Characterization of poly(diphenylamine)-gold nanocomposites obtained by self-assembly

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Abstract. Composites of poly (diphenylamine) and gold nanoparticles were chemically prepared from solutions which containing methane sulfonic acid (MSA) with the addition of gold chloride trihydrate as the oxidant as a source for initiation of polymerization and a generation of Au nanoparticles. Poly (diphenylamine) decorated with noble-metal gold nanoparticles were synthesized successfully and exposure of the solutions to caused polymerization of diphenylamine to polymerize with gold salt. The nanocomposites were characterized for the structure, morphology and electronic properties through X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR), Transmission electron microscopy (TEM) and UV–visible spectroscopy.

1. Introduction
Composites are a special class of materials originating from combinations of two or more compounds by a suitable technique, which results in materials having unique physicochemical properties and large potential for application in diverse areas. Novel properties of composites can be derived from successful combination of the characteristics of the parent constituents into a single material. Conventional polymers usually serve as the matrix, which result in a special class of hybrid materials termed “polymeric nanocomposites”. This composite material differs from the pure polymer with respect to some of the physical and chemical properties and hence it is useful for many applications in different field [1]. The synthesizes of polymer metal composites, however, arouse great interest among researchers because of their potential use in technological applications and have attracted much attention recently due to their curious interesting properties [2, 3].

Polymer, metal nanocomposite has received considerable attention due to potential possibilities to create suitable materials for electrocatalysts, chemical sensors and microelectronic devices [4]. In addition, the exceptional uniform shape and the wide range of polymer microspheres further extend their application potential. The metal particles formed on the surface of the polymer microspheres were mainly noble metal particles like rhodium, silver and palladium. This particle not only combine the advantageous properties of metals and polymers but also exhibit many new characters that single-phase materials do not have. To prepare the nanoscale materials successfully, several approaches have been employed like sol-gel technique [5], physical mixing [6], in-situ chemical polymerization in the
aqueous solution with the presence of polymer monomer and inorganic particles [7], sonochemical process [8], and γ-irradiation technique [9].

Poly (diphenylamine), (PDPA) composites and noble metal nanoparticles are currently of great research interest due to numerous applications arising from its good environmental stability and tunable electrical and optical properties [10]. Poly (diphenylamine) is polyaniline substituted derivatives and similar with polyaniline even this polyaniline has been studied exhaustively due to its unique properties and novel applications [11-14]. On the other hand, PDPA, an N-aryl substituted polyaniline, has been found to show many properties which are different from PANI and other N-substituted aniline derivatives [15, 16]. The utility of PDPA are known as sensor for alcohol [17], for modified electrode formation [18], as a glucose sensor [19], for light emitting diodes [20], and as a lithium battery [21] have been established. Such studies have revealed that PDPA can form an effective alternative to PANI, and PDPA is known to have better solubility than PANI [22]. Recent studies [23,24] have attempted to incorporate newer properties into PDPA by grafting a nonconducting polymer onto its backbone. In fact, this creates the possibility of the creation of new polymeric materials with interesting characteristics. Moreover, this technique is easily controlled and adaptable. In the present work, synthesis of poly (diphenylamine)-gold nanocomposites by oxidative polymerization of diphenylamine from a solution containing methanesulfonic acid (MSA) and gold (III) chloride trihydrate as the oxidizing agent and characterized using various techniques.

2. Experimental

2.1. Materials
DPA (diphenylamine), HAuCl₄ (gold chloride trihydrate), APS (ammonium persulfate), MSA (methanesulfonic acid) were obtained from Sigma-Aldrich. All chemicals were reagent grade and used as received. Solutions were prepared using Millipore water obtained from a MILLIPORE water purifying system.

2.2. Preparation of poly (diphenylamine)-gold nanocomposites
A typical polymerization method for poly (diphenylamine)-gold nanocomposites were carried out from a solution of 0.05 mol.L⁻¹ diphenylamine monomer and 0.025 mol. L⁻¹ MSA in deionized water. To this mixture, (0.025 mol.L⁻¹) auric acid was added drop wise to the reaction mixture for about 2 hour under ice cold condition with constant stirring. The polymerization started with the slow addition of auric acid as indicated by the color change of the solution from bluish to the green form immediately. The poly (diphenylamine)-gold nanocomposite was filtered and washed with deionized water, methanol several times. Finally, the obtained product was dried under a vacuum dryer at room temperature for 48 hours.

