Review

Polymer-noble metal nanocomposites: Review

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Polymer-noble metal nanocomposites have been extensively investigated due to their potential ability to provide materials with novel mechanical, electronic or chemical behaviour for technological applications. Many preparative procedures have been proposed and detailed characterizations have been carried out on conducting polymer-noble metal nanocomposites; thanks to the rapid improvement in analytical techniques on surface and nanoscale materials. This review focuses on the preparation, characterization of polymer-noble metal nanocomposites and some potential areas for applications such as sensors, batteries (fuel cells) and capacitors.

Key words: Polymer, noble metal, nanocomposites, preparation, characterization.

INTRODUCTION

The future progress in the field of science, technology, engineering, medicine etc will depend and be concerned with new knowledge-based nanostructured materials. Nanocomposites are a new class of materials in which the dimension of one of the dispersed particles occurred at the nanometer scale thus, in polymer-metal nanocomposites, metal particles are dispersed in the polymer matrix at the nanometer scale. These materials are of current interest because of their multi-functionality, ease of process-ability, potential for large-scale manufacturing, significantly lighter than metals, ease of synthesis when compared to the oxide/noble metal multi-layers (Gass et al., 2006; Lee et al., 2003; Avasthi et al., 2007).

By combining properties from the inorganic and the polymer components, they offer new performance hence, making them interesting functional materials with the possibility of novel mechanical, electronic or chemical behaviour (Zhu and Zhu, 2006; Corbierre et al., 2005; Sih and Wolf, 2005; Mayer, 2001). Small changes of the configuration of the composite concerning the metal

amount as well as the size and the shape of the nanoparticles can lead to dramatic changes in the electrical and optical properties of the material (Schurmann et al., 2005; Son et al., 2006). Therefore, in other to obtain nanocomposites for technological applications, the size, the shape and the amount of metal must be carefully controlled. One approach that had been employed by several groups for the control of size and shape of metal nanoparticles is ordered block copolymerization (Cole et al., 1999; Selvan et al., 1999), while the use of dendrimers had been employed by many research groups (Balogh et al., 1999). However, the most efficient method for particle size control is by sol deposition or zeolites where the metal component is introduced and retained within the pores (Hatchett and Josowicz, 2008). The nanoparticles exhibit unique properties which differ from their bulk materials, owing to the quantum size effects and the large number of unsaturated surface atoms. The polymeric matrices which are considered as good host materials for metal nanoparticles, provide additional qualities, such as the process-ability, solubility or thermal stability of the systems (Naka et al., 2004). In this way, nanocomposite materials possessing novel catalytic, conductive, magnetic or optical properties can be obtained (Balan and Burget, 2006; Huang et al., 2004). To maximize the excellent properties of polymer-metal nanocomposites, homogeneous dispersion of metal nanoparticles in the polymer matrix is required. This is a key challenge due to

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Abbreviations: PEDOT, Poly(3,4 ethylenedioxythiophene); **PSS,** poly styrene sulfonate; **PNVC,** poly(N-vinyl carbazole; **PANI,** polyaniline**; SERS,** surface-enhanced Raman spectroscopy.

their easy aggregation arising from their high surface free energy (Lee et al., 2006). In the design of nanocomposites, one must consider the properties of the polymer matrix as well as the stability of the nanoparticles and more importantly, the prevention of particle aggregation (Sangermano et al., 2007). Different approaches have been used to prepare polymer-metal nanocomposites. In the older approach (*ex-situ*), polymerization of organic monomer and the formation of metal nanoparticles are performed separately, and polymer matrix and metal nanoparticles are physically or mechanically mixed to form polymer-metal nanocomposites. The metal nanoparticles are not homogeneously dispersed in the polymer matrix (Zhu et al., 1998). Nowadays, the *in-situ* synthesis is employed in the preparation of polymer-metal nanocomposites. This method is based on the reduction of metal ions that are dispersed in polymer matrices or the polymerization of the monomer dispersed with metal nanoparticles (Zhang et al., 2004). Simultaneous polymerization-reduction approach is also another version of the *in-situ* synthesis. The polymerization of the organic monomers is carried out in parallel with the formation of the metal nanoparticles. However, successful synthesis of high performance composite depends largely on well-defined and control of particle size, content, dispersity and structure through the use of different physical and chemical methods (Zhang and Han, 2003).

A succinct survey of literature showed that there are two main kinds of nanosized composites of polymers with metals: (1) Metal core nanoparticles covered with a polymer shell, (2) Metal nanoparticles embedded into polymer matrix (Kang et al., 2005). Uniformly dispersed nanoparticles in a polymer matrix find application in the fabrication of functional materials with useful electrical (Delamarche et al., 2003; Luigi, 2005), catalytic (Demir et al., 2004; Zhong et al., 2004), magnetic (Delamarche et al., 2003; Baranauskas et al., 2005), optical (Porel et al., 2005; Lu et al., 2005) or sensory (Thurn-Albrecht et al., 2000) properties.

CONDUCTING POLYMERS

Polymers are traditionally regarded as electrical insulators and any conduction of electricity is regarded as an undesirable property. However, a new class of polymers known as intrinsically conducting polymers or electroactive conjugated polymers has emerged during the past two decades (Gerard et al., 2002; Malinauskas et al., 2005). These novel materials with interesting and unanticipated properties have attracted the whole scientific community including polymer and synthetic chemists, material scientists, organic chemists as well as theoretical and experimental physicists (Skotheim, 1986). They exhibit interesting electrical and optical properties previously found only in inorganic systems which include

good tunable conductivity, electrochromism, electroluminescence and chemosensitivity and this has led to the wide use of polymer electrolytes and polyelectrolytes in electrochemical systems, optical devices and sensors, rechargeable batteries and anticorrosion prime layers (Inzelt et al., 2000; Gerard et al., 2002; Suri et al., 2002; Sih and Wolf, 2005). The higher value of electrical conductivity of this class of organic compounds is different from that of metallic conductors because current is not caused by flow of electrons (He, 2004) but rather, conductivity is as a result of extended π-conjugated electron system present in their molecules and hence, the name "synthetic metals" (Gerard et al., 2002). These materials are by far lighter than metals and easy to fabricate into various forms. However, they exhibit not only limited conductivity when compared to metals, but also insoluble in common organic solvents, poor process-ability, poor mechanical properties, chemical sensitivity to oxygen, instability upon ultraviolet irradiation, reduced conductivity with increased pH, heat and other environmental conditions (Suri et al., 2002; Ballav and Biswas, 2003; Lee at al., 2003; Hatchett and Josowicz, 2008; Beyene et al., 2010); all these limit their applications.

