteins in serum when incubated in cell culture medium containing 10% serum (Figure 25). Furthermore, a much lower level of intracellular uptake by macrophage cells was observed with polysiloxane-containing diblock copolymers-coated IONPs, suggesting the reduction of non-specific cell uptakes and antibiofouling effect [57].

Au nanoparticles of size between 5 and 20 nm coated with densely packed polymer chain showed greater efficiency in cellular uptake [68]. The high grafting densities, surface properties, and size of the hybrid nanoparticles should be the only contributing factors in cellular uptake in epithelial Caco cells. Negatively charged AuNPs can be taken up easily by the cells with greater efficiency than the neutral AuNPs, most probably due to binding with membrane proteins. The positively charged AuNPs increase the uptake efficiency. The oxidation can be catalyzed by the metal@T-CoS-MIP nanocomposites at room temperature in water using air as oxidant. The Au nanocomposite particles show the enhanced catalytic activity for the oxidation of benzyl alcohol [68]. Moreover, it was found that the catalytic activity of the metal nanocomposite can be modulated by the volume transition of microgel particles for the oxidation reaction of benzyl alcohol [68]. Wu et al. studied the influence of the experimental parameters in the formation of silver/polypyrrole core-shell nanoparticles [39]. Core-shell-structured hybrid nanogels (40–80 nm) composed of Ag nanoparticles as core and smart gel of poly(N-isopropylacrylamide-co-acrylic acid) as shell have been synthesized by Wu et al. The pH-induced shrinkage of the nanogel increases the UV-vis absorption intensity and causes blue shift of the surface plasmon bands of the Ag NPs core. The smart nanogel can overcome cellular barriers to enter the intracellular region and light LIP the mouse melanoma B16F10 cells, including the nuclear regions. The surface property and concentrations of the hybrid nanogels influence their interactions with cells, resulting in different cell morphology and selective cell staining. The pH-responsive hybrid nanogels exhibit not only a high drug loading capacity but also a pH-controllable drug releasing behavior.

3.3.2. Thermoresponsive Properties. Core-shell structures with thermal responsive poly(N-isopropyl acryl amide) (PANIPAM) as core and gold nanoparticles as shell were synthesized [43]. The fabrication process is easy because there is no need to change or modify the structures of PANIPAM and AuNPs. The Au@polystyrene core-shell nanoparticles show an increase in the surrounding dielectric constant. Extinction spectra show red shift which is conformation of characteristic plasmon frequency (Figure 26). These particles can be synthesized by hydrogen reduction of silver oxide solution at elevated temperatures in the presence of polystyrene microspheres followed by acetone treatment [43].

Guo et al. synthesized size tunable degradable nanoparticles and they have studied thermal properties of these decreasing the Al2O3 shell thickness, the leakage current and high-field dielectric loss in these core-shell nanocomposites can be tuned [65].

