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REVIEW

Review on Polymer, Hydrogel and Microgel Metal Nanocomposites: A Facile Nanotechnological Approach

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The incorporation of metal nanoparticles into polymers has resulted in the origination of a new class of materials that have found fascinating interest in biomedical, catalytic, optical and electronic as well as quantum-size domain applications. This review article describes different strategies that have been adopted for the synthesis of metal nanocomposite materials with polymers and gel macromolecules (hydrogels and nanogels).

Keywords: hydrogels; microgels; metal nanoparticles; nanocomposites; transmission electron microscope; antibacterial activity; biomedical applications

1 Introduction

In recent years, colloidal scientists have shifted the focus of the research from micrometer-sized particles to nanometer-sized particles. In particular, studies of inorganic nanostructured materials have received much attention due to their unique optical, electronic and magnetic properties (1, 2) and biocompatible characteristics (3). Due to their small size, large specific surface areas, and tunable physico-chemical properties, they differ significantly from those of bulk materials (4). Because of their vast number of significant applications such as catalysis (5), electronics (6), high density information storage (7), photoluminescence devices (8), targeted drug delivery (9), enzyme immobilization (10) etc. in various disciplines (Figure 1); many efforts have been made for the synthesis of nanoparticles with different functionalities. Most recently, Bajpai et al. (11) have reviewed various methods employed for synthesis of coinage metals based nanostructures. The review explains in detail about various strategies to obtain metal nanoparticles i.e., spherical nanoparticles, nanocubes, nanorods, nanowires, nanodendrons, etc. Polymer-assisted or polymer template synthesis of metal nanoparticles have received substantial attention because of (1) very low concentrations of homopolymer and block copolymers capable of stabilizing nanoparticles effectively by steric stabilization, (2) the polymer containing appropriate functional groups serving as both reducing and stabilizing (capping) agent, (3) possibility of controlling the size, morphology of nanoparticles by varying the polymer/metal salt ratio, and (4) offers to prepare novel metal-polymer nanocomposites.

Hydrogels are constructed by polymer chains either physical or chemical crosslinking process. Due to their soft, rubbery, and high swelling nature in aqueous media they resembles tissues and exhibit stimuli responsive behavior in change of physical/chemical conditions of surrounding fluid such as pH (12), temperature (13), pressure (14), electric field (15), ionic strength (16) etc. The swelling and shrinking properties of hydrogels have been exploited in a number of applications including microfluidic flow (17), muscle-like actuators (18), biosensors (19), drug delivery (20) and switchable electronics (21). The incorporation of metal nanoparticles into hydrogel networks not only results in improved mechanical properties, but also imparts superior physico-chemical properties. For example, polymer containing magnetic nanoparticles shall exhibit magnetic character (22). Similarly, incorporation of silver or gold nanoparticles into a polymer matrix renders excellent

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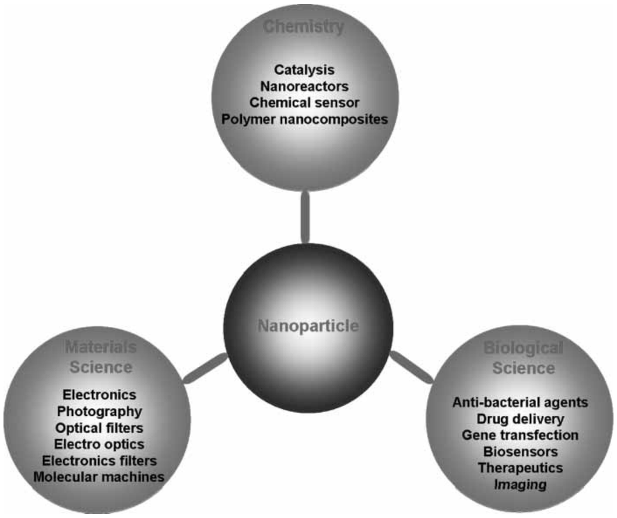

Fig. 1. Significant applications of nanoparticles in various disciplines.

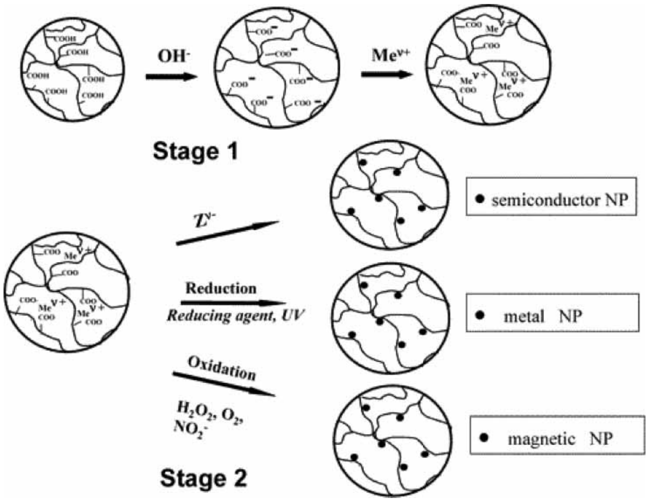

Fig. 2. Effective process showing semiconductor, metal and magnetic nanoparticles formation inside the gel networks Ref. (23).

antimicrobial property. In this way, combination of polymers or hydrogels and metal nanoparticles has resulted in generation of a new class of materials that have a wide spectral range of applications. The key aspect of hydrogel networks, is of course that, it is well suitable for *in situ* and *ex-situ* synthesis of nanoparticles. The free space between the gel networks act as nanoscopic domains or pots that provide excellent growth of the nanoparticles without any aggregations. As shown in Figure 2, gel networks are quite efficient to load or embed metal nanoparticles and/or metal oxides (magnetite) that not only provides stabilization to the particles but also readily prevents the oxidation (23).

In the following sections, we shall review various synthetic aspects of nanoparticle systems that have been discussed and how the hydrogel-nanoparticle systems are superior in terms of their synthetic strategies and overall properties that have been considered to develop new generation of materials for biomedical applications.

2 Natural Polymer–Metal Nanocomposites

Because of non-toxic and biocompatible nature, natural polymers have always been the first choice of material scientists for synthesis of their composites with metals. For example, chitosan, derived from chitin by partial deacetylation is a natural polymer with poly-cationic properties in dilute acidic solutions, enabling electrostatic attraction towards the negatively charged gold nanoparticle surfaces. Addition of aliquots of chitosan solution to gold colloidal solution results in a chitosan capped gold nanoparticles composite system (22), which is confirmed by transmission electron microscope (TEM) analysis. Gold nanoparticles, when embedded in a natural polymer like dextran, have been used as glucose sensor. To immobilize dextran on gold nanoparticles the first step is to modify gold nanoparticles dispersion with 16-mercaptohexadecanoic acid (16-MHDA) in the presence of tween-20 to obtain -COOH groups on the nanoparticles (24). Then, 2-(2-amino-ethoxy) ethanol (AEE) is allowed to react with -COOH groups using carbodiimide chemistry where we can receive -OH functionality through the nanoparticles (surface). These -OH groups are activated by epichlorohydrin and coupled through amino groups of dextran to yield dextran-coated gold nanoparticles (Figure 3).

