

Short Communication

A Simple Method To Synthesize Poly(Aminonaphthalene Sulfonic Acid) and Silver Nanocomposite and Its Characterization

Kun-Cheng Ho, A. Balamurugan, Shen-Ming Chen^{}, Kuo-Chiang Lin*

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan (ROC).

*E-mail: smchen78@ms15.hinet.net

Received: 19 August 2011 / *Accepted:* 15 September 2011 / *Published:* 1 October 2011

One-pot preparation of poly(amino naphthalene sulfonic acid) and silver nanoparticles (PANS-AgNPs) has been successfully performed in acidic aqueous condition. Using ANS monomer as a reductant and a particle stabilizer, the reduction of silver ions and polymerization of ANS occurred simultaneously in the absence of a commonly used reducing agent and initiator. Sulfonate group present in the PANS polymer acts as self dopant for polymer and a stabilizing agent. The produced PANS-AgNPs nanocomposite was characterized by UV-Vis spectroscopy and Fourier transform infrared spectroscopy. AgNPs showed its SPR band at 450 nm. AFM image revealed that AgNPs formed along with the PANS with an average particle diameter of 5 nm. The presence of AgNPs-PANS nanocomposite was analyzed by using cyclic voltammetry.

Keywords: Amino naphthalene sulfonic acid, silver nanoparticle, nanocomposite, particle stabilizer, electropolymerization, modified electrode, Electrochemistry

1. INTRODUCTION

Polyaniline [1] is a key material in the family of conductive polymers, and numerous studies have addressed its electrochemical property. Specifically, PANI was employed as redox polymer for the electrochemical activation of redox enzymes and for the development of electrochemical and optical sensors. But, the utility of PANI itself limits its broad use, above pH > 3 specifically in combination with biomaterial since PANI redox functions only in acid media. In order to switch the redox activity of PANI to neutral pH range values in aqueous media, doping of PANI with anionic species such as poly styrene sulfonate (PSS) [2] or through electro- copolymerization techniques self-doped polymers are synthesized by introducing sulfonic acid groups into the polymer backbone. These

negatively-charged groups act as intramolecular dopant anions that are able to compensate positive charges at protonated nitrogen atoms of the polymer backbone, thus replacing auxiliary dopant anions [3].

The preparation of noble-metal nanoparticles (NPs) has attracted extensive interest in modern materials chemistry due to their unique properties such as optical [4], electronic [5], and catalytic functions [6]. Noble metal NPs are particularly interesting due to their close lying conduction and valence bands in which electrons move freely which generate surface plasmon bands [7]. Among the different metals studied to date, silver NPs attract special attention due to their high electrical conductivity, antimicrobial effect, oxidative catalytic functions and unique Raman spectroscopic behavior [8-10]. Variety of reducing agent has been used to prepare AgNPs from its precursor. Conducting polymer monomer like aniline and its derivatives have also been used as reducing agent to AgNPs and obtained conducting polymer–AgNPs composite.

In almost all reported literature for the preparation of polyaniline (its derivatives)-AgNPs nanocomposite the external dopant like sulfonate containing groups have introduced to switch electrochemical properties of polyaniline to neutral pH and as a stabilizer for AgNPs [11]. In order to accomplish polyaniline (its derivatives)-AgNPs nanocomposite without using any external dopant for polymer and/or stabilizer for AgNPs, we have chosen ring substituted aniline derivatives, 5-amino-2-naphthalenesulfonic acid (ANS). The ANS monomer reduces AgNO_3 to silver nanoparticles while undergoing oxidation to form a polymer, PANS. The oxidation potential of ANS [12] (≈ 0.8 V vs Ag/AgCl in acidic condition) is close to that of aniline, which makes it possible for it to be used as a reducing agent in the preparation of AgNPs.

