proceedings

In-situ preparation of three types of noble metal nanoparticles-polyacrylonitrile nanofibers (NM NPs-PAN NFs, M=Pt, Au, and Ag) using electrospinning technique assisted with ultrasound irradiation

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Abstract:

In recently years, the many alluring methods to prepare the inorganic-organic hybrid nanomaterials have garnered great interest. The in-situ growth phenomenon is the most straightforward way to from these compounds with multiply dimensions. Here in, we demonstrate the in-situ synthesis of noble metal nanoparticles-polyacrylonitrile nanofibers (M NPs-PAN NFs) using electrospinning route. Synthesis includes two main paths in the presence of DMF. In the first path, the M NPs were prepared from the precursor solution using in-situ reduction route in the presence of ultrasound irradiation and DMF (as solvent and weak reducing agent) at 60 °C for 9 min. The mechanism of our second path exhibited that the polymer matrix solution (PAN/DMF) acts as an appropriate host solution for the MNPs, due to possessing high contents of effectiveness groups. These groups not only anchor NM NPs tightly in PAN fibers via dipole-induced dipole interactions but also they stabilize metal nanoparticles by good bonding interaction with their surface atoms. After preparing all nanofibers, TEM images revealed that both M NPs and their related nanofibers have particular and unique shape without agglomerated particles with different sizes. Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and Fourier-transform infrared (FT-IR) were also applied to verify the formation all samples. In this report, we tried to present a preparative synthesis strategy to preparation of nanofibers.

Keywords: In-situ method; Noble metal nanoparticles; Polyacrylonitrile; Electrospinning route.

1. Introduction

Over the past years, polymers and their related metallic compounds have been considered as promising and suitable materials to modify the enhancement energy and resolve the environmental crisis for many applications such as water treatment, air-batteries, and opto-electronics, due to the uniformly structures and their surface properties [1-4]. Several reports have shown that polymers act as stabilizers and hosts for metallic nanoparticles because the functional groups of the polymer chain contain electron-donor functional groups (hydroxyl, amine, etc.) [5,6]. There are many synthetic polymers used to generate a combination between them and metal nanoparticles with specific virtues. Among of those are polyacrylamide (PAA), polyaniline (PANI), poly (vinyl alcohol) (PVA), polyurethane (PU), poly (vinylpyrrolidone) (PVA), etc [7-9]. The ability to firm the metal particles on the surface of the polymer depends on: type of functional groups, particle size, abundance of these groups etc. There are a number of earlier studies on synthesis of metal-polymer such as Ag NPs-PMMA [2], Cu NPs-chitosan [10], Au NPs-polystyrene [11], Pd NPs-poly(3,5-dimethyl aniline) [12], Ag NPs-PVA [13], Cu NPs- poly(o-toluidine) [14], etc. The metal nanoparticles (M NPs)-polymer can be synthesized by various methods such as solvothermal, sonochemical, co-precipitation, electrospinning, and so on.

In this work, we revealed a novel synthetic protocol for the fabrication of noble metal nanoparticles - polyacrylonitrile (NM NPs-PAN, NM NPs=(Pt NPs, Au NPs, and Ag NPs) nanofibers using mixed method in which NM NPs are highly dispersed in a polymer fiber matrix. Moreover, the ultrasound irradiation, electrospinning route, and dimethyleformamide (DMF) were used as the assisted route to form metal nanoparticles and reducing agent for metal ion, respectively. During the reduction reaction, DMF undergoes oxidation and form its related radicals, which act as reducants for metal precursors, whereas the in-situ reduction of metal ions results in the formation of their corresponding zero-valent metal nanoparticles by ultrasound irradiations, the combining of this way with electrospinning way ultimately formation a “NM NPs-PAN” nanofibers material.

2. Experimental Section

2.1. General

All chemicals used were of analytical grade and were used as received.

X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (X’ pert pro. Analytical company) using Cu-Kα radiation. The morphologies of NM-PAN NFs were determined by field-emission scanning electron microscopy (FESEM-ZISS-Sigma VP-Germany) with an acceleration voltage 3 KV, and transmission electron microscopy (TEM-ZEISS- EMIOC, operating at 100 KV). A FESEM equipped with an energy-dispersive X-ray analyzer (Oxford Instrument company-England) were used to determine the morphology and composition the as-prepared samples. FT-IR analysis were carried out on a Shimadzu FT-IR-8400 spectrophotometer using KBr pellet for sample preparation. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation.