The fact that chitosan is insoluble above pH 6.0 has offered an excellent way to produce silver oxide nanoparticles (25). In a typical procedure, silver nitrate solution is added dropwise to the chitosan solution prepared in acetic acid, and the addition of sodium hydroxide (NaOH) to this solution results in the formation of black precipitate of silver oxide containing chitosan. The treatment of cotton fabric with the suspension of silver oxide-chitosan nanocomposites imparts excellent antimicrobial property to the fabric. Nanoparticles of ferromagnetic character (e.g. magnetite, maghemite) have been embedded into natural polymers such as chitosan for the purpose of wastewater treatment, and medicinal/biotechnological applications (e.g. separation of microorganisms, extracorporal blood detoxification and targeted drug delivery) (26). The magnetite nanoparticles containing chitosan microspheres are prepared by a suspension crosslinking technique (27). The magnetite nanoparticles are prepared by co-precipitation of ferrous and ferric salts in alkaline medium and the resulting product is mixed into acidified solution of chitosan, followed by addition of the crosslinker, glutaraldehyde. This suspension is now added dropwise into dispersion medium, which is composed of mineral oil, petroleum ether and emulsifier. The magnetic chitosan microspheres, so produced, are collected with the help of magnet. In fact, coating with natural polymers

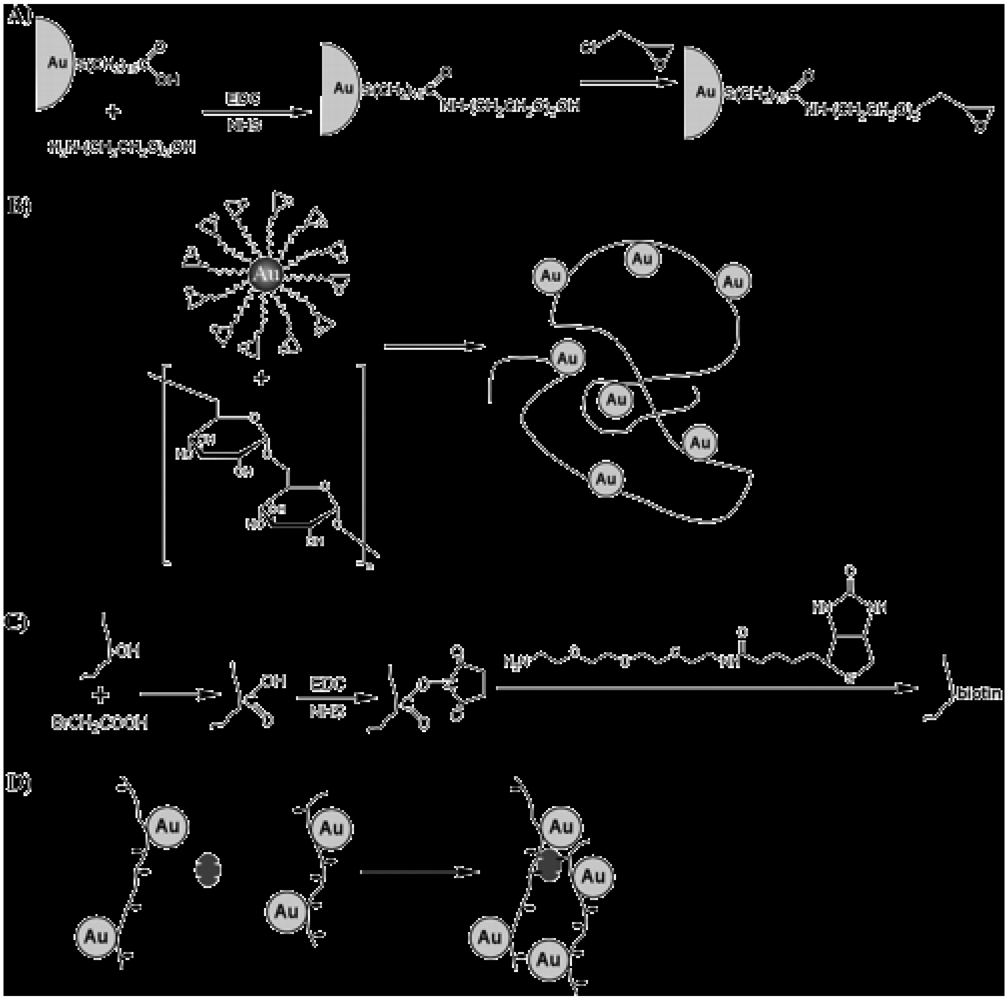

Fig. 3. Synthetic scheme for the preparation of the dextran-coated gold colloids Ref. (24).

ultimately improves the colloidal stability, oxidation resistance, mechanical stability and functionalization characteristics of the composite systems. A few formulations based on super-paramagentic nanoparticles coated by dextran polymer are being approved by the Food and Drugs Administration (FDA, USA) for clinical imaging applications and some of them are under clinic investigations. Recent critical reviews provide outstanding information about the magnetic nanoparticle formulations to a number of clinical applications (28, 29). These reviews suggest that superparamagnetic iron oxide nanoparticles (SPIOs) coated with or incorporated in the biodegradable polymers can serve as contrasting agents as well as targeted delivery applications. Gum arabic or gum acacia (GA) is widely known as natural polysaccharide. Few recent studies indicate that gum acacia is extensively useful as a stabilizer, as well as reducing agent for nanoparticles synthesis (30, 31). Our results support that the acacia polymer can produce 5–10 nm silver nanoparticles with good dispersion property over a long period of time. The reduction capacity of the acacia polymer progresses with higher amounts of polymer.

The catalytic properties of metal nanoparticles have also been exploited by preparing their nanocomposites with natural polymers. It is well known that silver is superior to other metals in electrical properties, antibacterial effects, optical property and oxidation catalysis (32). The catalytic properties of silver nanoparticles have been investigated by preparing silver nanoparticles containing cellulose acetate film (33). Silver nitrate and cellulose acetate are dissolved in 2-methoxy ethanol and the resulting mixture is boiled in a fume hood. The solution is cast on a glass plate and is allowed to stand till the formation of film. The silver ions, present in the film are now reduced with H_2 gas to get a light brown colored transparent film. The TEM analysis reveals that the size of Ag nanoparticles increases with the amount of silver salt used in film formation.

It has been reported that porous natural cellulose fibers could be used as nanoreactors and particle stabilizer for *in situ* synthesis of metal nanoparticles from metal precursor solutions (34). SnO_2 nanotubular materials have been prepared by using a natural cellulose substance (filter paper) as template (35). More recently, Se nanobelts have been synthesized by using a cellulose reducing method at low temperature in solution (36). Cellulose acetate films, containing iron and copper nanoparticles have demonstrated catalytic activity in hydrogenation of olefins, co-oxidation and NO reduction reactions (37). Antibacterial ultrafine cellulose acetate fibers with silver nanoparticles have been reported too (38). Most recently, Liu et al. (39) have successfully incorporated iron oxide nanoparticles in regenerated cellulose film. The nanocomposite film displayed apparently anisotopic magnetic particles. The good alignment of nanostructures within the film appears due to shrinkage of the film while drying. In this section, we have seen that a number of natural polymers used for the synthesis of polymer-metal nanocomposites that have potential applications in different fields.

3 Synthetic Polymers-Metal Nanocomposites

Poly(vinylalcohol), a versatile biocompatible polymer, has widely been used to form nanocomposites with metal nanoparticles (40). For instance, the addition of PVA solution to silver nanoparticles suspension, obtained via citrate reduction, can easily result in formation of yellow transparent poly(vinyl alcohol)-silver (PVA-Ag) nanocomposite film after solvent evaporation (41). Interestingly, the thermal stability of polymer-metal nanocomposites film is found to increase. Gao et al. (42) have synthesized silver nanoparticles by using a two-armed polymer consisting of a crown ether core i.e., [poly(styrene)]-dibenzo-18-crown-6-[poly(styrene)]. Due to the complexing effect of crown ether embedded in the polymer with the Ag^+, some aggregation composed of Ag^+ and polymer are formed. Subsequently, the Ag^+ ions in the aggregation are photochemically reduced by visible light to form Ag nanoparticles. The atomic force microscope (AFM) image of nanoparticles prepared by using different molecular weights of polymers reveal that size of Ag nanoparticles is affected by molecular weight of polymer (Figure 4).