The first conducting polymer, polythiazyl $(SN)_x$, was discovered in 1975, which possesses metallic conductivity and become superconductor at 0.29 K (Greene et al., 1975). The idea of using polymers based on their electrical conducting properties actually emerged in 1977 with the findings of Shirakawa et al. (1977) that the iodine doped trans-polyacetylene, $(CH)x$, exhibit conductivity of 10^3 S/cm. Since then, an active interest in synthesizing other organic polymers possessing this property has been initiated. As a result, other conducting polymers such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), polyfuran (PFu), poly(phenylene) and polycarbazole have been synthesized by chemical and electrochemical routes (Diaz and Bargon, 1986; Shirakawa, 1998) and studied extensively because of their process-ability and relative stability (Taylan et al., 2010). The most studied conducting polymers are shown in Figure 1. The conductivity and optical properties of these polymers have been tuned via chemical modification (Saxena and Malhotra, 2003; Beyene et al., 2010), by various degree and nature of doping. The resonance-stabilized structure of the polymers makes the incorporation of ions, nanoparticles, metal oxides, nanowires of metals, carbon or molecular species such as metallophthalocyanines or biologically active components such as enzymes, antibodies and antigens possible, giving rise to composites with different and enhanced physical and chemical properties (Hatchett and Josowicz, 2008).

Many of these polymers have sufficiently high reducing power with respect to some metal ions such as gold, silver, platinum and copper and can reduce these ions forming clusters or small particles within the porous
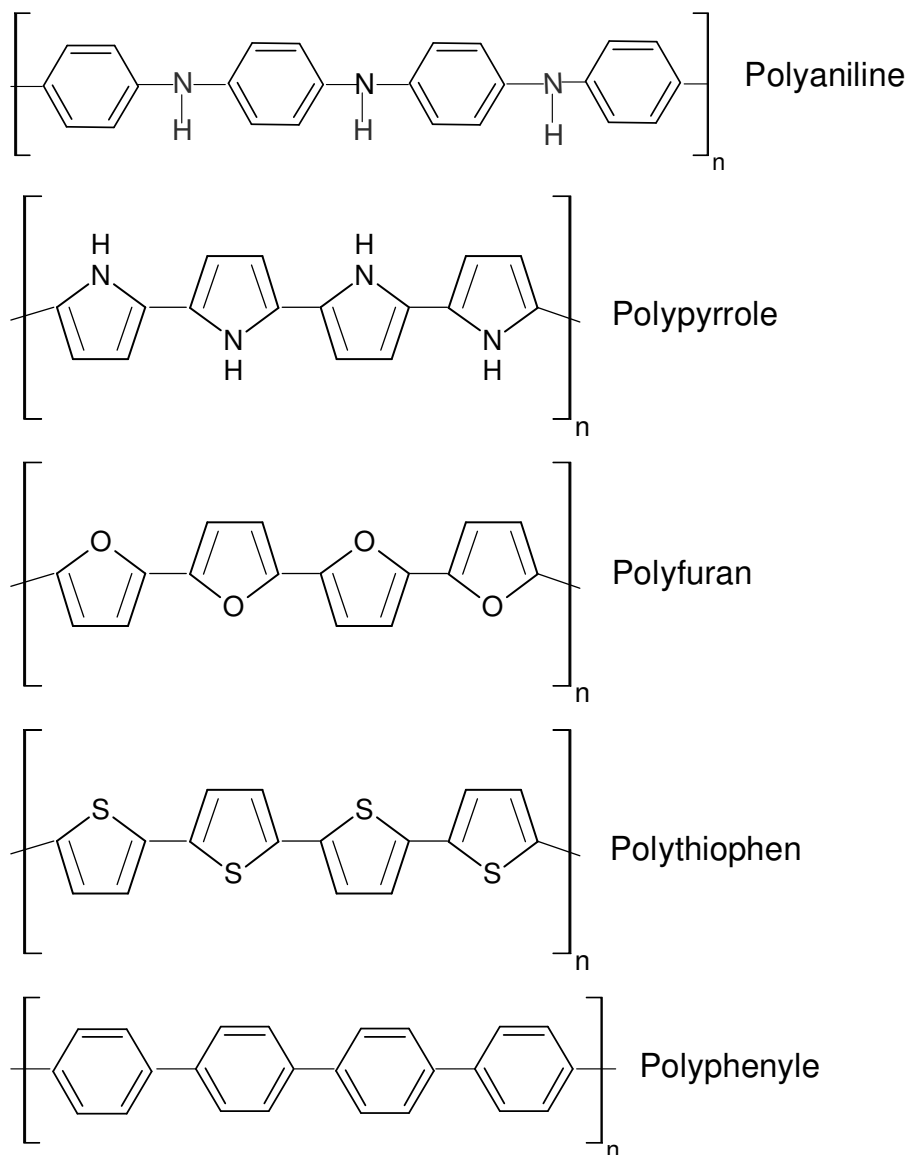
Polyaniline

Polypyrrole

Polyfuran

Polythiophen

Polyphenyle

Figure 1. Some examples of conducting polymers.

conducting polymer layer. This character (of conducting polymers) is explored in the preparation of polymer-metal nanocomposites.

METAL NANOPARTICLES

Nanoparticle is the term generally used to describe a solid particle in the range of 1 to 1000 nm that could be crystalline, an aggregate of crystalline or a single crystalline and possesses properties different from either atoms or bulk materials (Klabunde, 2001; Prasad, 2004). Metal nanoparticles have properties such as magnetic and optical polarizability, semiconductivity, Raman scattering, high porosity in sol form, good mechanical

properties, chemical reactivity due to the quantum size effect, which makes them attractive for applications in the fields such as catalysis, sensors, electronics, optics, medicine, biotechnology as well as in environmental refractive index sensing (Suri et al., 2002; Raschke et al., 2003; Naka et al., 2004; Pothukuchi et al., 2004; Hartling and Eng 2005; Sharma et al., 2009). The small size effect of nanoparticles is called the "quantum size effect" which was theoretically established by a Japanese physicist, Kubo (Kubo, 1962). Another feature of nanoparticles is the higher number of atoms located on the surface of the particles when compared to the number that are located in the bulk core.