2.2. Procedure

Our typical experiment contains two main stages. In the first stage, 1.2g of polyacrylonitrile was dissolved in 10 ml of DMF under continuous stirring for 3h. In the second stage, 0.25g of each raw metallic material was dissolved in 10 ml of DMF under vigorous magnetic stirring for 30 min. Then, this solution (M^{n+}/DMF) was irradiated with an ultrasonic horn for 9 min under air atmosphere at 25 °C. Then the resulted solution, NMPs/DMF, was slowly dropped into the PAN/DMF solution under the continuous magnetic stirring for 25 min at 60 °C. To prepare the electrospun NM NPs precursor PAN nanofibers, the prepared precursor solution was transferred into two syringes with a capacity 10 ml and an inner diameter of 0.8 mm.

3. Result and Discussion

XRD patterns, FT-IR spectra, FESEM images, EDS with SEM-mapping images and TEM micrographs provide the information on the structure of the whole nanofibers.

3.1. XRD patterns

The XRD patterns of the samples (PAN NFs, and NM NPs-PAN NFs; M= Pt, Au and Ag) were depicted in Figure 1. The PAN NFs a single unique and a broad peak diffraction with hexagonal lattice is observed at $2\theta=$

17.84°, which are in good agreement with the results reported by Xu et al [15]. Another two peaks at 17.22° and 27.06° can be related to the amorphous structure of these polymer nanofibers. X-ray diffraction patterns of modified electrospun nanofibers (PAN NFs embedded with three types of noble metals nanoparticles) show other characteristic peaks at different angles, as shown in Figure 1. Table 1 gives a brief of the whole XRD data of all samples. According to Table 1 and Figure 1, XRD data indicate well evidance for the successful rapid in-situ synthesis of PAN nanofibers loaded with noble metal nanoparticles. The intensity diffraction peak of polymer is larger than those diffraction peaks of metal, because the corresponding peaks of metals were covered by polymer peak [15].

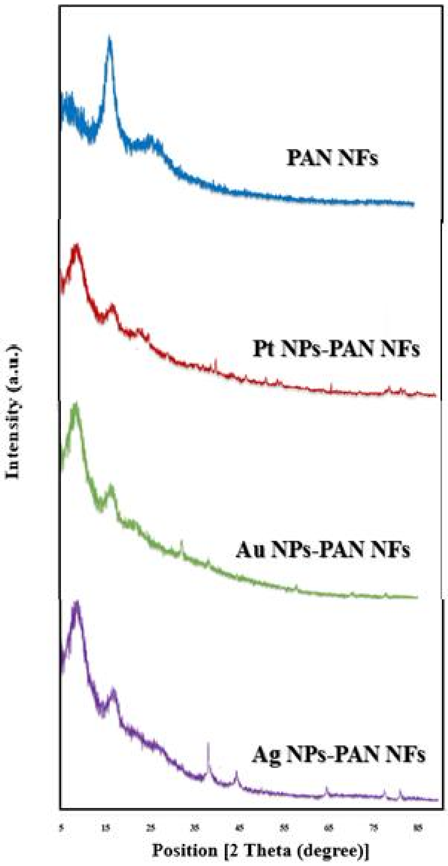

Figure 1. X-ray diffraction pattern of PAN NFs and NM NPs-PAN NFs (M NPs=Pt NPs, Au NPs, and Ag NPs)

Table 1. A brief of observed XRD data of all samples (NM NPs loaded on PAN NFs) with JCPDS cards, the lattice type, and crystallite size calculated by Scherrer formula

No. sample	Position [2 Theta (degree)]	(h k l)	Crystallite size (D, nm)
[1]PAN NFs	17.84, 27.06	(100), (020)	3.42
[2]Pt loaded on PAN NFs	39.92, 46.39, 67.70, 81.07, 86	(111), (002), (022), (113), (222)	50.14
[3]Au loaded on PAN NFs	38.34, 44.44, 64.68, 77.59, 81.93	(111), (002), (022), (113), (222)	19.52
[4]Ag loaded on PAN NFs	38.19, 44.37, 64.55, 77.48, 81.34	(111), (002), (022), (113), (222)	24.93

[1] This hexagonal structure can be indexed to its crystalline data (JCPDS card no. 96-432-8472, a=b=32.49 Å, c=16.32Å)
[2] This FCC structure can be indexed to its crysalline data (JCPDS card no. 96-101-1108, a=b=c= 3.911 Å)
[3] This FCC structure can be indexed to its crystalline data () JCPDS card no. 96-901-1613, a=b=c= 4.065 Å)
[4] This FCC structure can be indexed to its crystalline data (JCPDS card no. 96-101-1608, a=b=c= 4.079 Å)