In the present study, we reported that one-pot synthesis of PANS-AgNPs nanocomposite in acidic aqueous condition. The ANS has operated multiple roles which include as both a reducing agent, stabilizer for silver nanoparticles (AgNPs) and sulfonate group present in the ANS acts as a self dopant for polymer. The prepared polymer nanocomposite was exhibited electrochemically active polymer redox couple at neutral pH.

2. EXPERIMENT

2.1. Chemicals

5-amino-2-naphthalenesulfonic acid (ANS), AgNO_3 (Wako), and other chemicals were of analytical grade used as received. Aqueous solutions were prepared using Milli-Q water of 18 M Ω .

2.2. Measurements

Ultraviolet visible (UV-Vis) spectra were recorded on a model U-3300 UV-Vis spectrophotometer (Hitachi). FT-IR spectrum was taken by Perkin Elmer Spectrum GX FT-IR spectroscopy. Atomic force microscope (AFM) images were recorded by Beijing Nano-Instruments CSPM-4000 using tapping mode operation. Rectangle Si_3N_4 cantilevers with a normal force constant,

0.4 N m^{-1} , a radius of less than 10 nm were employed. Electrochemical experiments were performed with CH Instruments (Model CHI-400) using CHI-750 potentiostat. Glassy carbon electrode (geometric area = 0.07 cm^2) obtained from Bioanalytical Systems (BAS) served as a working electrode. Pt wire act as counter electrode and Ag/AgCl with the saturated KCl solution used as reference electrode. Indium tin oxide coated glass electrode (ITO electrode) was used to measure AFM images of PANS-AgNPs nanocomposite.

3. RESULTS AND DISCUSSION

3.1. Synthesis of PANS-AgNPs nanocomposite

Preparation of PANS-AgNPs was carried out in 1 M HNO_3 solution containing 0.01 M AgNO_3 and 2×10^{-3} M ANS. This solution was changed into slight yellow after stirring at room temperature in 15 minutes. The appearance of slight yellow color solution indicates that the formation of silver nanoparticles, which exhibit surface plasmon resonance (SPR) peak at 450 nm [13], as shown in Fig. 1A.