Recently, *in situ* preparation of inorganic nanoparticles in polyelectrolyte multilayer (PEM) film has been reported (43). PEMs, formed from the layer-by-layer adsorption of oppositely charged photoelectrolytes, have attracted much attention over the past decade. For example, PEM, composed of weak polyelctrolytes such as polyacrylic acid (PAA) and poly(allylamine hydrochloride) (PAH) are particularly employed for this purpose (44). The size of the in situ prepared nanoparticles and the overall metal concentration within PAA and PAH multilayer films are systematically controlled by multi-layer processing conditions (45). Figure 5, depicts the *in situ* formation of silver nanoparticles using PAA-PAH multi-layered film (44). Carboxylic acid groups in the PAH/PAA-based multi-layers bind silver cations by ion-exchange with the acid protons. Subsequent reduction forms silver nanoparticles. Since PAA has a pH-dependent degree of ionization, the multiplayer film can be fabricated with different concentration of free acid groups that are available to bind silver cations depending upon the multilayer assembly pH.

Metal nanoparticles have been used as catalysts in a number of chemical reactions that are very important from industrial point of view. However, the use of biometallic catalysts is more significant (46) as combining two metals may provide control over the catalytic activity, selectivity and stability and some combinations may exhibit synergistic effects (47). Moreover, by controlling the type of cluster synthesized one can improve the "catalyst atom economy" (48). Most recently, a facile microwave irradiation method has been reported (49), which accomplishes the crosslinking reaction of PVA with bimetallic systems such as Pt-In, Ag-Pt, Pt-Fe, Cu-Pd have been prepared by reacting the respective metal salts with 3 wt% PVA under microwave irradiation. This procedure is versatile and provides a

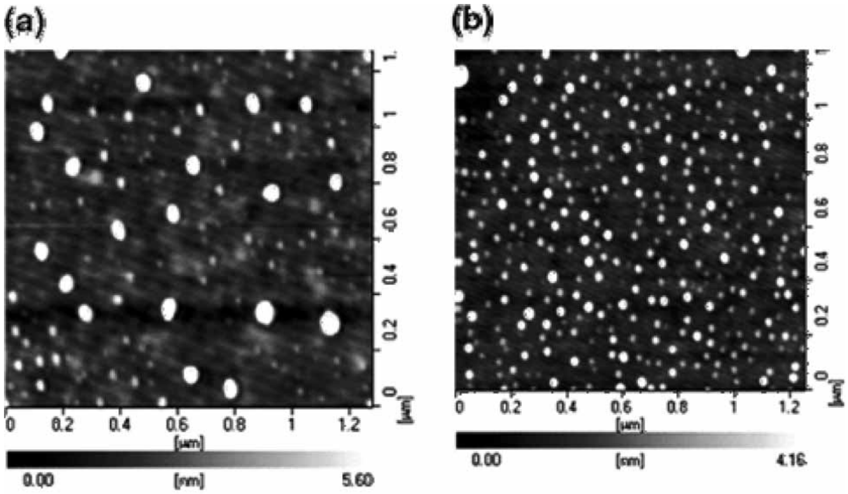

Fig. 4. AFM images of the silver particles synthesized with different molecular weights (MW) of the two-armed polymer with a crown ether core. (a) MW = 5700; (b) MW = 13600. The concentration of silver ions Ag^+ and polymer was 0.1 M and 0.25 wt%, respectively, Ref. (42).

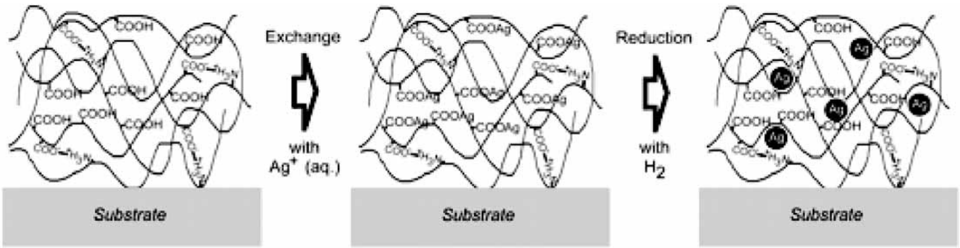

Fig. 5. Schematic illustration of the metal-ion exchange and reduction process flow Ref. (45).

simple route to manufacturing of biometallic nanocomposites with various shapes such as nanosphere, nanodentrides and nanocubes. Figure 6, depicts various metallic and biometallic-crosslinked PVA nanocomposites.

The incorporation of metal nanoparticles into polymer nanofibers can be achieved using either electrospinning the polymer solutions containing metal nanoparticles or by reducing the metal salts or complexes in the elecrospun polymer nanofibers (50). Recently, silver nanoparticles have been incorporated into poly(*N*-vinylpyrrolidone) (PVP) nanofibers using two distinct methods (51). The first method is electrospinning the PVP nanofibers containing Ag nanoparticles directly from the PVP solutions containing the Ag nanoparticles. *N,N*-dimethyl formamide was used as a solvent for PVP as well as reducing agent for Ag^+ ions. In the second method, the PVP containing Ag nanoparticles was used to prepare polymer fiber. The formation of Ag nanoparticles in the PVP fibers was demonstrated by scanning electron microscope (SEM) and TEM analysis (Figure 7).

In addition to nanoparticles of coinage metals, such as silver (Ag), copper (Cu), gold (Au); magnetic nanoparticles have also been exploited to prepare nanocomposites intended to be used in several biomedical applications like magnetic cell separations, drug delivery and diagnostics (52). Nanocomposite materials based on synthetic polymers such as poly(styrene) (PS) (53), poly(acrylic acid) (PAA) (54), and poly(*N*-isopropylacrylamide) (PNIPAM) (55) have been reported earlier. Although biopolymers based magnetic composite particles are also reported but synthetic polymers are less expensive. Recently, polyethylene (PE) magnetic nanoparticles have been synthesized by solvent: nonsolvent and temperature induced crystallization along with ultrasonication (56). Low molecular weight polyethylene wax and maghemite were used for forming the composite particles. Transmission electron micrograph obtained for particles formed with decalin:tetraglyme (1:1 ratio) showed that the particles had diameters in the 50–500 nm range with two types of distinct morphology (Figure 8). This clearly illustrates both elliptical and spherical morphologies were obtained. In most of the biomedical applications, magnetic nanoparticles have been embedded in a non-magnetic matrix to avoid aggregation and sedimentation of particles as well as to endow them with particular surface properties. This is usually done with silica as it screens the magnetic dipolar attraction between nanoparticles and the most important fact is that the silica layer provides a chemically inert surface for magnetic nanoparticles in biological systems. More recently, w/o microemulsions method has been proposed for preparing silica-coated magnetic nanoparticles (57), which employs non-ionic surfactant for formation of inverse microemulsion. Out of various methods proposed, sol-gel method have been adopted more widely for preparing silica-coated magnetic nanoparticles as this involves relatively mild reaction conditions, low-cost and surfactant free. Ohmor and Matijevic (58) prepared spindle type haemetite of about 400 nm and coated them directly with silica through the sol-gel process. Using surfactant-stabilized magnetic nanoparticles as seeds, Lu et al. (59) prepared

