SHORT COMMUNICATION

PREPARATION AND CHARACTERIZATION OF POLY(N-VINYLCARBAZOLE)/PLATINUM NANOCOMPOSITE VIA IN SITU SOLID STATE POLYMERIZATION

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ABSTRACT

A nanocomposite of poly(N-vinylcarbazole)(PNVC) and platinum (Pt) was prepared by simple solid state polymerization of N-vinylcarbazole (NVC) in the presence of platinic acid (H₂PtCl₆) at elevated temperature. The mechanism of the polymerization process was proposed. The nanocomposites, the extracted homopolymer and the Pt nanoparticles were characterized by FTIR, XPS, TEM and TGA. FTIR analysis confirmed the polymerization of NVC to PNVC in the presence of Pt ions. XPS studies revealed that the Pt nanoparticles formed contained both Pt(0) and Pt(II). The presence of polaron in the H₂PtCl₆ doped NVC during polymerization was confirmed by ESR. TEM analysis revealed the cementation of the Pt nanoparticles on the PNVC. Thermo gravimetric stability studies showed that PNVC-Pt nanocomposite is thermally stable than the homopolymer.

Keywords: Preparation, characterization, nanocomposite, nanoparticles, poly(N-vinylcarbazole).

INTRODUCTION

Hybrid organic-inorganic materials have emerged as a novel class of electronic and optoelectronic media for a number of potential technological applications. π -Conjugated polymers have great interesting high electrical conductivity, redox properties and extensive applications ranging from batteries to light-emitting devices (Zhou et al., 2002). Many inorganic nanoparticles have been encapsulated in π -conjugated polymers and the electronic structure of the polymer chain strongly influences the characteristics of the embedded metal nanoparticles (Sarathy et al., 2000). In this family of specialty polymers such as poly(N-vinylcarbazole) (PNVC), polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) etc, a considerable amount of research attention has been paid to the preparation and evaluation of nanocomposites using different nanomaterials. In recent years, there has been a substantial rise in interest regarding the use of nanosize metal particles as components of various composite materials intended to possess fine-tuned electrical and optical properties. The advantage of nanoparticles, as compared to more classical bulk homogeneous materials, is that they bridge a gap between the properties of these different classes of substances. On one hand, a nanoparticle may be regarded as a lump of bulk material and its properties may be derived by considering the spatial confinement imposed on electrons and excitations as a result of the particle's limited size. On the other hand,

a nanoparticle can be thought of as a big molecule that can be functionalized (capped) and that can interact with its surroundings in a way similar to conventional molecules (Choudhury et al., 2004). Among the nanoparticles, much interest has focused on some metal and semiconductor nanoparticles because of their unique optical properties. Nanoparticles of noble metals, such as platinum, gold, silver and copper, show intense colours that are quite different from those of their bulk phase. The coloration is caused by surface plasmon absorption of the particles (Link and El-Sayed, 1999). Nanoparticles are able to interact strongly with circumference owing to their large surface area. If semiconductor nanoparticles can be dispersed homogeneously in optically or electrically active materials and interacted with them, various enhanced or tuned optical or electrical properties may appear (Aita et al., 2007). Polymer-metal nanocomposites have an advantage over the oxide/noble metal multilayers in terms of ease of synthesis (Avasthi et al., 2007) and there are two main kinds polymer-metal nanocomposites of conducting polymers with metals (Malinauskas et al., 2005); (1) Metal core nanoparticles, covered with a conducting polymer shell. These composites are usually prepared by the chemical or electrochemical polymerization of a thin, nanometer-sized layer of a conducting polymer onto colloid metal particles. (2) Metal nanoparticles, embedded into a conducting polymer matrix. These composites can be easily obtained by the chemical reduction of metal ions

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from their salt solution at the conducting polymer/solution interface.