3.2. Morphology studies

The morphologies of as-synthesized samples were determined by FESEM and TEM micrographs. From Figure 2(A1), we can see that the smooth surface of pure PAN NFs was composed of different nano-size fibers in the range (300-320 nm). Figures 2(B1, C1 and D1) show the FESEM images of the Pt NPs-PAN NFs, Au NPs-PAN NFs, and Ag-PAN NFs, respectively. In all images, after loading NM NPs on the surface of polyacrylonitrile nanofibers, their nanofibers have a relatively rough surface, because the surface of polyacrylonitrile nanofibers was covered by a uniform compact layer of metal particles. TEM results (Figure 2(A2, B2, C2 and D2) are revealed both inner fiber surface and its external. The metal particles are uniformly embedded in both surfaces of the polymer chain.

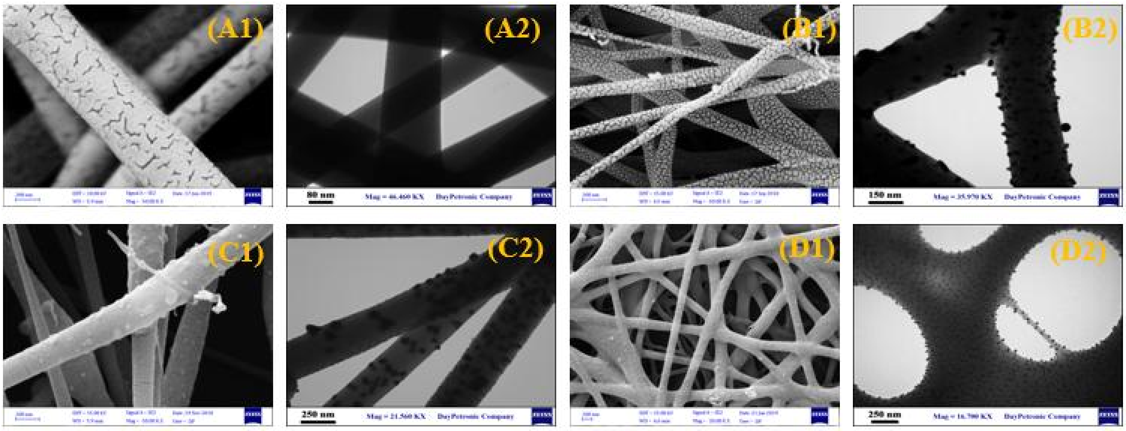

Figure 2. Field emission scanning electron micoscopy (FESEM) images of (A1) PAN NFs, (B1) Pt NPs-PAN NFs, (C1) Au NPs-PAN NFs, (D1) Ag NPs-PAN NFs, and Transmission electron microscope (TEM) images of (A2) PAN NFs, (B2)) Pt NPs-PAN NFs, (C2) Au NPs-PAN NFs, (D2) Ag NPs-PAN NFs

3.3. FT-IR studies

The FT-IR spectra of PAN NFs, and NM NPs-PAN NFs were shown in Figures 3(A-C). As seen in Figure 3(A), the corresponding vibration characteristic of the PAN nanofibers at 1668 cm^{-1} with strong intensity belong to the nitrile group, and the absorption peaks at 3452, 2870-2922, 1452-1460, 1350-1380, 1220-1270, 1093 cm^{-1} are assigned to vibrations modes of OH, the aliphatic CH in CH_2 and CH, respectively. The strong peak at 1988 cm^{-1} is due to C=O stretching, while the observed peak at 2244 cm^{-1} related to the stretching vibration of nitrile group. The vibration frequecies of 1065 cm^{-1} and 1161 cm^{-1} were associated with the symmetrical bending vibration of hydrogen bonds (OH…OH, CN…HO, etc.). These peaks for all groups are much shifted in the (NM NPs-PAN) NFs than the reported peak for PAN at 1988, 2242, and 1668 cm^{-1}[16,17].