2.3. Characterization
Transmission electron microscopy images were obtained using a Jeol JEM-1230 electron microscope operated at 120 kV equipped with a Gatan Ultrascan 4000SP 4K X 4K CCD camera. TEM samples were prepared by placing a droplet of a colloid suspension in water on a Formvar carbon coated, 300 mesh copper grid (Ted Pella) and allowed to evaporate in air at room temperature. The X-ray diffraction (XRD) patterns were measured at room temperature with an X’ Pert Philips materials research diffractometer using the CuKαR radiation. Infrared spectra were measured in the range of 400-4000 cm⁻¹ on pellets made with KBR by means of a Perkin Elmer 1600 FTIR spectrophotometer, taking 32 scans at a resolution of 4 cm⁻¹. The optical absorption spectra were measured using a HP-8453 spectrophotometer.
3. Results and Discussion

3.1. TEM analysis of poly (diphenylamine)-gold nanocomposites

The nanocomposites of poly (diphenylamine)-gold was successfully synthesized from an aqueous solution of methanesulfonic acid using HAuCl$_4$ as oxidant by means of a self-assembly process. A typical TEM image of poly (diphenylamine)-gold nanocomposite product is shown in Figure 1. It can be seen that the poly (diphenylamine)-gold nanocomposites were quite uniform in size and morphology. Dark spots of Au nanoparticles on the surface of polymer can be noticed from TEM image with an average size of approximately 5-16 nm.

![Figure 1. TEM images of poly(diphenylamine)-gold nanocomposites (a) and (b).](image)

The elemental gold, reduced from HAuCl$_4$ in the reaction with diphenylamine, precipitated onto the self-assembled PDPA spheres possibly hindering the elongation process of spheres into tubes. The Cl$^-$ anions, produced during reduction of the HAuCl$_4$ may be doping of the PDPA chain as well as doping with methanesulfonic acid. Firstly, the polymer of the composite, PDPA-MSA is amorphous, producing a characteristic ring in the diffraction pattern. Secondly, the Au nanoparticles can be seen in the form of dark spots superimposed on the polymer. Based on the above results, we can conclude that the poly (diphenylamine)-gold nanocomposites consist of amorphous PDPA spheres decorated with Au nanoparticles. This conclusion was further confirmed by XRD experiments.

3.2. XRD characterization of poly (diphenylamine)-gold nanocomposites

The XRD patterns of the self-assembly of polymerization of poly (diphenylamine)-gold nanocomposites prepared by oxidation with HAuCl$_4$. In case of PDPA, the broad peaks centered at $2\theta = 21 \sim 28^\circ$ are observed in the nanocomposites (Figure 2), which are ascribed to the periodicity parallel and perpendicular to the polymer chains of PDPA similar to PANI [25]. In the diffraction pattern of PDPA-MSA/Au nanocomposites of Figure 2, four additional sharp peaks at 38°, 45°, 64° and 78° revealed that represent Bragg’s reflections from the (111), (200), (220) and (311) planes for the presence of gold (Au), respectively [26]. The XRD patterns confirmed presence of poly (diphenylamine)-gold nanocomposites.
3.3. FTIR characterization of poly (diphenylamine)-gold nanocomposites

Figure 3 shows FTIR spectra of poly (diphenylamine)-gold nanocomposites. FTIR spectra of poly (diphenylamine)-gold peaks appear at 1592, 1502, 1303, 1285, 1170, 843, 580 cm\(^{-1}\). The characteristic peaks at 1592 and 1502 cm\(^{-1}\) are attributed to the C=C stretching of quinoid phenyl and benzenoid phenyl rings, respectively [27]. The bands at 1303 cm\(^{-1}\) can be assigned to the C-N modes of the secondary aromatic amine, the bands at 1170 cm\(^{-1}\) to the in-plane bending of C-H [28, 29] and the band at 843 cm\(^{-1}\) corresponds to the C-H out of plane bending vibration respectively [30]. A new peak at 1008 cm\(^{-1}\) related to a C-Cl vibration appears in the FTIR spectra of poly (diphenylamine)-gold is doped with the Cl\(^{-}\) from HAuCl\(_4\).