Recently, a few research articles on inorganic-inorganic/polymer-inorganic core-shell nanoparticles have been reported by Guo and coresearchers [68–75]. They found various improved functional properties like dielectric, thermal, magnetic, anticrocorrosion, and so forth. It was observed that Fe@SiO2 and Fe@SiO2/polyurethane nanocomposites have improved thermal stability and antioxidation capability compared to the Fe@FeO and Fe@FeO/polyurethane [69]. Fe@SiO2/Pu can absorb electromagnetic radiation with high extent. Carbonyl-iron-particles-(CIP-) silica/PU composites are very much potential for anticrocorrosive behavior than that of the CIP/PU composites [70]. In another work it was found that CIP-silica particles and CIP-silica/PU composites are quite thermally stab and with more enhanced antioxidation capability than that of their counterparts [72].
polymers which are also very important for high temperature applications [76]. The TGA thermograms of the triblock copolymers are shown in Figure 27. This thermal degradation behavior of polycaprolactone- emeraldine state aniline pentamer polycaprolactone (PCL-EMAPPCL) copolymers is similar to that of the AD-PCL (aniline dimer polycaprolactone) polymers. In the case of the PCL-EMAP-PCL copolymers, the first obvious weight loss took place in the temperature range between 310 °C and 440–460 °C, attributed to the decomposition of the less thermally stable PCL segments (Figure 27). They observed that if the temperature is increased from 440 to 460 °C and to 620 °C, there was a second evident weight loss of about 25–10 wt % of the copolymer, which corresponds to the degradation of the EMAP segment. Thermal degradation occurs at a lower temperature in the case of the AD-PCL polymers, this is indicating that the PCL-EMAP-PCL copolymers have a higher thermal stability.
3.3.3. pH Responsive Properties. pH responsive optical properties of core-shell materials have a potential in biomedical applications. Photoluminescence (PL) of the Ag nanocrystals can be tuned in multiple sensitive hybrid microgels. The microgels can be embedded with Ag nanoparticles or Ag@Au bimetallic nanoparticles. The multiple sensitive copolymer microgels of poly(n-isopropylacrylamide-co-acrylic acid-co-acrylamide with polyacrylamide fragments can serve as stabilizing. The photonization of poly(acryl acid) fragments shrinks the microgels resulting in the increment of photoluminescence intensity. Blue shift of the emission maximum of the AG nanoparticles conforms this phenomenon. The surface modification of small Ag nanoparticles with Au nanoclusters reduces the pH sensitivity of PL property changes but dramatically enhanced the PL signals in the near-infrared regime of the hybrid microgels [44]. Micrometer-sized silica sol stabilized polystyrene nanoparticles and submicrometer sized polystyrene nanoparticles were synthesized by Schmid et al. Initiator of polymerization has effect on the size of core-shell nanoparticles. When nonionic AIBN initiator is used, micrometer-sized polystyrene@silica sol core-shell nanoparticles are obtained. When this cationic initiator is used, the submicrometer and nanometer-sized polystyrene silica nanocomposites were obtained. Reduction of initial silica concentration results in the increase in the overall latex diameter. By calcinating these core-shell nanoparticles we can have hollow silica nanocapsules [31].

Yang et al. employed the pH sensitivity property of polymer microspheres/micelles with DOX (doxorubicine hydrochloride) as a model drug for cancer treatment [77]. The loading behavior of DOX in hollow P(MBAAm-co-MAA) microspheres depends on the pH of the medium. For
example, the loading capacity of DOX on hollow P(MBAAm-co-MAA) microspheres was 40 mg/mg at pH of 1, 321 mg/mg, at pH of 7, and 236 mg/mg at pH of 10, respectively. Therefore, the pH level has significant effects on the loading capacity of the DOX in hollow P (MBAAm-co-MAA) microspheres and is a controlling factor.

3.3.4. Surface Functionalization. Surface functionalization plays an important role in achieving the core-shell nanostructures. A study has been done in last few decades and proposed that in the synthesis of polystyrene@ZnO core-shell nanostructures, the interaction between the ZnO nanoparticles and beta-diketone groups present on the surface of the polystyrene particles leads to core-shell nanocomposite structures. In core-shell nanocomposites synthesis, the selection of suitable polymerization initiator decides the efficiency of aggregation of shell on the core. The synthesis of colloidal poly(2-vinylpyridine)-silica nanocomposite particles suitable
cationic azo initiator leads to a very high silica aggregation efficiencies (88%–99%) [32]. These nanoparticles, nanostructures and nanocomposites were synthesized using emulsion polymerization. In this the core material can be replaced with some materials like styrene, methacrylic comonomers to produce copolymer-silica core-shell nanocomposites [32]. The composite core-shell nanoparticles give improved properties than the individual nanoparticles. The ultrasonic irradiation synthesis of collagen-grafted PMMA/Ag@TiO$_2$ composite shows lower infrared emissivity value in the range from 8 to 14 µm than that of pure collagen or grafted collagen (Table 2) [34]. This is the result of strong interfacial synergism forces inside the composite. The thickness of the TiO$_2$ shell is varied with concentration of Ti precursor. The Ag core diameter produced is around 50 nm [34].