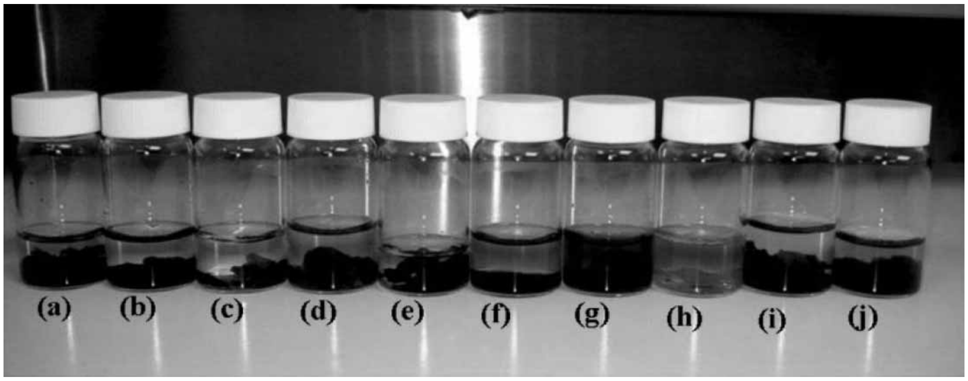

Fig. 6. Photographic image of crosslinked PVA with various metallic and bimetallic systems: (a) Pt; (b) Pt-In; (c) Ag-Pt; (d) Cu; (e) Pt-Fe; (f) Pt with higher concentration ratio; (g) Cu-Pd; (h) In; (i) Pt-Pd and (j) Pd-Fe Ref. (49).

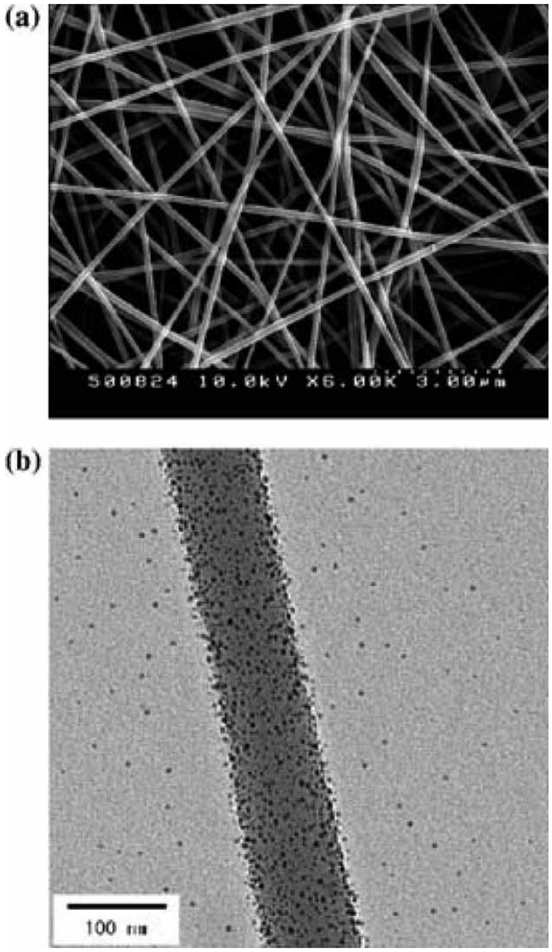

Fig. 7. (a) SEM image and (b) TEM image of a PVA nanofiber electrospun with 47 wt.% PVP solutions containing 15 wt.% of $AgNO_3$ 1 h after preparation Ref. (51).

silica-coated magnetite particles via the sol-gel approach. Most recently, magnetite nanoparticles, prepared by co-precipitation of ferrous and ferric salts, have been coated with silica in basic alcohol/water mixture by using magnetic fluid as seeds (60). TEM image and electron diffraction pattern of the synthesized magnetite nanoparticles show that most of the particles are quasi-spherical with an average diameter of 15 nm. Magnetite particles obtained from various alcohols showed different morphologies as shown in Figure 9.

In fact, synthesis of nanoparticles with a controllable size and size distribution still remains a great challenge, particularly in the aspect of small sizes (<5 nm). An effective economic scalable and non-toxic monodisperse synthesis of magnetite nanoparticles is highly desirable for potential biomedical applications. Monosize PVP coated magnetite particles (5 nm) have been synthesized by one-potpolyol synthesis (61). The results from the structural characterization and magnetic measurements revealed higher crystallinity. These monodispersed Fe_3O_4 nanoparticles with tailorable size and tunable magnetic properties are promising for biomedical applications such as MRI and biosensors.

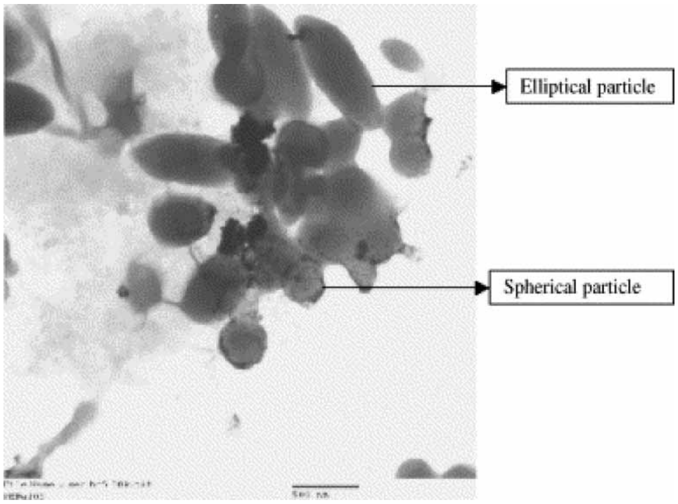

Fig. 8. TEM of particles in decaline/tetraglime system at 80% amplitude of ultrasonication Ref. (56).

4 Hydrogels Assisted Formation of Nanocomposites

Continuous research efforts by material scientists and polymer chemists has revealed that polymeric hydrogel/microgel/nanogel networks can also act as a template for the synthesis of smaller sized nanoparticles with fair stability (62). Indeed, the synthesized products using these approaches have worked

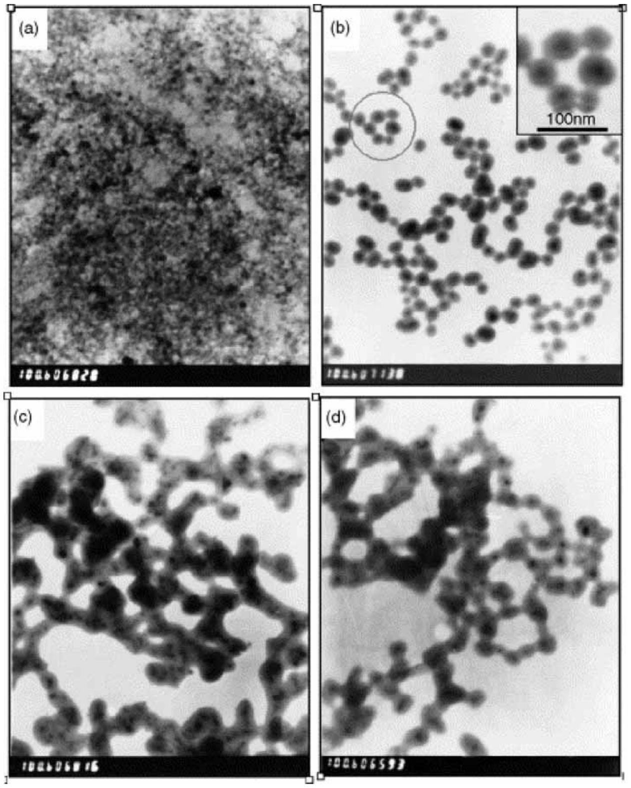

Fig. 9. TEM images of silica-coated magnetite particles obtained in (a) methanol, (b) ethanol, (c) isopropanol, and (d) n-propanol Ref. (60).