The relatively broad peak at 3427 cm\(^{-1}\) can be attributed to the N-H stretching vibration mode. In addition, the characteristic bands of the parent PANI, the spectrum showed distinctive broad peaks of the 1005 ~ 1068 cm\(^{-1}\) assigned to the asymmetric and/or symmetric 0=S=0 stretching vibrations. The shifts to the lower energy of these peaks are directly related to the differences in electron density,
which may originate from structural differences of these two materials or Au, as the electron density
 donator makes the electron cloud of PDPA more delocalized.

Table 1. Summarized for FTIR spectral data of poly (diphenylamine)-gold nanocomposites

| Poly(diphenylamine)-gold nanocomposites | Peak Assignment                                      |
|----------------------------------------|-----------------------------------------------------|
| 3427 cm\(^{-1}\)                      | N-H stretching vibration mode                        |
| 1592 cm\(^{-1}\)                      | C=C stretching of quinoid phenyl rings               |
| 1502 cm\(^{-1}\)                      | C=C stretching of benzenoid phenyl rings             |
| 1303 cm\(^{-1}\)                      | C-N modes of the secondary aromatic amine            |
| 1170 cm\(^{-1}\)                      | in-plane bending of C-H                              |
| 1008-1068 cm\(^{-1}\)                 | related to a C-Cl vibration appears in the spectra of PDPA-MSA/Au is doped with the Cl\(^{-}\) from HAuCl\(_4\) |
| 843 cm\(^{-1}\)                       | C-H out of plane bending vibration                   |
| 580 cm\(^{-1}\)                       | absorption of the -SO\(_3\)-H group                  |

3.4. UV-Visible analysis

The UV-Vis absorption spectra of poly (diphenylamine)-gold nanocomposites obtained by chemically synthesized which shown in Figure 4. The characteristic bands of poly (diphenylamine) that appear at 310~370 nm are attributed to \(\pi-\pi^*\) and polaron-\(\pi^*\) transitions, respectively. The bands associated with the PDPA/Au products are located at 370 nm and 570 nm (region of interchain excitation). There is no variation in the position of the band at around 310 ~ 370 nm corresponds to the \(\pi-\pi^*\) transition of the neutral form of PDPA. Conversely, the electronic spectra of composites shows a band at around 570 nm and inform that PDPA is present in the diphenosemiquinoneamine form. This assignment is based on earlier reports on the doping of PANI with acids [31, 32]. PDPA-Au nanocomposites exhibit the surface plasmon resonance absorption band of Au at 520-570 nm.

This is because Au particles are incorporated into the polymer chain. The breadth of the 520 - 570 nm Plasmon resonance peak indicates a vary poly disperse Au nanoparticle solution [33]. Therefore, the wide band should also be attributed to the Plasmon resonance adsorption of Au particles, which provided a piece of evidence for the formation of Au particles. So, the broad absorption should
 originate from combined effect of the benzenoid to quinoid transition and plasmon resonance absorption of the gold particles.

4. Conclusions
We have described a new route for synthesis of poly (diphenylamine)-gold nanocomposites using HAuCl₄ as the oxidant in a solution of methanesulfonic acid. The presence of Au particles was confirmed by transmission electron. XRD study evidenced the presence of Au in the polymer sample in nanometer scale. FTIR spectra showed that the incorporation of gold seems to be easier with methanesulfonic acid. The synthesized nanocomposites can be taken for further application studies, depending upon their properties. Thus, the present work gives a simple and facile method of synthesis of poly (diphenylamine)-gold nanocomposites.

5. Acknowledgements
This work was supported by the BK21 plus program.

6. References
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