Metal nanoparticles are excellent chromophores in the visible and near infrared regions of electromagnetic

spectrum; hence gold, silver and copper nanoparticles show plasmonic band in the visible region of the electromagnetic spectrum (Toshima and Yonezawa, 1998; Huang et al., 2004; Namboothiry et al; 2007; Dahal, 2010). The spectra of platinum and palladium nanonparticles lack significant plasmon absorption maximum (Bigall and Eychmuller, 2010) while nano-particles of metals such as iron, cobalt and nickel have their magnetic properties changed from ferromagnetic to superparamagnetic (Dahal, 2010). The core-shell or alloyed bimetallic nanoparticles of noble metals also show plasmonic behavior (Toshima and Yonezawa, 1998). The surface plasmon band arises from the coherent existence of free electrons in the conduction band due to the particle size, shape and spacing of the particles and on the dielectric functions of the substrate and the surrounding medium (Tessier et al., 2000; Burda et al., 2005; Namboothiry et al., 2007). Nanoparticles of noble metals such as gold, silver, platinum and copper are the most studied as they form stable dispersions that found applications in photography, biological labeling, catalysis, sensors, optoelectronics and photonics (Sharma et al., 2009). The most remarkable features of metal nanoparticles are their specific chemical and physical properties.

A survey of the literature revealed that there are two types of metal nanoparticles (Toshima et al., 1993; Toshima and Yonezawa, 1998; Nadagouda and Varma, 2007; Beyene et al., 2010): Namely monometallic and bimetallic nanoparticles. Bimetallic nanoparticles are composed of two different metal elements that are alloyed or core-shell structured (Toshima and Yonezawa, 1998; Beyene et al., 2010), while monometallic nanoparticles are formed from single metal elements. The properties of bimetallic nanoparticles are usually superior to that of the particles of the constituent metals wherein they exhibit improved catalytic, surface plasmonic and magnetic properties, resulting from electronic and structural effects of the bimetal (Liang et al., 2004; Hatchett and Josowicz, 2008). Metal nanoparticles are prepared in two ways which are: Physical and chemical methods (Toshima et al., 1993; Toshima and Yonezawa, 1998; Beyene et al., 2010). The physical methods involve vapour deposition, which in principle is a subdivision of bulk metals to nanoparticles. The cohesive energy of noble metals is about 2 orders of magnitude higher than that of polymers hence, they have low solubility in polymers under equilibrium conditions thereby exhibiting a high agglomeration tendency (Giesfeldt et al., 2005). Despite noble metals weak chemical interaction with polymers, they have been shown to diffuse into polymers during vapour deposition (Beyene et al., 2010). The chemical method is associated with the reduction of metal ions to metal atoms at zero-valent state. The latter preparative technique allows the control of size and shape of the nanoparticles, hence it is more suitable. The bulk of

bimetallic nanoparticles are prepared by chemical methods, which could, however, be divided into two, namely: (1) Co-reduction and (2) Successive reduction. Co-reduction is suitable for the preparation of alloyed bimetallic nanoparticles while core-shell structured bimetallic nanoparticles are usually prepared by successive reduction process. The composition of bimetallic nanoparticles can be varied by changing the salt ratio used during the particle synthesis (Hatchett and Josowicz, 2008; Beyene et al., 2010). It has also been reported that metal nanoparticles can be obtained by the decomposition of organometallic precursors in the zero oxidation state using a reactive gas such as CO and H_2 under mild conditions (Scheeren et al., 2003). This has made possible the preparation of stable mono- and bimetallic nanoparticles using polymers as stabilizing agents. The synthesis of small, monodispersed nanoparticles is a major challenge in the field of nanotechnology. Smaller particles experience increased driving forces to aggregate (Sardar et al., 2009), so a stabilizer or a protective coating or 'capping is necessary to keep them in a finely dispersed state and also keep them from other modes of decay. Conducting polymers have been employed as the supporting matrix in different nanocomposites for intercalation of nanoparticles so that their activities could be retained in the composite (Park et al., 2005; Qi et al., 1998).

METHODS OF PREPARING POLYMER-METAL NANOCOMPOSITES

Different methods have been reported in the literature for the synthesis of polymer-metal nanocomposites. These methods can be grouped into two: Chemical and electrochemical methods.

Chemical methods

Many chemical techniques have been developed to prepare polymer-metal nanocomposites. In many of these approaches, the monomer or polymer acts as a reductant for the metal.

Polymerization of the monomer in the presence of the metal nanoparticles

This method gives metal core nanoparticles covered with a polymer shell. It leads to inhomogeneous mixing of the polymer and metal particles and aggregation of metal particles, which can create the uneven properties in the composites (Zhu and Zhu, 2006; Corbierre et al., 2005). In addition, relatively high temperatures or pressures are needed, which make the preparation complex, difficult and costly.

The reduction of metal ions from their salt solution at the polymer-solution interface (*In situ* reduction method)

In this method, the reduction of the metal ions is achieved by the use of a reductant, heat treatment, UV-light or a polymer having sufficiently high reducing power with respect to the metal ions (Roth et al., 2001; Lin and Yang, 2005; Wang et al., 2006). The nanocomposites are obtained from the dispersion of nanoparticles in polymer solution by solvent evaporation, co-precipitation or electrospinning. This method gives metal nanoparticles embedded into a polymer matrix and the metal nanoparticles are well-dispersed. A judicious choice of the polymer facilitates environmentally-safe synthesis without the requirement of additional reducing/stabilizing agents (Nadagouda and Varma, 2007). The polymeric matrix provides additional qualities, such as the processability, solubility or thermal stability of the system. In this way, nanocomposite materials possessing novel catalytic, conductive, magnetic or optical properties can be obtained (Balan and Burget, 2006). It is suitable for synthesizing polymer-metal nanocomposites involving metal ions such as copper, gold, platinum and silver that have relatively high positive redox potentials.