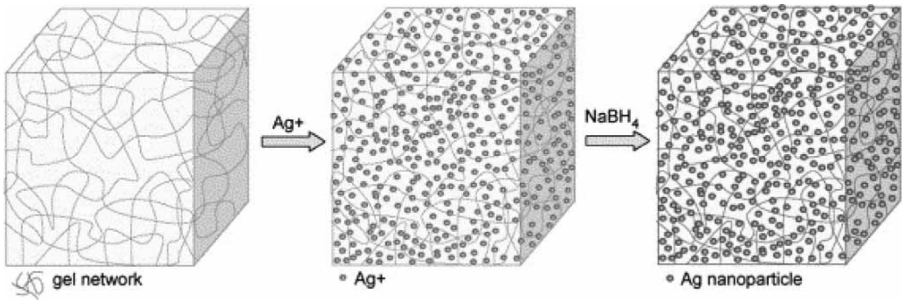

Fig. 10. Silver nanoparticles formation inside the hydrogel Ref. (67).

out as a new class of materials that have a wide range of applications, in chemistry, biomedical engineering and other related fields. Free space available between the crosslinked networks, can act as nanoreactor to the nucleation and growth of nanoparticles. Recently, silver nanoparticles deposition into microgels such as poly [(*N*-isopropylacrylamide)-*co*-(acrylic acid)-*co*-(2-hydroxy ethylacrylate)], poly[(vinyl caprolactum-*co*-aceto acetoxy methacrylate)] hydrogel system has been reported (63, 64). In a typical approach, Au nanoparticles have been stabilized in the hydrogel network through thiol-ester bonds by employing *N,N′*-cystamine bisacrylamide (CBA) as a crosslinking agent (65). Looking into the wide spectral antimicrobial activity of silver nanoparticles; efforts have been made to immobilize them in hydrogel network to produce composite materials with antibacterial surface. Poly(*N*-vinyl-2-pyrrolidone)/Ag nanoparticles composite have been applied as bacteriacide in infected burns and purulent wounds (66). Murali Mohan et al. (67) successfully developed a poly(*N*-isopropyl acrylamide-*co*-sodium acrylate) hydrogel network for synthesis of small silver nanoparticles. In this novel approach, gels are allowed to swell completely in distilled water, and then placed in $AgNO_3$ solution for Ag^+ ions to enter inside

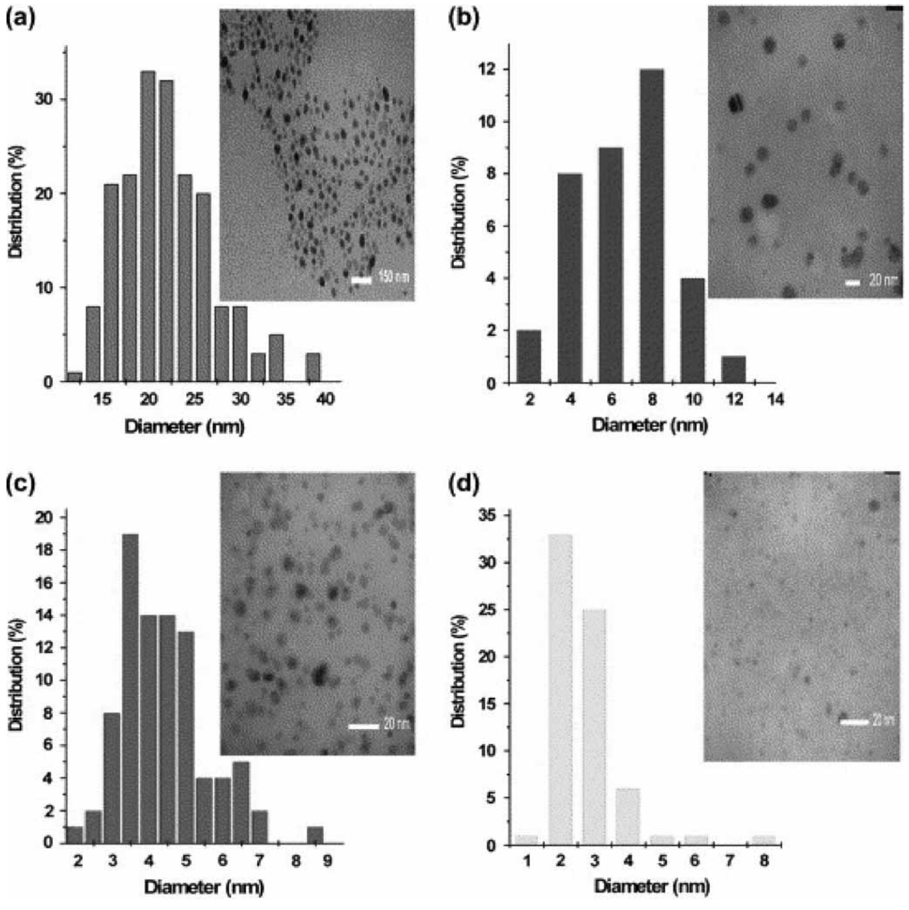

Fig. 11. TEM and histograms of Ag nanoparticles synthesized using (a) 4.50, (b) 6.00, (c) 8.50, and (d) 13.00 mM MBA-crosslinked hydrogels, respectively Ref. (67).

the swollen network and finally, transferred into solution of sodium borohydride ($NaBH_4$) for reduction of silver ions to silver nanocomposite. A schematic representation of silver nanoparticles formation inside the gel networks has been presented in Figure 10. It was observed that the diameter of the Ag nanoparticles decreased with an increase in degree of crosslinking of hydrogels (Figure 11). These hydrogel-silver nanohybrids showed fair antibacterial activity. The other synthetic methods for metal nanoparticle immobilized hydrogel composites involve the preparation of nanoparticles and hydrogels separately, and then physically combining the two, or mixing pre-made nanoparticles with a hydrogel precursor followed by gelation (19). Pardo-Yissar et al. (68) prepared crosslinked polyacrylamide (PAM) hydrogels on Au wire electrodes by the elecropolymerization of acrylamide monomer in the presence of $ZnCl_2$ and *N,N″*-methylene bisacrylamide (MBA). Gold nanoparticles were introduced into the hydrogels by a breathing mechanism, whereby the shrunken hydrogel was allowed to swell in an aqueous Au nanoparticle solution and the structure was then re-shrunk in acetone. Likewise, radical polymerization of acrylamide at 70°C in an aqueous dispersion containing pre-made γ-Fe_2O_3 particles using polyoxometalate (POM) results in the formation of ferrogels (69). In a recently developed approach (70), solution state polymerization of monomer acrylamide into PAM hydrogel is carried out in aqueous medium containing Ag^+ ions. The Ag^+ ions functionalized PAM hydrogel matrix is then hydrolyzed to yield colloidal Ag nanoparticles within the hydrogel network. Thermosensitive PNIPAM has also been exploited to produce hydrogel coated gold nanoparticles (71) by surfactant free emulsion polymerization (SFEP) method. The structural and optical properties of this new class of hybrid nanoparticles consisting of small gold core (~60 nm in diameter) coated with a biocompatible hydrogel polymer shell varying from 20 to 90 nm in thickness, have been studied. The attractive feature of these nanoparticles derives from the fact that the hydrogel can be thermally activated by exposure to light via exploitation of the strong plasmon absorption of the gold nanoparticle core. The bare and hydrogel coated Au particles are clearly visible in the FE-SEM micrographs (Figure 12).