Many research groups have reported on the preparation and characterization of various types of polymer-metal nanocomposites because the incorporation of various nano-structured materials into the polymer matrix leads to improvement in the properties of polymer. In the search for platinum-containing nanocomposites, Hepel (1998) prepared polypyrrole-platinum nanocomposites by having $PtCl_4^{2-}$ anion trapped into a polypyrrole film during its electrochemical preparation, and after solution exchange, these anions were reduced cathodically to yield platinum metal particles of average size 10 nm, included in a 3D polypyrrole matrix. The resulting composite film showed an electrocatalytic effect on the electrochemical methanol oxidation. Grzeszczuk and Poks 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. Smith et al prepared polyaniline-gold nanocomposites by the spontaneous chemical reduction of gold from tetrabromoaurate ions in solution onto a polyaniline an acidic laver electropolymerized at a platinum electrode. It was pointed out that although the amount and size distribution of the gold clusters vary with the reaction time, it was difficult to control both of these parameters. PNVC is well known for its exceptionally high thermal stability, high photoconductivity and opto-electronic properties and these desirable properties are derived from a complex interplay between the building blocks and the interfaces separating the building blocks (Maity et al., 2008; Wang et al., 2000). It is a good hole transporting material and the fabrication of its nanocomposites by covalent inclusion of inorganic nanoparticles is highly topical and find applications in the electronics, optics, and energy sectors (Feng et al., 2008). It has been established that Nvinylcarbazole monomer is a fairly good electron donor (Ballav and Biswas, 2003), its ability to reduce Pt ions to nanoparticles and form polymer-metal nanocomposite is not in doubt, hence our choice of NVC.

Various methods for the preparation of the PNVC/metal nanocomposites have been used; in situ solid state polymerization of the monomers in the presence of H_2PtCl_6 at an elevated temperature without any external oxidant has not been reported. The reduction of Pt ions to Pt atoms at the zero-valent state in the presence of polymers had been reported (Toshima *et al.*, 1993; Ahmadi *et al.*, 1996), this necessitated our choice of metal. Our intention is to carry out direct oxidation of *N*-vinylcarbazole (NVC) with hexachloroplatinic acid. Obviously, hexachloroplatinic acid will serve both as an oxidizer for NVC polymerization and as a source of platinum in the subsequent cementation of platinum metal on poly(*N*-vinylcarbazole). In this work, we report for the

first time, PNVC-platinum nanocomposite synthesized by simple solid state polymerization of a mixture of NVC and H_2PtCl_6 nanoparticle at an elevated temperature.

MATERIALS AND METHODS

Materials

The NVC monomer and H_2PtCl_6 used in this study were purchased from Sigma-Aldrich Chemicals (USA). The NVC monomer was recrystallized from n-hexane and kept in a dark place prior to use. H_2PtCl_6 was used as supplied. All solvents used were of analytical grade and were freshly distilled before use.

Preparation of the nanocomposite

Simple solid state polymerization technique was employed for the preparation of PNVC/Pt nanocomposite. A mixture of 0.5g of NVC and 0.1g of H₂PtCl₆ was taken in a conical flask and heated at 70°C for 1 h. 5ml of distilled THF was added to the reaction mixture and stirred. The whole reaction mixture was added to an excess ethanol (EtOH). The separated gravish black mass was filtered and washed with ethanol to remove any unreacted NVC monomer (Ellinger, 1964), followed by a wash with acetone. The resulting mass was dried at 100°C for 6 h under vacuum until the total mass became constant. For the extraction of the PNVC homopolymer from the nanocomposite, the dried nanocomposite powder was refluxed with 20ml of benzene at 70° C for 6h. Thereafter, the solution was poured into an excess methanol to yield a white precipitate, i.e., PNVC homopolymer. The white mass was filtered and washed with methanol, followed by acetone and finally dried at 100°C for 6h until the total mass became constant.

Characterization of the PNVC/Pt nanocomposites

The formation of PNVC from the NVC/H₂PtCl₆ polymerization system and its presence in the nanocomposites were confirmed by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy, using a Perkin-Elmer Spectrum 100 spectrometer, equipped with IR microscopy accessory and a germanium crystal. Elemental mapping was performed, using an X-ray photoelectron spectroscopy (XPS) on a Kratos Axis ultra device, with an Al monochromatic X-ray source (1486.6 eV). The morphology of Pt nanoparticles and nanocomposites was studied by TEM (JEOL JEM 2100). The TGA was carried out with Perkin Elmer TGA 7 thermal analyzer under N₂ at the heating rate 10° C min⁻¹.

RESULTS AND DISCUSSION

Table 1 summarizes the FTIR absorption peaks for the nanocomposite and the extracted polymer as they appear in the figure 1. The results of the Table and the Figure clearly prove the formation of PNVC polymer in the

presence of H_2PtCl_6 and that of PNVC/Pt nanocomposite. The PNVC/Pt composite shows the characteristic peaks (cm⁻¹) of PNVC moieties at 717, 745, 1155, 1218, 1330,