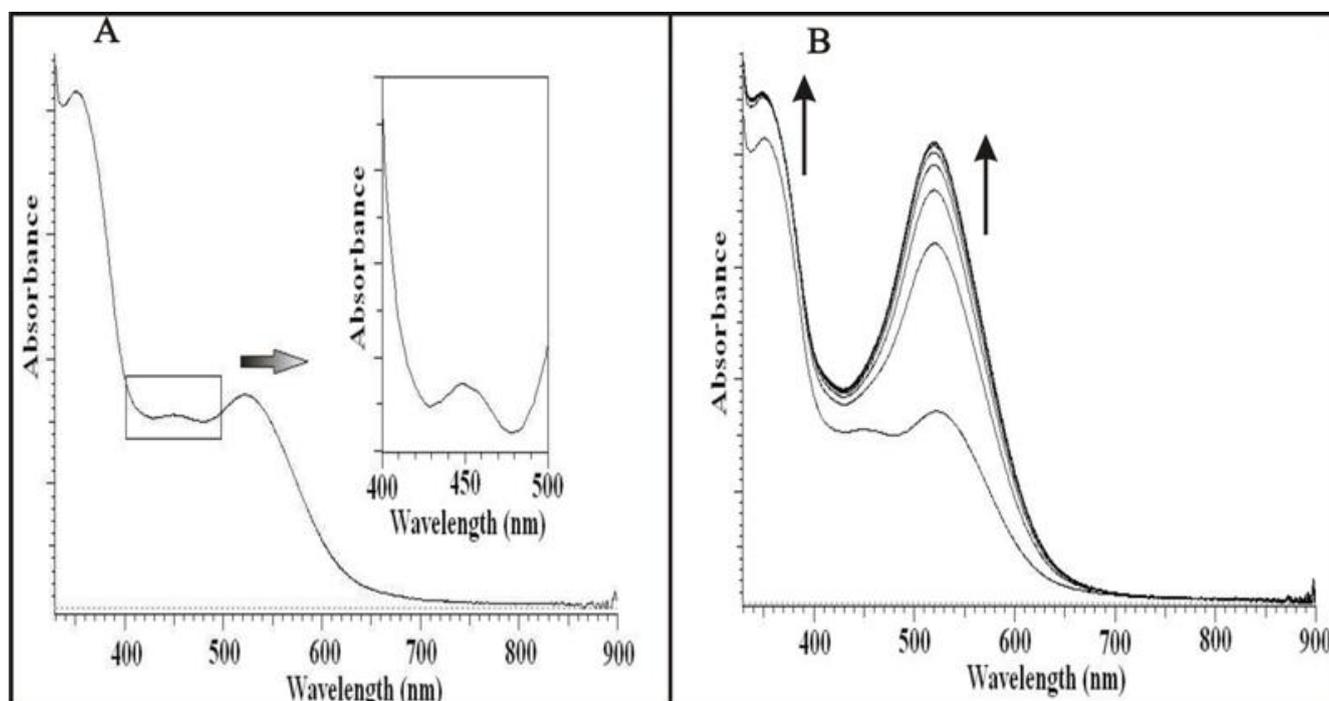
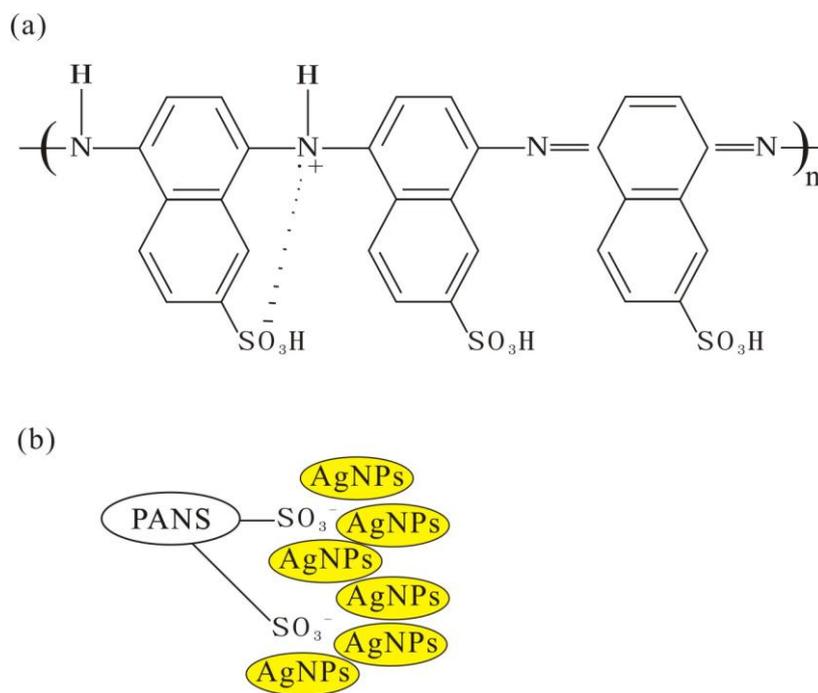


Figure 1. (A) UV-Vis spectra of PANS-AgNPs nanocomposite synthesized using 1 M HNO_3 solution containing 2×10^{-3} M ANS and 0.01 M AgNO_3 . (B) UV-Vis spectra obtained in the formation process of PANS-AgNPs nanocomposite at different time intervals.

For clarity, the magnified image of Ag nanoparticles SPR peak was shown as the inset of Fig. 1A. In addition, another two absorption bands at 340 nm and 530 nm was appeared. These two bands

were used to examine for the formation of PANS (in situ) during polymerization process. These two bands at 340 and 530 nm were associated with characteristics π - π^* transition of benzenoid type rings and n - π^* transition of the quinoid type rings presented in the PANS, in agreement with Singa et al [14]. The mechanism for the formation of polymer, PANS and AgNPs were given in Scheme 1.