It is well known that the polyacrylamide hydrogels adopt highly swollen structure in water, but undergo phase transition to a collapsed state on exposure to less polar solvent as acetone (72). This property has been exploited to introduce metal and semiconductor nanoparticles for the fabrication of a nanoparticle/hydrogel composite with interesting solvent switchable electrical and photoelectrochemical properties on macroscopic Au electrodes (69). A different strategy has been extended to a hydrogel-nanowire-assisted technique to obtain highly dispersed nanoparticles in the channels of porous anodic aluminium oxide films as well as in the hydrogel nanowires (73). The Au particles are introduced into PAM when a shrunken PAM nanowire array is allowed to swell in an aqueous solution of Au nanoparticles. Upon the next breathing out cycle, the nanoparticles remain fixed inside the PAM probably due to physical entanglement of the polymer. TEM investigation provides direct observation of the morphology and distribution of an Au nanoparticle in the Au/PAM composite nanowires and reveals that a number of Au nanoparticles in the PAM nanowire increases with an increase in the number of breathing cycles, Figure 13 illustrates the formation of nanoparticles on the nanowires.

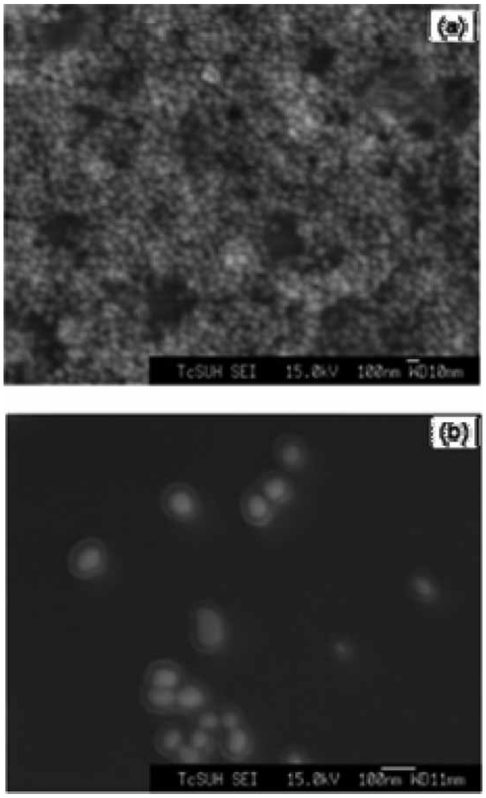

Fig. 12. FE-SEM micrographs of (a) bare gold nanoparticles (60 nm) and (b) hydrogel-coated 60 nm gold nanoparticles with overall diameter 100 nm Ref. (71).

Temperature is an important triggering signal for stimulating phase transition in hydrogels (74). Nanoparticles/hydrogel composites provide unique materials for controllable electronic properties. Phase transition of these composite materials may

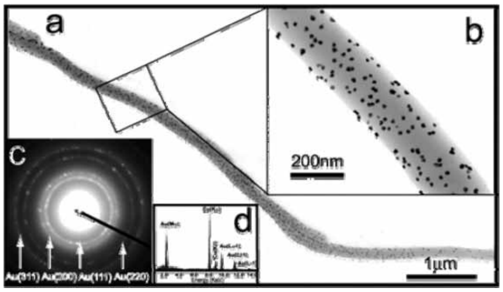

Fig. 13. (a) Typical TEM image of Au-nanoparticle-containing PAM nanowires, (b) High-magnification TEM image from the framed area in (a), (c) ED pattern, and (d) EDAX profile of the composite nanowire Ref. (73).

be exploited as a means of controlling interparticle distances in the polymer matrices and therefore one may envisage tunable electronic and/or optical properties of them (72). The Au nanoparticles have been incorporated into PNIPAM hydrogel by using cyclic swelling/shrinking thermal transition of hydrogels (21). The presence of nanoparticles in the polymer decreases the resistance of the shrunken polymer interface and also decreases the electron transfer resistance for redox transformation at the Au-nanopartcle/poly(NIPAM)-functionalized electrode.

Coating of superparamagnetic nanoparticles with biocompatible polymer is a promising approach to generate core-corona particles for biomedical applications (75). The polymer such as polyethylene glycol (PEG) has proved to be effective in suppressing the opsonisation process (76) due to its ability to prevent protein adsorption. This feature is particularly interesting for particles that are intended for intravenous injections, because their half-life in blood circulation will be extended. This is usually done by 'PEG-ylation' of surface of magnetic nanoparticles by grafting process (77). Alternatively, the surface of magnetic nanoparticles, e.g., maghemite can also be coated by free radical copolymerization of methacrylate-functionalized PEG macromonomers and surface immobilized methacrylate groups. Copolymerization reactions at the surface of inorganic particles have previously been reported. Recently, methacrylate-functionalized poly(ethylene glycol) macromonomer has been copolymerized at the surface of methacrylate-derivatized maghemite nanoparticles. After silylation of magnetic core with methacryloxypropyl-trimethoxysilane, two grafting procedures, based on either a direct copolymerization reaction in water or an inverse emulsion polymerization were compared (78). It is reported that the latter process greatly increases the amount of surface immobilized polymer, up to 8 g/g maghemite. The polymer is strongly retained on the surface and its amount remains unchanged even after stirring the nanoparticles for 2 h in boiling water.

For the synthesis of nanoparticles within the polymer matrix, there must be nanoscale reactors to generate nanoparticles within the polymer matrix. These reactors are generally formed by microphase-separation between hydrophilic and hydrophobic segments in amphiphilic polymer chains (79). The amphiphilic polyurethane network, synthesized through coalescence polymerization of amphiphilic urethane acrylate (AUA) non-ionomer emulsions possess highly microphase separated structures which have been used to disperse magnetic nanoparticles (80). Magnetic nanocomposites are also prepared using amphiphilic urethane acrylate non-ionomer (UAN) precursor chain. The UAN gel films, having the same UNA content, were prepared under different synthesis conditions. As a consequence, magnetic composites, prepared with these films, exhibited different size and morphology of nanoparticles (81). The AFM analysis revealed that UAN gel film (UANH) synthesized via UAN/water mixture had the highly microphase separated structure, whereas the gel film synthesized via UV-curing (UANV) or polymerization of UAN/DMAc mixture (UAND) had relatively homogeneous structure (Figure 15). Moreover, the largest ellipsoidal particles were formed in UNAH gel films and the smallest ellipsoidal particles and rod-shaped particles were made up in UANV gel and UAND gel films. Magnetic particles can be tailored using functionalized natural and synthetic polymers to impart surface reactivity. Most recently, Shamim et al. (82) have modified Fe_3O_4 nanoparticles using thiodigycolic acid as the primary surfactant and 4-vinylaniline as secondary surfactant. These double surfactants coated particles were used for seed polymerization using NIPAM as the main monomer. The particles so obtained were single domain magnetic dipole, which shows no preferred directional ordering in the absence of applied magnetic field. A schematic representation of magnetic nanoparticle coated PNIPAM system shown in Figure 14. The size, structure and magnetic properties of resulting magnetite/poly (*N*-isopropylacrylamide) nanocomposites were characterized by TEM, x-ray diffraction (XRD) and VSM.