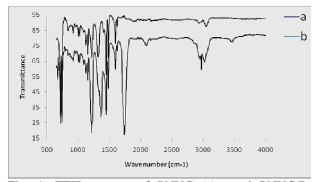
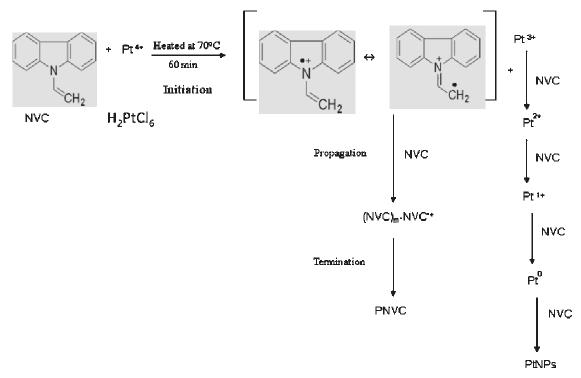


Fig. 1. FTIR spectra of PNVC (a) and PNVC/Pt nanocomposite (b).

1453 – 1484, 1600 and 2928 – 3036. These peaks are due to the following vibrations: ring deformation of the substituted aromatic structure, CH₂ rocking vibration due to tail-to-tail addition, out-of-plane deformation of the vinylidene group, C-H in-plane deformation of the vinylidene group, ring vibration of the NVC moiety, C=C stretching vibration of the vinylidene- group, and =C-H stretching, respectively (Ballav and Biswas, 2003; Maity and Ray, 2008). In addition, the composite has two peaks at 1736 cm⁻¹ and 2079 cm⁻¹. The peak at 1736 cm⁻¹ is attributable to stretching vibration of carboxylic acid (C=O) that was formed via the oxidation of alcohols used during the preparation of the nanocomposite by platinum. 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 $2060-2100 \text{ cm}^{-1}$. The observed peak of the PNVC/Pt nanocomposite at 2079 cm^{-1} could be attributed to CO molecules produced during the preparation of the nanocomposite.

Mechanism of polymerization of NVC

The mechanism for the polymerization of NVC by various metal salts/oxides had received a good deal of research attention. Ballav and Biswas (2005) and Maity and Ray (2010) reported the cationic initiation of the polymerization of NVC by a variety of transition metal compounds via the formation of π -complex between the vinyl π -bond (CH₂=CH-X) and the transition metal ion centres. On the other hand charge-transfer polymerization of NVC (via the participation of the lone pair of N atom) is also well established in several systems (Baibarac et al., 2007) where PNVC was obtained as coloured polymer. Chen et al. (2000) reported that polymerization of NVC in the presence of [60] fullerene (C₆₀) involved electron transfer between the electron-rich NVC and the acceptor (C_{60}) . In the presence of H₂PtCl₆, polymerization of NVC at elevated temperature occurred via electron transfer from the electron-rich NVC to Pt ions. This process produces an intermediate charged complex leading to the



Probable mechanism for the solid state polymerization of NVC in the presence of H₂PtCl₆

Observed peaks (cm ⁻¹)				
Extracted PNVC	PNVC/Pt	Assignment		
	Nanocomposite			
720	717	Ring deformation of substituted aromatic structure		
744	745	>CH ₂ rocking vibration due to tail to tail addition		
1154	1155	Out of plane deformation of vinylidene group		
1217	1218	C-H in-plane deformation of aromatic ring		
1316	1364	>CH ₂ deformation of vinylidene group		
1452 -1484	1453-1484	Ring vibration of NVC moiety		
1600	1600	C=C stretching vibration of vinylidene group.		
-	1736	C=O stretching vibration of carboxylic acid		
-	2079	Stretching vibration of CO molecule		
3060	2928-3036	=C-H asymmetric stretching of aromatic structure		

Table 1. Observed FT-IR characteristic peaks for PNVC extracted from nanocomposite and PNVC/Pt nanocomposite along with their probable assignments.

Table 2. Binding energies of the PNVC/Pt nanocomposites and Pt nanoparticles.

Binding energy (eV)					
	Pt species	Pt 4f _{7/2}	Pt 4f _{5/2}	Rel. Intensity (%)	
PNVC/Pt	Pt^0	72.03	75.33	39.61	
nanocomposite	Pt ²⁺	73.47	76.77	60.39	
Pt nanoparticle	Pt ⁰	72.12	75.42	38.97	
	Pt ²⁺	73.41	76.71	61.03	

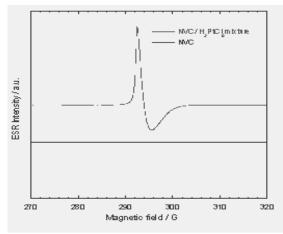


Fig. 2. ESR spectrum of NVC/H₂PtCl₆ mixture.

formation of radical cation and subsequent reduction of Pt ions to Pt nanoparticles. As we know, polaron and bipolaron as charge carriers can be distinguished by the ESR measurements, ESR spectrum of H₂PtCl₆-doped NVC (Figure 2) shows ESR signal whose *g*-value and line width (Δ H_{pp}) are 2.0026 and 1.8 G respectively, indicating the presence of polaron in H₂PtCl₆ and NVC mixture.