Simultaneous formation of metal nanoparticles and polymerization of the monomer

This usually involves direct oxidation of the monomer with the metal ions precursor. In this case, the metal ion precursor serves as an oxidizer for the monomer polymerization and also as a source of metal nanoparticles in the subsequent cementation of metal on polymer colloids (Malinauskas et al., 2005; Folarin et al., 2011). In some version of this method, the simultaneous polymerization and reduction process occur in the presence of an initiator. This technique involves heating or irradiation with γ-ray/uv radiation or both (Zhu and Zhu, 2006). The method had been reported to lead to a homogeneous distribution of metal nanoparticles in the polymer matrix.

Co-sputtering of the polymer and the metal nanoparticles using different magnetron sources and/or atom beam

This technique, also known as physical vapour deposition (PVD), is suitable for preparing polymer-metal nano-composite films (Schurmann et al., 2005). In the magnet-ron co-sputtering process, if the number of samples is large, the presence of a magnetic field results in higher sputtering from a narrow circular region, resulting in non-uniformity in the sample. Such non-uniformity does not occur in the wide source atom beam co-sputtering due to the large size of the atom beam (Avasthi et al., 2007). The technological advantage of the sputter technique over other techniques is the possibility of realizing a higher deposition rate (Schurmann et al., 2005).

Electrochemical methods

Electrochemical technique is well established for the synthesis of films of polymers via oxidative coupling of monomers, particularly polymers with functional side groups as the monomers could be modified prior to electro-oxidation (Sih and Wolf, 2005). This technique has proved to be effective in incorporating metal nanoparticles in either pre-deposited polymers or in growing polymer films. Based on the metal, the desired size of the nanoparticle and the type of polymer, different electrochemical techniques had been developed for preparing polymer-metal nanocomposites. Earlier attempts to electrochemically prepare polymer-metal nanocomposites involved a two-step process (Sigaud et al., 2004). In the first step, the polymer is deposited on an electrode by electro-oxidation of the appropriate monomer. Films of the polymers are then dipped in a solution containing metal ions followed by electrochemical reduction of the ions yielding metallic clusters embedded in the polymer (Sih and Wolf, 2005). This technique has the disadvantage of producing nanocomposites having large nanoparticles, a wide size distribution, particle confinement to the polymer surface and uneven particle distribution within the polymer matrix. To circumvent some of these drawbacks, cation were attached to the polymer backbone to complex the metal ions wherein the metal complex acts as a template to facilitate metal particle nucleation (Sigaud et al., 2004; Zouaoui et al., 1999).

An alternative approach is to carry out the electropolymerization of the monomer in the presence of pre-synthesized colloidal dispersion of the nanoparticles. This leads to the particles being trapped within the growing polymer instead of being confined to the surface as observed when metal particles are deposited onto pre-deposited polymers by reduction of metal ions. The technique gives room for the effective control of the embedded nanoparticles. Three-dimensional distribution of metal particles within the polymer matrix also facilitates improved charge shuttling throughout the material. The major drawback of this approach is that the nanoparticles used are passivated by thiols, amines or citrates which prevent them from being directly chemically bound to the polymer, hence, it is difficult to prevent leaching of the particles from polymer matrix (Katz et al., 2004).

CHARACTERIZATION OF POLYMER-METAL NANOCOMPOSITES

Here, some characterization methods of polymer-metal

nanocomposites will be discussed; however, the bulk of these methods provide information on sizes, shapes and physicochemical properties of the nanoparticles.

Electron micrographic analysis

The question frequently asked about metal nanoparticles in polymer-metal nanocomposites is concerned with aggregation state, size and morphology. Many techniques have been used to reveal the size and dispersity of nanoparticles in polymer-metal nanocomposites since the homogeneity of particle size and shape on the atomic scale is quite important to the physical and chemical properties of the nanostructured materials. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the two important electron micrographic techniques employed in the characterization of polymer-metal nanocomposites. The microstructure and crystalline morphology of nanocomposites are often evaluated by SEM (Xia et al., 2006). Samples for SEM analysis could be sputtercoated with gold layers and micro sprayed on a mica foil (Ballav and Biswas, 2003) or the nanocomposites could be cut into strips and etched with the solution of potassium permanganate in a mixture of equal volumes of orthophosphoric and sulphuric acid. An energy dispersive X-ray spectrometer (EDX) mounted to a scanning electron microscope can be used to determine the amount of constituent metal nanoparticles in the composite. TEM had been used frequently in establishing the crystalline morphology of polymer-metal nanocomposites better than SEM. Sample preparation of polymer-metal nanocomposites for TEM observation is very simple, involving evaporation of a small drop of the prepared nanocomposites from appropriate solvent onto a carbon-coated copper grid (Tian et al., 2006; Huang et al., 2004; Toshima and Yonezawa, 1998). Improvement in high-voltage electron beam technique had brought about high resolution TEM (HRTEM). HRTEM can now provide information on the particle size and shape as well as on the crystallography of the nanoparticles in the nanocomposites (Toshima and Yonezawa, 1998). The use of TEM has been severely criticized due to the fact that it reveals morphology in a small region, however, this can be overcome by taking images at different magnifications and from different locations and orientations until a representative picture of the morphology is established (Paul and Robeson, 2008).

UV/visible spectroscopy

Colour is the most immediate observable properties for certain metal nanoparticles dispersions. This colour effect is based upon the surface plasmon resonance or particle plasmon resonance. Noble metal nanoparticles such as Au, Ag and Cu have characteristic colours that are related to their particle size, shape, and particle distance and on the matrix material (Schurmann et al., 2006; Huang et al., 2004; Toshima and Yonezawa, 1998). For these metals, observation of uv-visible spectra will be a useful complement to other methods in characterizing the nanomaterials. For example, information on the formation of bimetallic nanoparticles can be derived from this technique. The uv-visible spectra of the bimetallic nanoparticles are not simple sum of the two monometallic nanoparticles. If two separate metallic phases are present, the absorption spectrum would be characterized by double peaks due to the SPR of single metal nanoclusters (Beyene et al., 2010; Nadagouda and Varma, 2007) provided the two metals have characteristic SPR. Comparison of spectra of bimetallic nanoparticles with the spectra of physical mixtures of the respective monometallic particles can confirm the formation of bimetallic nanoparticles.