4. Applications

Synthetic polymeric core-shell nanomaterials can be used in medical fields like disposable supply, prosthetic materials, dental materials, implants, dressings, extracorporeal devices, encapsulants, polymeric drug delivery systems, tissue engineered products, and orthodoses as that of metal and ceramics substituents. The core-shell nanoparticles have
shown a wide range of new applications in the fields of chemistry, bioscience, and material sciences because of their improved physical and chemical properties over their single-component counterpart. Core-shell nanomaterials play important roles in developing biological and medical applications. Proper core-shell materials can provide biocompatibility, safety, and surface functionalization that is required for specific in vitro and in vivo applications.

4.1. Drug Delivery. Buxton and Nigel studied the drug delivery efficiency of polymer core-shell nanoparticles using computer simulations [78]. In particular, they investigated the effects of shell swelling on drug release rates. Polymer core-shell nanoparticles are attractive drug-delivery systems because the drug can be encapsulated inside the core, while the shell properties can be assigned to optimize drug-delivery needs. An elegant approach to such particles is to use polymer gels, which have swelling properties that depend upon conditions such as pH. In this way swelling of the shell, and the drug release, can be targeted to occur at the desired location. Furthermore, they studied the thermodynamic feasibility and investigated both the physical and chemical barriers to drug release from the core shell. Through a combination of structural and fluid simulations, they are able to explain the physics behind polymer core-shell nanoparticles to use it in drug delivery applications [78].

Systems with no enthalpic interactions (Figures 28(a) and 28(b)) are compared with systems which penalize with both drug diffusion out of and bulk fluid into the polymer core. Cross-linked sites are depicted as red (core) and blue (shell) spheres, and the drug molecules are depicted as red mist. Both physical structure and enthalpic interactions play an important role in releasing of the drug from the core-shell nanoparticles. In particular, the amount of drug that has been diffused out of the core-shell particles appears to be larger for the open particle (Figure 28(a)) than for the closed particle (Figure 28(b)) [78]. Poly( amidoamine)(PAMAM)-poly(2-(N,N-diethylamino)ethyl methacrylate)(pDEA)-ethoxy-poly(ethylene glycol)2000 (mPEG) is also a promising nanocarrier for the delivery of anticancer drugs [79]. The pH sensitive and thermosensitive biocompatible polymer core-shell nanoparticles are also a potential for drug delivery and cancer therapy [43, 77].

4.2. Biomedical Application and Drug Carrier. Core-shell nanoparticles play an important role in biomedical applications. The core-shell nanoparticles can be used as drug carriers with sustained release. The drug uptake and release profile can be altered by changing the structuring morphology of core and shell materials. In surfactant-free self-assembled iron nanoparticles (SAIO)@SiO$_2$ core-shell nanocrystals, the hydrophobic drug molecules can be encapsulated within the SAIO-PVA (surfactant-free self-assembled iron nanoparticles-polyvinyl alcohol) core and then further covered with a thin shell of SiO$_2$. The structure of the core can
be distinguished when an external magnetic stimuli is applied resulting in burst release of the drug. After removing external magnetic stimuli drug profiles showed linear and controlled releases. These core-shell nanocrystals also showed high uptake efficiency from the HeLa cancer cells [23].

Fe$_3$O$_4$/Polypyrrole/Au nanocomposites with core/shell/shell structure were synthesized by Zhang et al. [52]. These core-shell nanocomposites show magnetism in addition to being easily controllable by an external magnetic field. They also show good conductivity and excellent electrochemical and catalytic properties of PP and Au nanoparticles. Additionally, these nanocomposites showed excellent electrocatalytic activities to biospecies such as ascorbic acid [52]. Some core-shell nanocomposites of PANI and Fe$_3$O$_4$ show improved conductivity than that of their individual particles and they can also exhibit multifunctional properties. Fe$_3$O$_4$/PANI core-shell nanocomposites showed higher conductivity (6.4–9.2 × 10$^{-2}$ S/cm) than that of pure PANI (3.7 × 10$^{-3}$ S/cm). These particles also show superparamagnetism behavior. The method for the preparation of Fe$_3$O$_4$/PANI core-shell nanocomposites provides new strategy for the synthesis of multifunctional core-shell nanocomposites (i.e., conducting polymers and metal nanoparticles) [80].