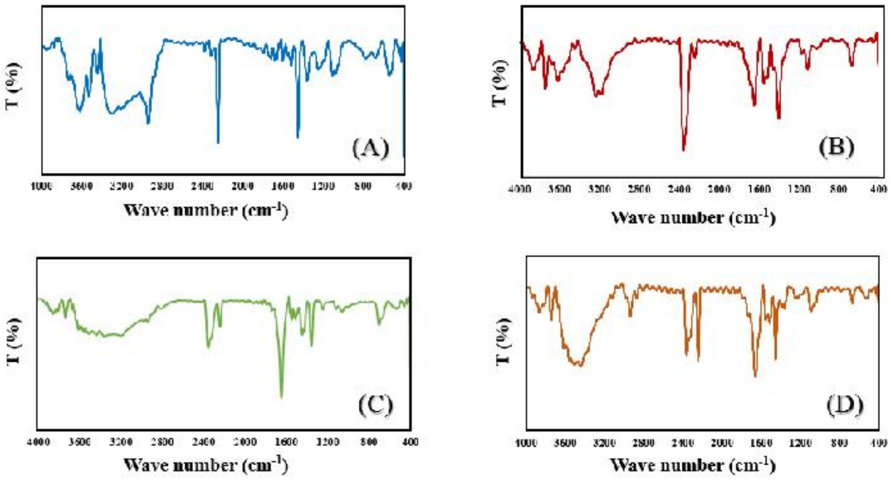

Figure 3. FT-IR spectra of (A) PAN NFs, (B) Pt NPs-PAN NFs, (C) Au NPs-PAN NFs, (D) Ag NPs-PAN NFs

3.3. Elemental alnalysis study

The chemical analysis of the pristinse PAN NFs and NM NPs-PAN NFs enabled by EDS (Figures 4(A-D). By mentioned to results in Figure 4(A), which were derived from PAN NFs, C, N, and O were only found associated with this sample. The nominal chemical compositions of the NM NPs-PAN NFs estimated using the EDS analysis are positioned in Figure 4(B-D), show that all their corresponded metallic elements are in equiatomic proportion.

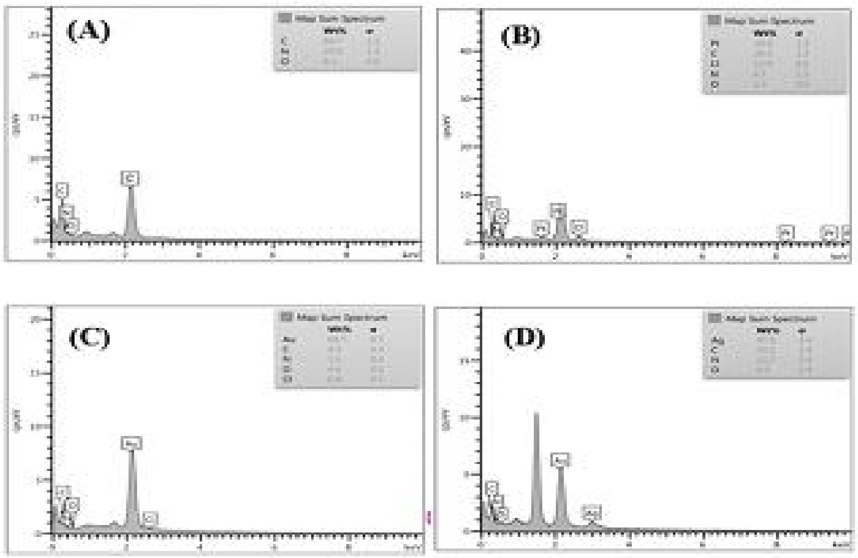

Figure 4. EDS spectra of (A) PAN NFs, (B) Pt NPs-PAN NFs, (C) Au NPs-PAN NFs, (D) Ag NPs-PAN NFs

4. Conclusion

In summary, the synthesis of three types of noble metal nano-particles has been described in polyacrylonitrile nanofibers (NM NPs-PAN NFs) by a simple and easy route (as-called in-situ method). The XRD patterns indicate well defined crystallinity and lattice structure type of all as-prepared nanofibers. The reduction of H_2PtCl_6, $HAuCl_4$, and $AgNO_3$ by DMF in the presence of ultrasound irradiation is considered to be a key step in formation of such system. The particles diameter of the NM NPs by the current methodology is varied that depended on the type of particles. SEM and TEM revealed that the particle dimension is in nanometer regime and the calculations made by the XRD match well with the observations made by TEM. The functional groups such as –CN and hydroxyl groups act as capturing agents by electrostatic interaction and stabilizers them by strong bonding interaction between NM NPs and their polar groups of PAN polymer.