Infrared spectroscopy (**IR spectroscopy**)

IR spectroscopy is one of the methods most extensively used for the investigation of polymer structure (Sandler et al., 1998) as IR bands characteristics of the polymers are readily observed. It is very helpful in the characterization of nanocomposites prepared by the polymerization of the monomers as the formation of the polymer in the nanocomposite is confirmed by this method (Zhu and Zhu, 2006). To prevent agglomeration of nanoparticles during polymerization and to achieve their compatibility with the polymer, the surfaces of some nanoparticles had been coated with oleic acid (Gyergyek et al., 2008). IR spectroscopy gives evidence of the surface coating and is used to investigate the surface chemistry of the nanoparticles as polymer-stabilized nanoparticles give IR bands characteristics of the polymer. The formation of CO molecules had been reported during the preparation of Pt nanoparticles from platinum compounds (Dablemont et al., 2008). The produced CO molecules were reported trapped on the platinum particle surface, with the IR stretching vibration occurring in the region 2060 to 2100 cm^{-1}. Figure 2 shows IR spectrum of Poly(N-vinylcarbazole)-Platinum (PNVC-Pt) nanocomposite characterized by Poly(N-vinylcarbazole) (PNVC) absorption bands and an absorption band at 2079 cm^{-1} characteristic of CO molecules adsorbed on the surface of the Pt nanoparticles. IR spectroscopy of CO on the surface of bimetallic nanoparticles can also give some information about the surface structure of bimetallic nanoparticles. By comparison of IR spectra of CO on a series of bimetallic nanoparticles at various metal compositions, the surface micro-structure of bimetallic nanoparticles can be elucidated (Toshima and Yonezawa, 1998). This technique can also investigate chemisorptions of the polymer on the surface of the nanoparticles.
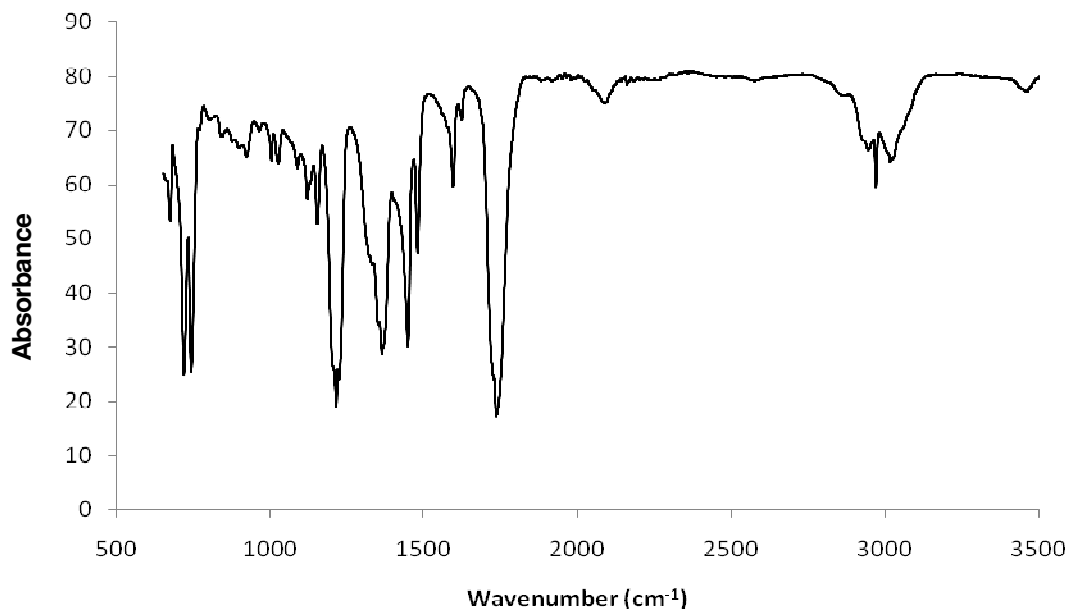
Figure 2. IR spectrum of PNVC-Pt nanocomposite.

X-ray methods

X-ray methods are versatile and non-destructive techniques that reveal detailed information about the chemical composition and crystallographic structure of natural and synthetic materials; hence X-ray techniques had been used in the characterization of polymer-metal nanocomposites. X-ray diffraction (XRD) and X-ray photospectroscopy (XPS) are the most frequently used X-ray methods for characterization of polymer-metal nanocomposites.

X-Ray diffraction (XRD)

X-ray diffraction (XRD) is a method of choice to investigate the solid structure of metal nanoparticles and morphology of polymer in polymer-metal nanocomposites. The phase changes with increasing diameter of nanoparticles and the crystal structure can be determined with XRD. The polymer and the metal nanoparticles can be identified by their characteristics peaks in XRD patterns. This technique can investigate the formation of bimetallic nanoparticles as opposed to a mixture of monometallic nanoparticles, since the diffraction pattern of the physical mixtures which may consist of overlapping lines of the two individual monometallic nanoparticles and is distinct from that of the bimetallic nanoparticles (Toshima and Yonezawa, 1998; Beyene et al., 2010). Information on the morphology of the polymer constituent of the composite could be derived also from XRD. The technique can reveal the degree of crystallinity in the polymer component of the nanocomposites as sharper peaks with increased relative peak intensity implies a more ordered arrangement (Gangopadhyay and De, 1999). Figure 3 shows XRD spectrum of PNVC-Au nanocomposite. The broad reflection in the range of $2\theta = 15 - 35$ indicating a low order of crystallinity is attributed to poly(N-vinylcarbazole) of the nanocomposites while sharper reflections at $2\theta > 35$ are attributed to gold nanoparticles.