Scheme 1. Structure of (a) PANS, poly(amino naphthalene sulfonic acid); and (b) PANS-AgNPs.

The sulfonate group in the PANS acted as both a stabilizer for AgNPs and the negatively charged sulfonate group of PANS acted as self dopant for the polymer to compensate positive charge generated during formation of polymer. Also, sulfonate group in the PANS was very effective to inhibit the agglomeration of AgNPs, the consonance was found with AFM images.

The formation of PANS-AgNPs nanocomposite was followed by UV-Vis spectroscopy at various time intervals as shown in Fig. 1B. When AgNO_3 was added into nitric acid solution containing ANS, the absorption peaks at 355 nm and 540 nm developed and increased gradually with time as shown in Fig. 1B. This result indicates that the simultaneous formation of AgNPs and PANS. However, SPR band of AgNPs at 450 nm appeared during first scanning of UV-Vis spectrum. When increased scanning time, Ag nanoparticle SPR peak was not observed in the composite spectrum probably due to reduction of absorption intensity by the surrounding polymer.

3.2. Morphology of PANS-AgNPs nanocomposite by AFM

From AFM image (Fig. 2), it can be seen that the Ag nanoparticles have white bright fine spheres and uniformly dispersed throughout polymer, PANS, which indicates that the AgNPs were formed along with PANS.

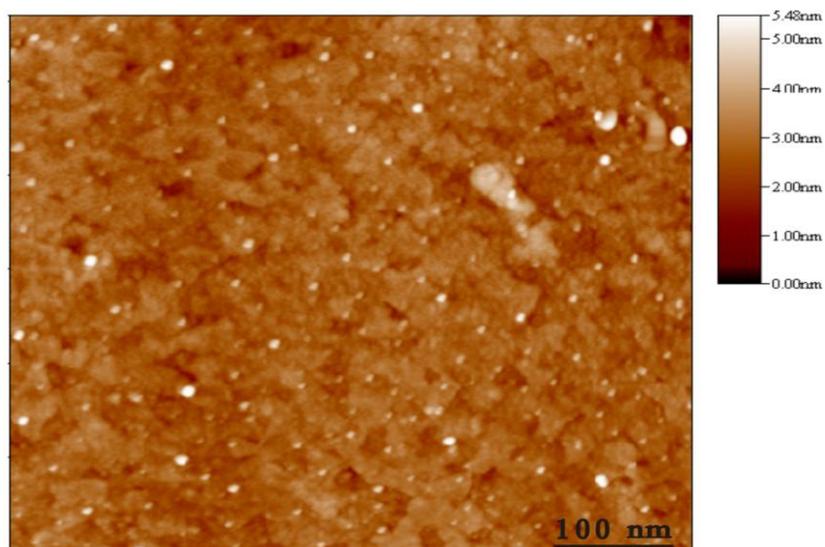


Figure 2. AFM image of PANS-AgNPs nanocomposite.

Also, no apparent aggregation of Ag nanoparticles on the PANS can be observed. These can be explained by the localization effect of PANS sulfonate group with AgNPs. The average diameter of AgNPs was about 5 nm on the basis of the AFM image.

3.3. FT-IR spectrum of PANS-AgNPs nanocomposite

Fig. 3A showed FT-IR spectrum of PANS-AgNPs nanocomposite with strong absorption bands at 1175, 1260, 1485, and 1550 cm^{-1} .