4.3. Molecular Bioimaging. Molecular bioimaging is one of the most powerful techniques of noninvasive imaging methods utilized in medical sciences, and it is based on the relaxation of protons in tissues. Upon accumulation in tissues, SIONPs enhance proton relaxation of specific tissues compared with that in surrounding tissues, serving as an MR contrast agent [81]. The iron oxide nanoparticles allow the nanocarriers to be used as agents for magnetic resonance imaging (MRI), magnetic targeting with the assistance of external magnetic field gradients and hyperthermia treatment in an alternating magnetic field [14, 15]. The core-shell has tunable magnetic and biocompatible properties and it can
be used in various types of bioimaging technique (e.g., CT scan, MRI, etc.). Several types of polymer DDS have been exploited, including polymer prodrugs [73], micelles, and vesicles based on amphiphilic and double-block copolymers [82, 83], dendrimers [84], and hydrophobic polyester-based nanoparticles [85] molecular bioimaging. Yathindranath et al. synthesized surface-modified iron oxide core-shell nanocomposites with different biocompatible polymers along with an excipient during freeze-drying. They observed that bovine serum albumin (BSA) was physically adsorbed onto the surface of iron oxide nanoparticles along with excipient during the freeze-drying. The BSA attached with iron oxide nanoparticles when applied the magnetic field of an MRI instruments was observed in vitro due to the mass transport [86]. The designed polymer core-shell materials, as shown in Figure 29, are used for bioimaging under the magnetic field.

The schematic of the IO CS-NPs is represented in Figure 29. PEG is chosen as coating, since, it is a neutral, hydrophilic polyether. PEG is known to form stable protein conjugates. PEG is also nonimmunogenic and nonantigenic with a long in vivo circulation lifetime [86].

Achieving the dual functions of MRI and magnetic targeting, a strategy was developed to synthesize CMD (carboxymethyl dextran) coated, iron oxide-based core-shell magnetic nanoparticles with controlled sizes. Characterization demonstrated that the nanoparticles thus synthesized possessed a shell-core structure consisting of a thin polymer shell coating on a self-assembled magnetic core made of...
Figure 31: Fluorescence imaging of HeLa cells after incubated with rabbit anti-CEA Ab-conjugated UCNPs (a), amino-modified NPs without linking any antibody (b), and rabbit anti-goat Ab-conjugated UCNPs (c) for 1h. Left rows are images in bright field; the middle rows are fluorescent images in dark field; and right rows are overlays of the left and middle rows [88].

4.4. PhotoSensitive Applications. In some core-shell hybrid nanoparticles, the photochromic properties can be changed by changing the precursor ratios synthesis. In spiropyran@silica core-shell nanoparticles, the chemical nature and porosity can be changed by changing the precursor ratio. Depending upon the content of the MTEOS the optical response can be tuned from reverse to direct. The nanoporous shell in which silylated spiropyran-derived chromophore is grafted [19]. The core-shell structure can be modified by the fluorescence molecules. By changing the content of ZnO particles into polymer-coated ZnO, the strong blue fluorescence with quantum yield more than 80% is achieved. In this, the different fluorescence mechanism is suggested for pure ZnO. The surface of the ZnO was modified by methacrylic group to initiate the polymerization by reacting with liquid monomers. The core-shell microgels consist of a polystyrene core and a network made of poly(N-isopropylacrylamide) (PNIPA) cross-linked by N,N'-methylenebisacrylamide which are used as “nanoreactors” for the immobilization of metal nanoparticles like those in [89]. Core-shell materials can be used as plasticizers to improve toughness and stiffness of the matrix material [49]. PMMA(PBA) core-shell nanoparticles can be used to improve the degree of dispersion and compatibility of the phosphors like SrAl(2)O(4) Eu(2+), Dy(3+) in the PVC matrix. The results for PVC plastics characterized by SEM show that the interfacial adhesion was enhanced with filling the polymer/phosphor composite particles, and the compatibility of phosphor with PVC matrix was improved by coating with PMMA(PBA). The luminescent PVC plastics filled with PMMA(PBA)/phosphor composite particles show improved mechanical properties and higher phosphorescence when the filling content was more than 3 phr compared with the unmodified phosphor [90].