X-ray photospectroscopy (XPS)

The structure and surface composition are indispensable information and quantitative XPS analysis provides valuable information on the surface composition, structure and charge transfer between metals and adsorbed ligands at the surface (Liu et al., 2006; Qiu et al., 2006; Fu et al., 2001; Toshima and Yonezawa, 1998)). When metal nanoclusters are modified, the binding energies of nanoparticles change relative to those of the bulk atoms (Giesfeldt et al., 2005). Knowing the energy of the X-ray photons and measuring the kinetic energy of the extracted electrons, the binding energy of the extracted electrons can be determined. The binding energies of the particles provide information on the particle sizes as metal particles with sizes less than certain critical size have less binding energies than bulk atoms while metal particles with sizes more than this critical size have binding energies greater than those of bulk atoms. This transition is attributed to the fact that smaller particles act as electron acceptors while larger particles act as electron donor with consequent effect on their binding energies. The increased binding energy of the nanoparticles is a confirmation of interaction between the nanoparticles and the polymer matrix in the
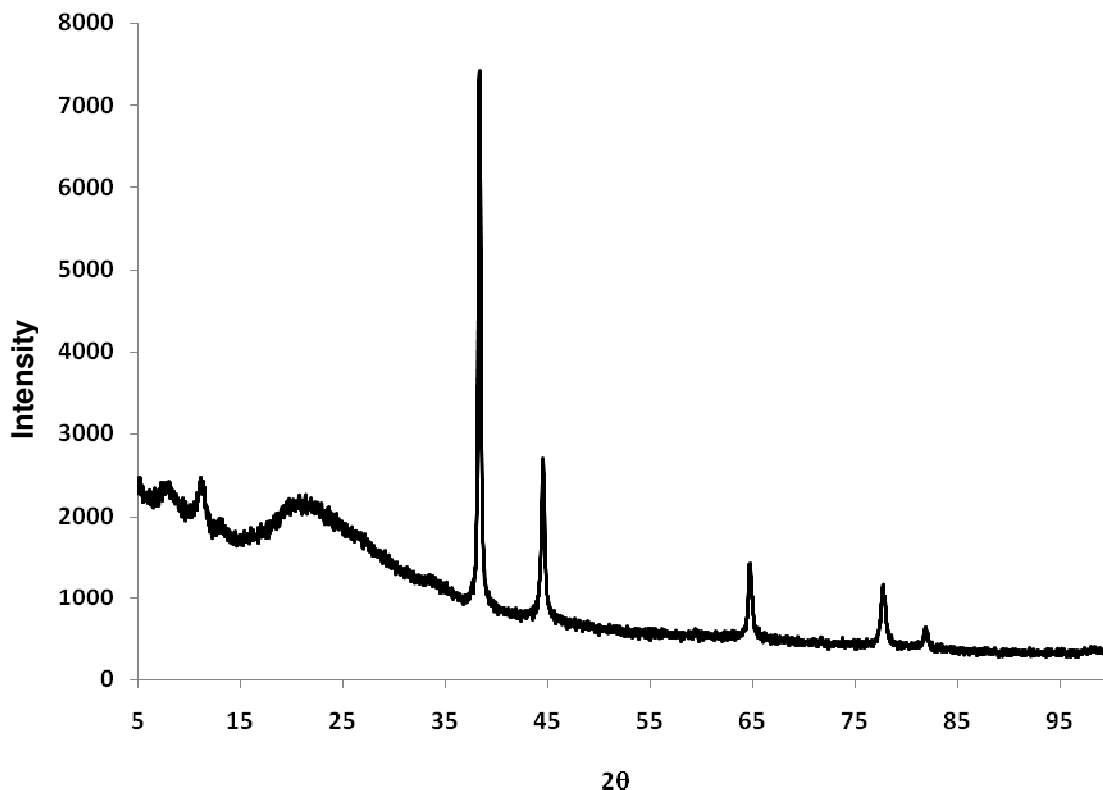
Figure 3. XRD spectrum of PNVC-Au nanocomposite.

nanocomposite. The technique gives information on the change of the nanoparticles content corresponding to the matrix depth from the surface of the nanocomposites.

Energy-dispersive X-ray (EDX)

Energy-dispersive X-ray (EDX) analysis normally used as additional technique to SEM and TEM finds application in characterizing bimetallic nanoparticles. The technique reveals the shell structure, the composition and the size of the bimetallic particles. Each element in the chosen nanoparticles emits X-rays at characteristic energies by electron beam irradiation, and their intensity is proportional to the concentration of each element in the particle (Beyene et al., 2010).

Thermogravimetric analyses

Thermogravimetric analysis finds application in the characterization of polymer-metal nanocomposites as it provides information on the thermal stability of the nanocomposite relative to the polymers. During composite formation, stabilizers (polymers/surfactants) make organic coating on the nanoparticles surface, TGA can be used to evaluate the amount of stabilizer

chemisorbed on the surface of the nanoparticles (Zhu and Zhu, 2006; Xia et al., 2006). Figure 4 represents the thermogram of Pt nanoparticle, PNVC-Pt nanocomposite and PNVC. The thermogram shows that the Pt nanoparticle lost about 28% weight due to loss of polymer coating on the surface of the nanoparticle.

POLYMER-NOBLE METAL NANOCOMPOSITES

Noble metals are widely used as catalysts for many reactions. However, catalysis at metal surfaces embedded in conducting polymers is enhanced due to the conductive polymer environment. Among the variety of polymer-metal nanocomposites, the coinage metal group, Ag, Au, Cu and Pt is the most extensively studied. Incorporating metals in conducting polymers enhances electron transfer through a direct or mediated mechanism with improved conductivity and enhanced stability (Muraviev et al., 2006). The electron-rich polymer acts as a chemical receptor or scaffold for the nanoparticles or providing stability to the metal ions that are deficient in electron. The polymer provides high surface and protection against the fouling of the metal surface and a scaffold for high dispersion and anchoring of the metal particle (Hatchett and Josowicz, 2008). The availability of the finely dispersed particles in the polymer ensures high
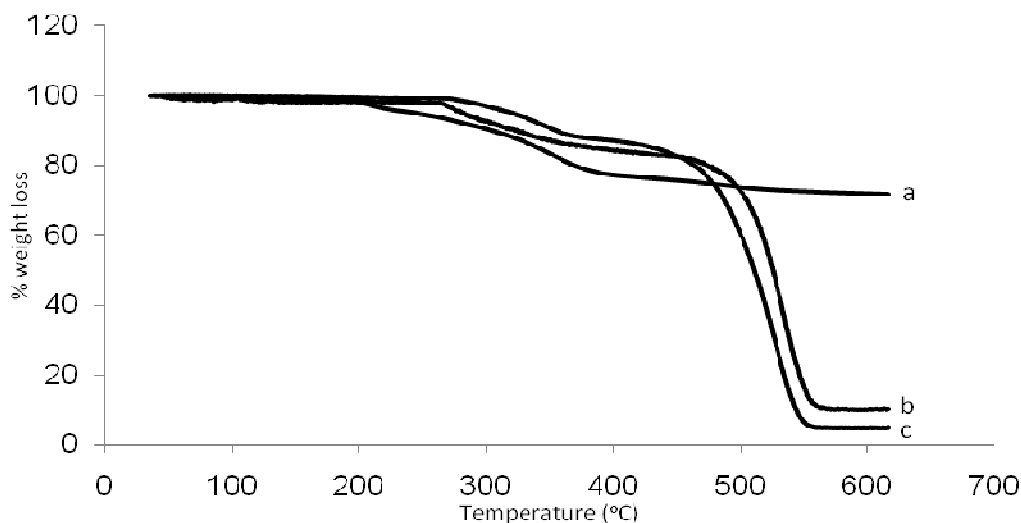
Figure 4. Thermograms of Pt-nanoparticle (a) PNVC/Pt nanocomposite (b) and PNVC (c).