Probable mechanism for the solid state polymerization of NVC in the presence of H_2PtCl_6

XPS provides valuable information on the charge transfer between metals and adsorbed ligands at the surface (Qiu *et al.*, 2006). The main peaks observed in the survey scans

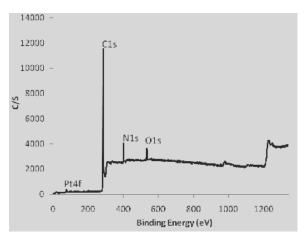


Fig. 3. X-ray photoelectron spectrum of PNVC-Pt nanocomposite.

of the PNVC/Pt nanocomposites and Pt nanoparticles are: Pt 4f, Cl 2p, C 1s, N 1s and O 1s peaks centered around 72, 200, 285, 400 and 530 eV respectively (Figs. 3 and 4). Figure 5 shows the Pt(4f) of the XPS spectrum of Pt in the nanocomposites while figure 6 shows that of the extracted Pt nanoparticles. The Pt(4f_{7/2,5/2}) peaks are usually deconvoluted into three sets of spin-orbit doublet. Accordingly, Pt (4f_{7/2,5/2}) peaks at 71. 1, 74.4; 72.8, 76.1; 74.3, 77.6 eV could be assigned to Pt⁰, Pt²⁺ and Pt⁴⁺ respectively (Liu *et al.*, 2005; Tian *et al.*, 2006). Previous studies (Fu *et al.*, 2001; Tu *et al.*, 2003) showed an influence of the organic ligands on the Pt 4f binding energy of platinum nanoparticles. The Pt 4f binding

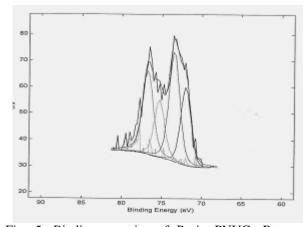


Fig. 5. Binding energies of Pt in PNVC- Pt nanocomposites.

energies in the Pt nanoclusters modified with different ligands (S, N) are 0.5-0.8 eV higher than those of a bulk Pt sample (71.1 eV) (Fu et al., 2001). Table 2 summarizes the distribution of Pt species in the PNVC/Pt nanocomposites and the Pt nanoparticles. From the table, it is evident that platinum occurred in two states (Pt⁰ and Pt^{2+}) in the nanocomposites and the nanoparticles. In the Pt^0 state, the binding energies of $Pt (4f_{7/2})$ and $Pt (4f_{5/2})$ are 72.03, 75.33 eV and 72.12, 75.42 eV in the nanocomposites and nanoparticles respectively, which shift to higher binding energies compared with those of bulk Pt (Pt(4f_{7/2}), 71.1 eV; Pt(4f_{5/2}), 74.4 eV) (Tian et al., 2006). Similarly, the binding energies of $Pt(4f_{7/2,5/2})$ in Pt^{2+} state shifted to higher values (Table 2). On the basis of the areas of peaks, the relative intensities of Pt⁰ and Pt²⁺ were calculated to be 39.61%, 38.97% and 60.39%, 61.03% in the nanocomposites and nanoparticles respectively, this indicates that the majority of Pt species in PNVC/Pt nanocomposites and Pt nanoparticles exist as Pt^{2+} . The shift of binding energies of Pt to higher values is an indication of interaction of Pt with nitrogen which may lead to the formation of polaron in the polymer thereby supporting electron transfer mechanism proposed for the polymerization. The binding energies and relative intensities values of Pt confirmed chemical interaction between Pt and PNVC with the formed Pt⁰ atoms acting as electron donors (Qiu et al., 2006). This is further confirmed by higher relative intensity of Pt²⁺. The C 1s spectra of the nanocomposites and Pt nanoparticles appear to be composed of graphitic carbon (284.8 eV) and a small amount of surface functional groups with high oxygen content (286.5 eV) (Liu et al., 2005). This corroborated the absorption bands of 1736 cm⁻¹ and 2079 cm⁻¹ in the IR spectrum of the nanocomposites corresponding to the stretching vibrations of carbonyl group of carboxylic acid and carbon mono-oxide respectively. The N 1s core-level spectrum of the nanocomposites has been deconvoluted by assigning binding energy 400 eV for the (N^+) polaron species (Kong