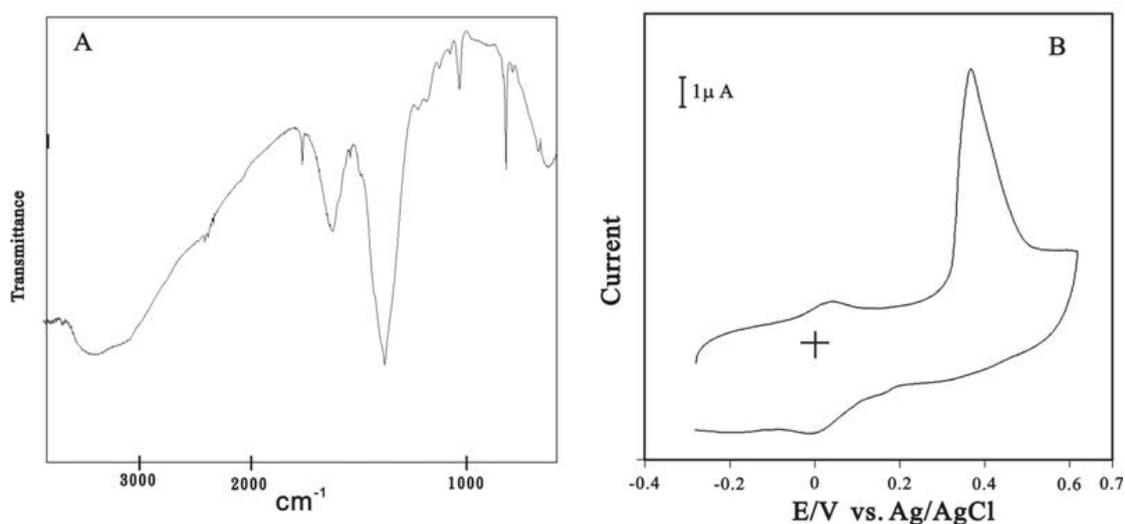


Figure 3. (A) FT-IR spectra of highly stable PANS-AgNPs nanocomposite. (B) Cyclic voltammogram of PANS-AgNPs nanocomposite in 0.1 M PBS (pH 7). Scan rate: 50 mV s^{-1} .

All of the spectra exhibited absorption peaks corresponding to the stretching of quinonoid (1550 cm^{-1}) and benzenoid (1485 cm^{-1}) rings. Finally, the presence of a couple of sharp bands in the $1000\text{--}1030\text{ cm}^{-1}$ range can be clearly related with the presence of sulfonate moieties; the higher frequency feature being assigned to the asymmetric S=O stretching and the low frequency one to the symmetric S=O stretching vibration of those groups [15].

3.4. Cyclic voltammogram of PANS-AgNPs nanocomposite

Fig. 3B shows the cyclic voltammogram of the PANS-AgNPs nanocomposite. There were two redox couples with $E^{0'}$ of 0 V and 0.23 V which corresponding to PANS and AgNPs, respectively. The redox couple at $E^{0'} = 0\text{ V}$ was originated from PANS polymer in accordance with our previous study [12] and the redox couple at 0.23 V corresponding to AgNPs. The small cathodic peak current of silver was due to small adsorption on ITO electrode surface. From above result, it can be concluded that the composite consisting of PANS polymer and silver nanoparticles.

4. CONCLUSION

We presented a simple method to form the PANS-AgNPs nanocomposite while PANS acted as reducing and stabilizing agents. The positive charge of silver ions can be attracted and stabilized by the negative charge PANS to form PANS-AgNPs nanocomposite without other reducing, dopant or stabilizing agents. The mixture of AgNPs and PANS was examined to monitor the formation of PANS-AgNPs nanocomposite by UV-Vis absorption study. This nanocomposite was characterized by the AFM images revealed the Ag nanoparticles of approximately 5 nm in size were well distributed along with polymer. FT-IR result exhibited the specific absorption peaks corresponding to the stretching of quinonoid and benzenoid rings. It was also clearly related with the presence of sulfonate moieties. This nanocomposite can be well modified on electrode surface and exhibited two redox couples corresponding to PANS and AgNPs, respectively.

ACKNOWLEDGEMENTS

This work was supported by the National Science Council of Taiwan (ROC).

References

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