4.5. Immunolabeling and Imaging of HeLa Cells. Wang et al. worked on upconversion fluorescent nanoparticles [88]. Upconversion nanoparticles can convert a longer wavelength radiation (e.g., near-infrared, NIR light) into shorter wavelength fluorescence (e.g., visible light) and thus have emerged as a new class of fluorescent probes for biomedical imaging. The cells exhibited bright green UC fluorescence, confirming the attachment of the antibody-UCNP conjugates on the surface of cells (Figure 30). This fact indicates that the UCNPs
with good biocompatibility recognized the targets on the cell membrane due to the antibody conjugation, and the UC fluorescence was strong enough for the cell imaging. The shape and position of the cells in bright field and dark field overlapped very well, showing good specific interactions between the UCNPs and the cells. As drawn in Figure 31, amino-modified NaYF$_4$:Yb, Er UCNPs were first cross-linked with the rabbit anti-CEA8 antibody (Ab), which involves a simple condensation reaction between carboxyl groups of antibody and amino groups on the surfaces of the NPs by the aid of NHS and EDC [88]. Surface modification of gold nanorods using bovine serum albumin (BSA) and polyethyleneimine (PEI) enabled cellular imaging using light scattering from the NRs [91]. Polymeric liposomes-coated superparamagnetic iron oxide nanoparticles (SPIONs) show better T(2)-weighted images than uncoated nanoparticles [92]. In conclusion, polymer-based UCN core-shell nanoparticles have better prospect as fluorescent probe marker and light sensitive materials for therapeutic application.

4.6. Cancer/Tumor Treatment. Hyperthermia therapy with SIONPs (size-dependent iron oxide nanoparticles) involves a local increase in temperature (up to 45°C) when external magnetic field is applied on SIONPs. Such a temperature increase can be lethal for temperature-sensitive cells, such as cancer cells. Recent studies using calorimetry shows that the heating rate depends on the particle size of the SIONPs, consistent with theoretical predictions. This result suggests that the SIONPs should be designed to have optimal particle size with narrow-size distribution for enhanced hyperthermia therapy [93].

5. Conclusions and Future Aspects

There are different types of core-shell structures. Based on these metal, nonmetal, and polymers core-shell nanostructures, they can be categorized in many. The core-shell structures maintain their integrity when redispersed in water. The core-shell structures represent a new class of metal-polymer composite materials that can be used for photonic and biomedical applications exploiting optical properties.

The primary focus in research and technology develop significant contributions to the modern civilization through the invention of the new types of core-shell nanostructure. The core-shell nanostructure, pure polymer nanoparticles, and core-shell hybrid nanoparticles with functional properties can be utilized for the various types of applications and molecular materials, which can gradually “disappear,” that is, degrade to harmless small molecules and fragments, after successful performance of their task in various biomedical and environmental applications. Core-shell and hybrid core-shell nanoparticles will be playing a key role in the design of the medical devices, especially in drug delivery, tissue engineering, and plastic surgery. Researchers are involved more to use the core-shell nanoparticles as structure materials to use them in drug delivery, drug targeting, bioimagination, sensor applications, dielectric properties-based devices, and so forth. These materials show good future aspects in all the fields of biotechnology such as cancer therapy, sustained and targeted drug delivery. Recently, much attention has been focused on metal nanoparticles such as gold, platinum, and palladium because their properties may markedly differ from the ones of the respective bulk metals. Authors of this paper predict that the polymer-based core-shell functional nanoparticles have potential future compared to the inorganic-inorganic nanoparticles in biomedical applications because, polymers are very soft materials, a great number of polymer particles are biocompatible, as well as biodegradable. Polymer shell is easy to modify chemically to develop the functional properties specially for the site-specific target-oriented delivery. On the degradation of the polymers, they only produce C-and-N based components in the living system which is less toxic compared to the inorganic complex formed in the biochemical reactions.

Authors Contribution

K. S. Kumar and V. B. Kumar contributed equally to this paper.

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