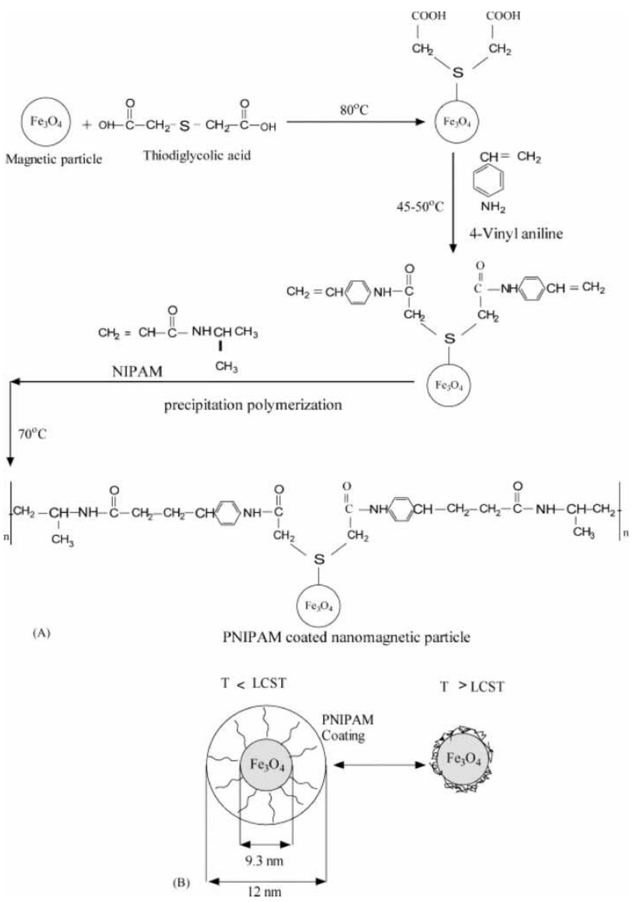

Fig. 14. Preparation of thermosensitive (PNIPAM) coated nanomagnetic particles Ref. (82).

5 Microgel Containing Nanoparticles

Microgels are nanoscopic objects in themselves, in that they are crosslinked macromolecules with a globular shape, of a

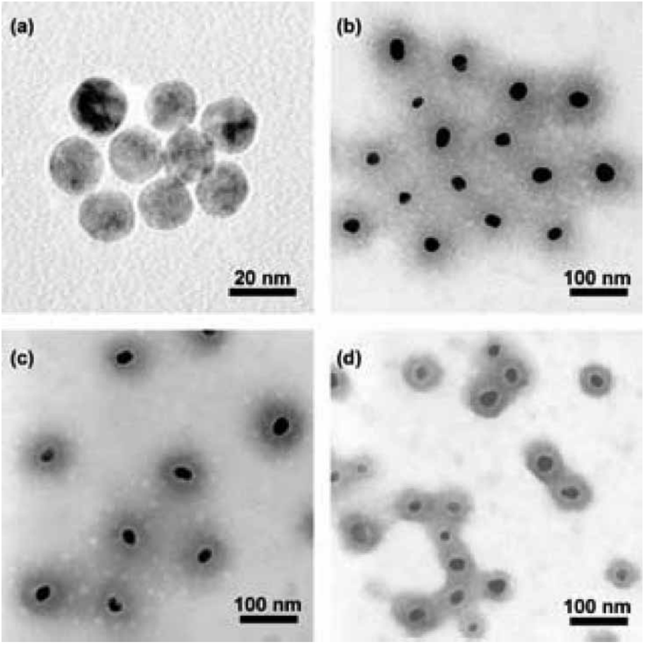

Fig. 15. TEM images of (a) AuNPs, (b) brush-type AuNP/PNIPAAm hybrids, (c) cross-linked AuNP/PNIPAM hybrids (5 mol% crosslinker), and (d) crosslinked AuNP/PNIPAM hybrids (10 mol% crosslinker) Ref. (93).

size 50–100 nm. Such macromolecules can be prepared by slight modification of standard polymerization techniques. Microgels can be tailored to bear pendant functional groups able to interact with metal ions that are precursors of metal nanoclusters. In this way, microgels can be loaded with metal precursors, which are subsequently reduced inside the microgel to yield metal particles. Antonietti and coworkers (83) were the first to employ microgels as 'exotemplates' for the preparation of soluble metal nanoparticles. They prepared polystyrene based microgels by microemulsion polymerization and sulfonated them by concentrated sulfuric acid. The microgels were soluble in water and could be loaded with metal ions, which were subsequently reduced thus forming microgel stabilized metal nanoclusters. Recently, poly(aminoethyl methacrylate hydrochloride), covalently bound to polystyrene core, have effectively immobilized aurate ions by counter ion exchange and complexation (84).The immobilized ions were then reduced to yield a 3 nm sized particle. Using a similar technique, Pt nanoparticles (ca. 2 nm in diameter) have been synthesized in spherical polyelectrolyte brushes consisting of a solid core of polystyrene onto which long chains of poly(2-methylpropenoyloxyethy) trimethyl ammonium chloride have been grafted (85). Similarly, the surface of poly(styrene sulfonate)-doped polyaniline/poly(allylamine hydrochloride) capsules has also been used for photoreduction of silver ions to yield well-defined microgel particles containing silver nanoparticles (86). The polystyrene core, grafted with thermosensitive poly[*N*-isopropylacrylamide] shell has also been exploited for the incorporation of Ag nanopartcles (87). This system has lead to the formation of a smart catalyst system. The catalytic activity of hybrid Ag nanoparticles for the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ can be tuned by temperature. Kawaguchi et al. (88) have reported novel thermosensitive hybrid co-shell particles via *in situ* gold nanoparticle formation using core-shell particles as template. The authors succeeded in the preparation of gold nanoparticles only at the interface region between the core, which had a reactive site to bind metal ions, and the thermoresponsive shell. Recently, poly[vinylcaprolactum-*co*-(aceto acetoxtethyl methacrylate)] (VCL/AAEM) microgels, functionalized with Ag nanoparticles have been studied for their physio-chemical properties (64). Incorporation of silver nanoparticles content results in the decrease of size of microgel particles. Moreover, the thermo responsiveness also decreases with AgNP content. Such hybrid microgels are excellent catalytic systems where AgNP are separated from each other within the microgel network, thus providing an extremely large surface area. Localization of AgNP in microgel template allows easy separation from the reaction mixture.