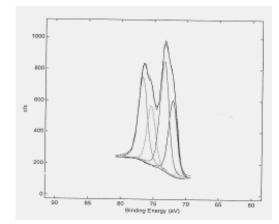


Fig. 6. Binding energies of Pt in Pt nanoparticles.

et al., 2008). This is consistent with the electron-transfer mechanism proposed for the polymerization. From the spectrum, the weight ratios of the elements present in the nanocomposites are as follows: C, 90.5%; Cl, 0.1%; N, 5.8%; O, 3.4% and Pt, 0.2%.

To have insight into the morphology of Pt nanoparticles and nanocomposites, TEM analysis was carried out. Figure 7 shows the TEM micrograph image of the cubic Pt nanoparticles. The "squares", the "triangles", and the "hexagons" represent the cubic, tetrahedral, and the icosahedral and cubooctahedral (depending on their orientation with respect to the electron beam) particles respectively. This image is taken from a randomly chosen part of the substrate and it is a good representation of the overall sizes and shapes of the particles. This pattern of TEM micrograph is similar to those reported earlier for colloidal Pt nanoparticles (Ahmadi et al., 1996). The TEM analysis of the PNVC/Pt nanocomposite showed a preponderance of stringy particles that were transformed into discrete spherical particles during composite formation with PNVC (Fig. 8). This indicates that superimposition of globular polymer particles (dark regions in the photograph) occurred nonuniformly and the tendency towards cluster formation was clearly evident (Maity and Biswas, 2003). The thermogram of Pt nanoparticles, PNVC-Pt nanocomposite and PNVC is shown in figure 9. Two stages of weight loss can be observed in the TG curve (C) of the polymer. The first weight loss between 250 and 360°C may correspond to the evolution of NH₃ (Zhu and Zhu, 2006). The second weight loss appears sharply above 450°C due to the pyrolysis of the polymer. The decomposition pattern of the nanocomposite is similar to that of the polymer. The incorporation of Pt nanoparticles into the polymer increased the thermal stability of the polymer moderately. The decomposition temperature onset of the homopolymer (388°C) increased to 508°C for the PNVC-Pt nanocomposite. It is also interesting to point out that

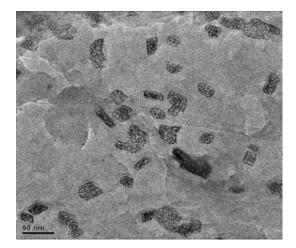


Fig. 7. TEM image of Pt nanoparticle.

the residual weight of the nanocomposite at 600°C was much higher than the total amount of the residual weight of PNVC, that is, the residual weight of PNVC was increased due to the presence of a small quantity of Pt nanoparticles. The different residual weights between PNVC and PNVC-Pt nanocomposites may be another proof of the improvement of the thermal stability of PNVC by Pt nanoparticles. The weight fraction of the polymer in the Pt nanoparticles was also measured with TGA giving a total weight loss of about 27% indicating that the polymer is chemisorbed on the surface of the nanoparticles.

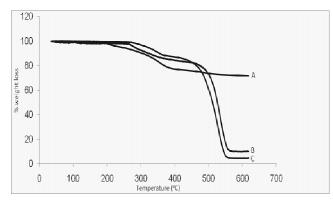


Fig. 9. Thermograms of Pt-nanoparticle (A) PNVC/Pt nanocomposite (B) and PNVC (C).

CONCLUSION

We have successfully prepared PNVC/Pt nanocomposite at elevated temperature by redox reaction between NVC and H_2PtCl_6 as a Pt metal precursor. This technique does not require the use of oxidant as the Pt metal precursor serves both as an oxidizer for NVC polymerization and as a source of Pt in the subsequent cementation of Pt metal on poly(*N*-vinylcarbazole). The synthesis of the PNVC/Pt nanocomposites from the polymerization system was

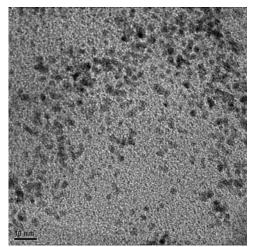


Fig. 8. TEM image of nanocomposite.

confirmed by both FTIR and XPS analyses. TEM analysis was used to confirm the cementation of the *in situ* prepared Pt nanoparticles on the PNVC. The incorporation of Pt nanoparticles into the polymer matrix improved its thermal stability.

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