References

1. Bounor-Legare, V., Cassagnau, P. (2014). In situ synthesis of organic–inorganic hybrids or nanocomposites from sol–gel chemistry in molten polymers. *Progress in Polymer Science*, *39*(8), 1473-1497.
2. He, J., Kunitake, T., Nakao, A. (2003). Facile in situ synthesis of noble metal nanoparticles in porous cellulose fibers. *Chemistry of Materials*, *15*(23), 4401-4406.
3. Yang, X., Liu, Q., Zhang, Y., Su, X., Huang, Y., Zhang, T. (2018). In situ synthesis of metal clusters encapsulated within small-pore zeolites via a dry gel conversion method. *Nanoscale*, *10*(24), 11320-11327.
4. Adnan, M. M., Dalod, A. R., Balci, M. H., Glaum, J., Einarsrud, M. A. (2018). In Situ Synthesis of Hybrid Inorganic–Polymer Nanocomposites. *Polymers*, *10*(10), 1129.
5. Singh, N., Khanna, P. K. (2007). In situ synthesis of silver nano-particles in polymethylmethacrylate. *Materials chemistry and physics*, *104*(2-3), 367-372.
6. Guo, Q., Ghadiri, R.1, Weigel, T., Aumann, A., Gurevich, E., Esen, C., etal (2014). Comparison of in situ and ex situ methods for synthesis of two-photon polymerization polymer nanocomposites. *Polymers*, *6*(7), 2037-2050.

7. Panaitescu, D. M., Frone, A. N., Chiulan, I. (2016). Nanostructured biocomposites from aliphatic polyesters and bacterial cellulose. *Industrial Crops and Products*, *93*, 251-266.
8. Zeng, F. R., Xu, J., Xiong, Q., Qin, K. X., Xu, W. J., Wang, Y. X., Zan-Jiao Liu, Zi-Long Lia, Li, Z. C. (2019). Aliphatic polyketones via cross-metathesis polymerization: Synthesis and post-polymerization modification. *Polymer*, 121936.
9. Carrado, K. A., Xu, L. (1998). In situ synthesis of polymer− clay nanocomposites from silicate gels. *Chemistry of materials*, *10*(5), 1440-1445.
10. Haider, S., Kamal, T., Khan, S. B., Omer, M., Haider, A., Khan, F. U., Asiri, A. M. (2016). Natural polymers supported copper nanoparticles for pollutants degradation. *Applied Surface Science*, *387*, 1154-1161.
11. Tian, J., Jin, J., Zheng, F., Zhao, H. (2010). Self-assembly of gold nanoparticles and polystyrene: a highly versatile approach to the preparation of colloidal particles with polystyrene cores and gold nanoparticle coronae. *Langmuir*, *26*(11), 8762-8768.
12. Mallick, K., Witcomb, M. J., Dinsmore, A., Scurrell, M. S. (2005). Fabrication of a metal nanoparticles and polymer nanofibers composite material by an in situ chemical synthetic route. *Langmuir*, *21*(17), 7964-7967.
13. Porel, S., Singh, S., Harsha, S. S., Rao, D. N., Radhakrishnan, T. P. (2005). Nanoparticle-embedded polymer: in situ synthesis, free-standing films with highly monodisperse silver nanoparticles and optical limiting. *Chemistry of Materials*, *17*(1), 9-12.
14. Mallick, K., Witcomb, M. J., Scurrell, M. S. (2006). In situ synthesis of copper nanoparticles and poly (o-toluidine): A metal–polymer composite material. *European polymer journal*, *42*(3), 670-675.
15. Xu, Z., Wei, C., Jin, J., Xu, W., Wu, Q., Gu, J., Xu, X. (2018). Development of a Novel Mixed Titanium, Silver Oxide Polyacrylonitrile Nanofiber as a Superior Adsorbent and its Application for MB Removal in Wastewater Treatment. *Journal of the Brazilian Chemical Society*, *29*(3), 560-571.
16. Alarifi, I., Alharbi, A., Khan, W., Swindle, A., Asmatulu, R. (2015). Thermal, electrical and surface hydrophobic properties of electrospun polyacrylonitrile nanofibers for structural health monitoring. *Materials*, *8*(10), 7017-7031.
17. Wang, H., Zhang, X., Zhang, Y., Cheng, N., Yu, T., Yang, Y., Yang, G. (2016). Study of carbonization behavior of polyacrylonitrile/tin salt as anode material for lithium-ion batteries. *Journal of Applied Polymer Science*, *133*(36).