The functional groups, present in the microgel structure play a significant role in controlling the growth of nanoparticles. In a study, hybrid fluorescent microgels were prepared via photoactivated synthesis of Ag nanoparticles in PNIPAM microgels (89). It was found that the presence of carboxylic groups in the microgel structure allowed the effective uptake of Ag^+ ions and controlled nucleation and growth of small nanoclusters. These florescent microgels are attractive candidates for the fabrication colloidal crystals for sensor applications. Apart from the presence of functional groups, the degree of crosslinking of the microgel also affects the size of the nanoparticles. For example, the size of the palladium (Pd) and platinum nanoparticles in microgels can be varied by a slight variation in the degree of crosslinking of microgels prepared by copolymerization of methylmethacrylate (MMA), ethylene dimethacrylate (EDMA) with small amount of *N,N'*-diethylamminoethyl methacrylate (90). The average size of Pd nanoclusture was decreased from 9 to

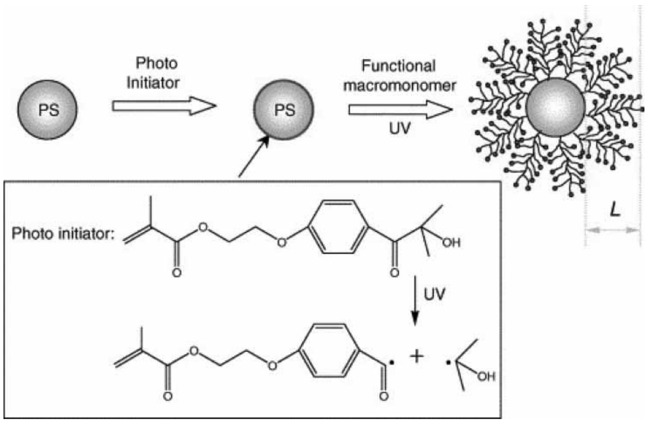

Fig. 16. Schematic representation of the the 'Nano-tree' type PS-PEGMA functional microgels Ref. (95).

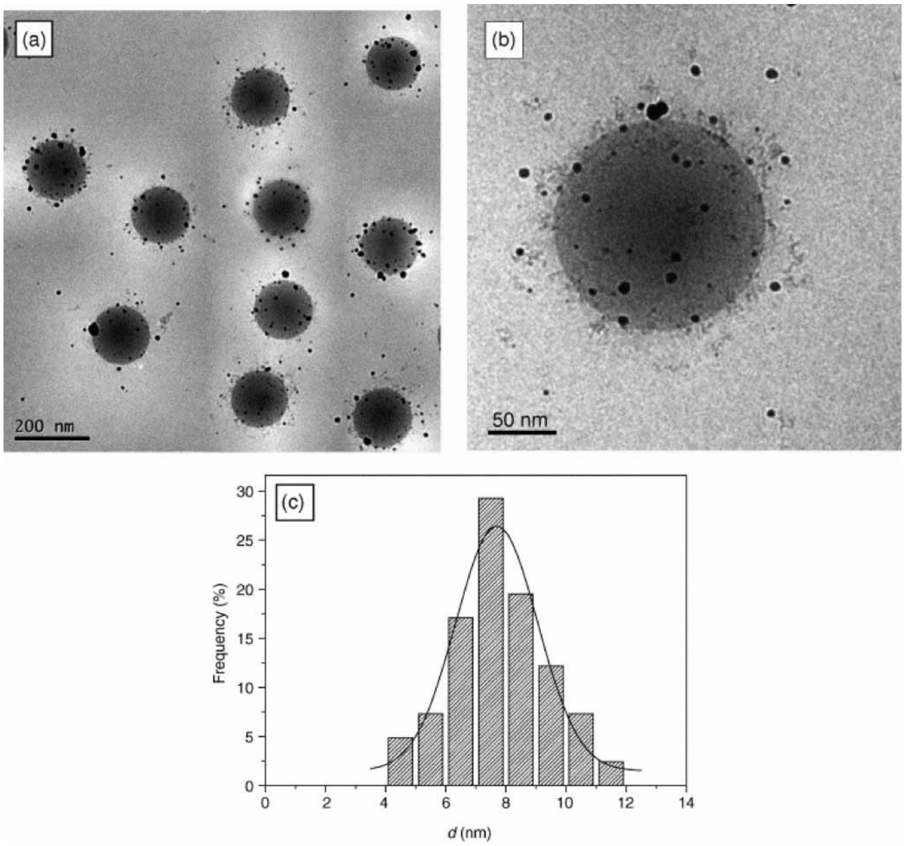

Fig. 17. (a–b) Cryo-TEM images for PS-PEGMA-Ag composite particles and (c) particle size distribution histogram of Ag particles evaluated from the cryo-TEM image Ref. (95).

3 nm by increasing the concentration of crosslinker (EDMA) from 5 to 20 mol%. The poly(*N,N′*-dimethylacrylamide) microgels have been loaded with Pt and Pd ions followed by reduction with NaHBEt$_3$ (23). The relatively weaker interactions of *N,N′*-dialkylamide groups with the surface of metal nanoparticles through carbonyl oxygen enhance the stability. The Pd nanoculsters were successfully treated as a catalyst in Suzuki coupling of aryl bromide and chloride with phenylboric acid.

The entrapment of magnetic nanoparticles into porous microgels has been reported by various workers. The PNIPAM microgels, with diameter 200 to 600 nm, containing acrylic acid and 2-hydroxyethyl acrylate units for better integration of magnetic nanoparticles, have been synthesized recently (91). The particles have average diameter below 12 nm, possess excellent magnetic properties and preserve thermo-responsiveness of microgels. The free-radical polymerization of acrylamide and MBA in inverse emulsion in the presence of maghemite nanoparticles has also resulted in the formation of hydrophilic magnetic microgels (92). The loading of maghemite nanoparticles depends upon the degree of crosslinking of microgels. The size of the microgels has also been reported to depend upon the nature of the solvent used.

The surface initiated atom transform radical polymerization (ATRP) method is also successful in obtaining the nanoparticles covered by polymeric chains (core-shell nanostructures) (93). In such a process, the disulfide containing an ATRP initiator was attached to the surface of the nanoparticles (gold nanoparticles) and the thermosensitive monomer, NIPAM was polymerized using a crosslinker, ethylene diacrylate, in aqueous media at room temperature. The formed core-shell morphological thermosensitive nanohydrbids i.e., crosslinked AuNP/PNIPAAm hybrids were characterized by Fourier-transform infrared spectroscopy, transmission electron microscopy and variable temperature dynamic light scattering experiments. Figure 15 shows the TEM images of gold and gold-thermosensitive nanohybrides. These kinds of nanosystems exhibit longer stability over a period of time.

In another most recent report (94, 95), the use of microgel particles containing functional monomers, which are capable to hold the generated metal nanoparticles in their structures (Figure 16), is demonstrated. Figure 17 illustrates the TEM image of the nanoparticles throughout the functionality on the microgels. In more detail, nanocomposite hydrogels are composed by 'nano-tree' type polymer brush particles and metal nanoparticles. Nano-tree type polymer particles are chemically entrapped in a poly(vinyl alcohol) (PVA) matrix by means of the disulfone reaction. This reaction allows crosslinking between the nano-tree brush particles within the PVA hydrogel. The resulting composite hydrogels are used as a template for the deposition of silver nanoparticles. A few microgel systems composed of cholesterol-pullulan and modified with amino groups are well advanced materials. (96, 97). The combination of these hybrid nanogels particles and quantum dots or metal nanoparticles is quite effective in delivering them at human cells bio-imaging applications.

6 Conclusions

Gel family (hydrogels and microgels) and metal nanoparticles are two distinguished classes of materials that have attracted much attention in recent years due to their ideal properties in various fields including chemistry, and materials and biological sciences. The combination of these two materials are not extensively studied so for. Therefore, this critical review serves the purpose of finding numerous approaches to make gel-metal nanoparticles composite or hybrid materials. In fact, metal colloidal particles or quantum dots loaded/incorporated/encapsulated in polymer or nanogel network structures submit exclusive rheological, optical, magnetic or electrical properties that are highly suitable for different applications, especially of therapeutic and diagnostic applications in biomedical fields.

7 References

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