surface area and possible enhancement of the unique characteristics of the composites. When nanocomposites with noble metal nanoclusters are exposed to light, they exhibit a strong absorption maximum at a particular wavelength due to photon induced oscillation of the electron charge density (Hutter and Fendler, 2004). This oscillation of the surface electrons is called surface plasmon resonance (SPR) in the case of thin films, or particle plasmon resonance (PPR) for nanoparticles (Lance Kelly et al., 2003). The type of metal and the surrounding dielectric medium play a significant role in the excitation of the plasmon resonance (Takele et al., 2006). Light scattering is markedly reduced in polymer-metal nanocomposites and this renders them attractive for optical studies and applications. Some of the applications are colour filters (Biswas et al., 2004), optical switching and optical limiting devices, optical and biosensors, absorption elements of solar cells, photonic bandgap tuning, Bragg reflectors, surface enhanced Raman spectroscopy and laser technology.

Polymer-silver nanocomposites

Incorporating silver nanoparticles into a polymer matrix has received more attention within the past decade, because the resulting nanocomposites exhibit applications in catalysts, drug and wound dressings, optical information storage, electrochromic devices, surface enhanced Raman scattering as well as data storage (Wang et al., 2006; Sangermano et al., 2007; Namboothiry et al; 2007). Wang et al (2006) prepared polyvinyl pyrrolidone (PVP)/silver nanocomposites in two steps. In the first step, silver nanoparticles were prepared through the reduction of $AgNO_3$ by ethanol under refluxing conditions in PVP ethanol solution. At the

second stage after the reaction, the solution was spun directly to prepare PVP nanofibre film dispersed silver nanoparticles by electrospinning. Schurmann et al (2005) synthesized polytetrafluoroethylene (PTFE)-silver nanocomposite films by co-sputtering of the polymer and silver. The synthesis involved the use of two magnetron sources, one for PTFE and the other for silver. The films formed were reported to be of relatively high deposition and the uniformity of the deposited films was enhanced. The metal filling factor in the nanocomposites was controlled by adjusting the DC power of the metal sputter source thereby giving nanocomposite films of varying silver content. Near the percolation threshold, the electrical and optical properties of the nanocomposite films were reported to change drastically from insulating to metallic. Biswas et al. (2004) prepared (using vapour phase co-deposition process) Teflon AF-Ag nanocomposites with tunable optical properties. The optical nanocomposites produced containing nanoparticles of extremely narrow size distribution show a shifting of the plasmon resonance wavelength in the uv-visible region with potential application as ultrathin colour filters. Namboothiry et al. (2007) investigated the electrochromic properties of some conducting polymer blends-Ag nanocomposites wherein they reported the enhanced absorbance of the nanocomposites in the visible region of the electromagnetic spectrum. The absorbance enhancement depended on the loading of the nanoparticles in the polymer blend and the dielectric properties of the surrounding medium. The nanocomposites find applications in the fabrication of electrochromic devices for full colour electrochromic displays. Reddy et al. (2008) prepared poly(o-toluidine)-Ag nanocomposites in two stages: Firstly, the citrate reduction of the Ag ions to form citrate-stabilized Ag colloids was flowed by *in-situ* chemical oxidative polymerization of

o-toluidine. The electrical conductivity of the nanocomposites compared to that of the polymer was reported to increase by the order 10^3. The nanocomposites find applications in electronic devices.

Polymer-gold nanocomposites

The excellent and unusual properties of gold nanoparticles coupled with their ability to tune the properties of conducting polymers leading to the fabrication of materials with varied applications have continued to attract interest from researchers. The optical properties of the nanoparticles and composites are often unique with absorption peaks at around 520 and 580 nm (Sih and Wolf, 2006; Hatchett and Josowicz, 2008).

Owens 111 et al. (2007) synthesized gold-polymer nanocomposites of gold and some thermally responsive interpenetrating polymer network. The resulting biocompatible nanocomposites were described as intelligent therapeutic nanocomposites that exhibit intelligent therapeutic functions. Giesfeldt et al. (2005) prepared polydimethylsiloxane-Au nanocomposites with improved surface-enhanced Raman scattering (SERS) via physical vapour deposition. The nanocomposites exhibit affinity for amine and nitro-based compounds that are biologically active and point towards their potential applications as substrates for biologically based SERS experiments. Poly(ethylene glycol)-Au nanocomposites prepared via simultaneous photo-induced electron transfer and free radical polymerization processes was investigated by Yagei et al. (2008). The resulting nanocomposite displayed long-term stability and has potential application in electron and energy storage.

Polymer-platinum nanocomposites

Platinum have catalyzed many processes that are important for technologies of energy production and environmental protection. However, interactions between the metal and its support are known to maximize the performance of proton exchange membrane and minimize the use of the metal (Grzeszczuk and Poks, 2000; Seger and Kamat, 2009). Nanomaterials with a high surface area and porosities are known to function as better electrode materials for direct methanol fuel cell application, consequently, the synthesis of high surface area nanocomposites of platinum had been attempted extensively in the recent past (Liu et al., 2007; Malinauskas et al., 2005; Prasad and Miura, 2004). Grzeszczuk and Poks (2000) studied the incorporation of platinum nanoparticles into polyaniline matrix. The polyaniline-platinum nanocomposite electrodes grown potentiostatically were used to study electrochemical process of hydrogen evolution. The authors reported that the performance of polyaniline with Pt nanoparticles and bulk Pt electrodes are similar. Liu et al. (2007) prepared

polyaniline-poly(styrene sulfonic acid)-Pt nanocomposite through an interfacial polymerization route. The composites consisting of Pt nanoparticles loaded into conducting PANI-PSS polymers was reported to find applications in direct methanol fuel cell. Sanchez et al. (2010) prepared poly(pyrrole-alkylammonium)-Pt nanocomposites by potentiostatic oxidative electro-polymerization process, wherein they reported the incorporation of Pt nanoparticles into the polymer matrix. These nanocomposites coated onto carbon electrodes possessed strong electrocatalytic properties towards the oxidation of arsenite to arsenate. Conductive polymer-platinum composites find applications primarily in fuel cell and catalysis. Direct methanol fuel cells (DMFCs) are considered to be important and the most promising options for addressing future energy needs (Lin et al., 2005), therefore polymer- Pt nanocomposites will definitely play major role in this regard.

APPLICATIONS OF POLYMER-NOBLE METAL NANOCOMPOSITES

The combination of a wide range of polymeric materials with noble metals had led to the fabrication of nanocomposites with unique electrical, magnetic, catalytic and optical properties. These nanocomposites find applications in electrocatalysis, gas separation and optoelectronic devices such as high refractive index wave guide materials (Kelly et al., 2003); organic batteries, microelectronics, nonlinear optics, sensors (Kang et al., 2005); drug delivery (Owens III et al., 2007) and anti-bacteria reagent (Panacek et al., 2006; Kvitek et al., 2008). Based on its stability and tunable electric properties, polyaniline-metal nanocomposites showed enhanced sensing and catalytic applications when compared to those of pure polyaniline (Pillalamarri et al., 2005). Polyaniline-Ag and polyaniline-Au composite nanofibres prepared by Pillalamarri et al. (2005) were reported to have 50 times the electrical conductivity of pure polyaniline nanofibres. In the one-pot synthesis of the nanocomposites, polyaniline nanofibres were decorated with the noble metal particles via γ-irradiation and the electrical conductivity increased with the increased loading of the metal particles in the nanocomposites. Polyaniline-Au nanocomposites for example, find application as sensor for dopamine detection (Kongkanand et al., 2006). In the field of laser technology, polymer-metal nanocomposites are gaining prominence. The excitation by light of the nanoparticles embedded in a dielectric matrix causes the electric vector of the electromagnetic wave to induce a charge density oscillation which corresponds to the plasmon frequency of metal particles, leading to strong absorption of light at a particular wavelength (Avasthi et al., 2007). The light absorption and subsequent surface plasmon oscillations lead to the strongly enhanced electric field within the nanoparticles and the Interparticle gaps. Composites

Table 1. Applications of polymer-noble metal nanocomposites.

Polymer matrix	Nanoparticle	Application (Reference)
Polyaniline	Gold	Sensor (Paul and Robeson, 2008)
Natural rubber	Silver	Latex gloves (Paul and Robeson, 2008)
PET	Silver	Bandpass filter (Avasthi et al., 2007)
Polypyrrole	Platinum	Fuel cell (Malinauskas et al., 2005)
Poly(vinyl chloride)	Copper	Biotechnology (Cioffi et al., 2005)
Polyaniline	Copper	Sensor (Sharma et al., 2002)
Polytetrafluoroethylene	Silver	Optical filler/sensor (Schurmann, 2005)
PEDOT: PSS	Silver/gold	Electrochromic device (Namboothiry, 2007)
Bisphenol A	Silver	Capacitor (Pothukuchi et al., 2004)
Polydimethylsiloxane	Gold	SERS (Giesfeldt et al., 2005)
PANI-PSS	Platinum	Fuel cell (Liu et al., 2007)
Polysulfone	Platinum	Sensor (Muraviev et al., 2006)
Polymethylmethacrylate	Gold	Sensor (Hanisch et al., 2008)

absorbing light over a broad range extending from the visible to the infrared region is of technological importance as these find applications for high efficiency solar cells having absorption in the range 330 to 2500 nm (Granqvist, 2003), infrared photodetectors and sensors and solar control glazing windows (Schelm and Smith, 2003; Liu et al., 2005) and such a composite will also be of interest in surface-enhanced Raman spectrometry (Shalaev, 2002). Recently, Avasthi et al. (2007) prepared Ag-PET nanocomposites via atom beam co-sputtering and reported that the nanocomposite films have two uv-visible absorption bands. First, a narrow band around 320 nm, which is a wavelength of considerable interest, being the same wavelength as that of a HeCd laser. The second broad uv-visible absorption band from 500 nm and extending to IR region implies that the nanocomposites will have applications as mentioned previously. The application of polymer nanocomposites to emerging biomedical and biotechnological field is growing rapidly. One area of intense research involves electrospinning to produce bioresorbable nanofibre scaffolds for tissue engineering applications (Paul and Robeson, 2008). Polymer-metal nanocomposites equally find applications in fuel cell as the incorporation of platinum nanoparticles into the polymers in the proton exchange membrane brings improved proton conductivity and mechanical properties over the conventional carbon black-based electrodes (Kongkanand et al., 2006). Some of the applications of polymer-noble metal nano-composites are presented in Table 1.

CONCLUSION

Nanostructured materials are novel materials with improved and unanticipated properties that will continue to dictate the pace in the field of science and technology. Polymer-metal nanocomposites will remain materials of

interest to researchers in this field for the next decade. Within this period, nanocomposites of bimetallic nanoparticles are likely to receive more attention as less attention is presently focused on them. This will lead to emergence of new materials with properties that are superior to some of the presently known polymer-metal nanocomposites. This review attempted to summarize preparation methods, characterization and some applications of polymer-noble metal nanocomposites suggested by researchers working in this field.

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