



HAL
open science

Electrochemical Detection of Dopamine at Poly (o-anisidine)/Silver Nanocomposite Modified Glassy Carbon Electrode

D Sangamithirai, V Narayanan, A Stephen

► **To cite this version:**

D Sangamithirai, V Narayanan, A Stephen. Electrochemical Detection of Dopamine at Poly (o-anisidine)/Silver Nanocomposite Modified Glassy Carbon Electrode . Mechanics, Materials Science & Engineering Journal, 2017, 9 (1), 10.2412/mmse.91.86.223 . hal-01500528

HAL Id: hal-01500528

<https://hal.science/hal-01500528v1>

Submitted on 3 Apr 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Electrochemical Detection of Dopamine at Poly (o-anisidine)/Silver Nanocomposite Modified Glassy Carbon Electrode

D. Sangamithirai¹, V. Narayanan², A. Stephen^{1,a}

1 – Materials Science Centre, Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai, India

2 – Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai, India

a – stephen_arum@hotmail.com



DOI 10.2412/mmse.91.86.223 provided by Seo4U.link

Keywords: poly (o-anisidine), silver nanoparticles, electrochemical sensor, dopamine.

ABSTRACT. Poly (o-anisidine) and silver nanoparticles based nanocomposite (POA-AgNPs) modified electrode was used for the electrocatalytic detection of dopamine (DA). POA-AgNPs nanocomposite was synthesized via simple and cost-effective chemical oxidative polymerization method. The composite was characterized by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The face centred cubic structure of silver and the semi-crystalline nature of poly (o-anisidine) is evident from XRD studies. The formation of polymer matrix-type nanocomposite with the embedment of silver nanoparticles is determined from HRTEM. The synthesized POA-AgNPs nanocomposite was found to exhibit electrocatalytic activity towards the detection of DA at a potential of +0.45 V. Under the optimal conditions, the modified electrode showed enhanced catalytic current and a linear response was observed in the concentration range of 10.0-140.0 μM with a detection limit of 0.2 μM (S/N=3). The results revealed the potential application of the fabricated sensor for other such biomolecules.

Introduction. The arrival of conjugated materials with π -conjugated backbones is a landmark in analytical science and they have been widely used as signal-enhancing elements in electroanalytical applications [1]. Conducting polymers consist of a troop of compounds (such as polyaniline, polypyrrole, polythiophene and their derivatives) with very distinct properties which have been employed in many fields of electrochemical research. In recent times, poly (o-anisidine) (POA), a new electrically conducting polymer of polyaniline derivatives have received a significant attention towards electrochemical studies owing to their good electrochemical activity, biocompatibility, cost effective and most importantly its ability to dissolve in common organic solvents [2-4]. However, pure POA had few limitations such as low sensitivity, poor selectivity and interference from other species which is why they have not been commercialized to date. Thus, recently conducting polymer nanocomposites with improved properties have been developed to overcome the limitations of pure conducting polymers.

Silver nanoparticles (AgNps) are extensively used due to their variety of applications including antibacterial activity, inhibition of diseases like HIV and tumor, sensing of various biomolecules, ions and pH [5-7]. Though silver is a promising material, the disadvantages arise by the agglomeration of silver, the primary one being the increase of particle size. These disadvantages can be overcome by the combination of AgNps with conducting polymers in the form of polymer matrix type nanocomposite enabling the growth and spatial arrangement of nanoparticles, which is highly desirable to inquire the peculiar properties and applications of both the moieties.

The major advantage of poly (o-anisidine)-silver nanocomposite is that the drawback brought up by the usage of poly (o-anisidine) and silver separately are overcome. Based on the aforementioned facts,

the present work is focussed on the preparation and characterization of poly (o-anisidine)-silver nanocomposite (POA-AgNPs). The prepared nanocomposite was characterized by XRD and HRTEM. The employment of the prepared nanocomposite towards the detection of dopamine has also been studied and analyzed.

Detection of dopamine (DA) is important since dopamine is a significant neurotransmitter in the mammalian central nervous systems. Several nervous system diseases are found to be encountered due to the dysfunction of DA including Parkinson's disease, schizophrenia and HIV infection [8]. Thus, the sensitive and accurate determination of DA is highly significant in the clinical diagnosis to conveniently trace and treat such diseases. Here, poly (o-anisidine)-AgNPs has been successfully utilized for the determination of DA using cyclic voltammetry.

2. Experimental

2.1 Materials

The o-Anisidine, β -naphthalene sulfonic acid (β -NSA), ammonium persulfate [(NH₄)₂S₂O₈, APS] and dopamine (98% purity) were purchased from Sigma Aldrich. AgNO₃ (99.9% purity) and NaBH₄ were received from Finar reagents. Doubly distilled water was utilized for all the experiments.

2.2 Synthesis of POA-AgNPs Nanocomposite

Silver nanoparticles (AgNPs) were chemically synthesized by reduction of AgNO₃ using NaBH₄. POA-silver nanocomposite (POA-AgNPs) was prepared by insitu polymerization of o-anisidine in the presence of AgNPs. In a typical procedure, a required amount of AgNPs was added to 100 mL of 0.2 M of β -naphthalene sulfonic acid (β -NSA) solution holding 1 mL of o-anisidine monomer and allowed to stir for 30 min. Then, 20 mL of 2.5 g of ammonium persulfate (APS) solution was prepared and added dropwise to the o-anisidine suspension mixture and the solution was continued to stir for 12 h at 5 °C. The obtained dark green product was filtered and washed with methanol and deionized water to remove the impurities. The POA with AgNPs was synthesized under the same conditions.

2.3 Instrumentation

The X-ray diffraction studies of the prepared materials were done by GE X-ray diffraction system – XRD 303 TT. HRTEM was carried out using Tecnai instrument operating at 200 kV. The electrochemical experiments were performed on a CHI 1103A electrochemical instrument comprising of the conventional three electrode system; glassy carbon electrode (GCE), saturated calomel electrode (SCE) and platinum wire was used as working electrode, reference electrode and counter electrode, respectively.

3. Results and Discussion

3.1 Structural Investigation

The XRD patterns of pure POA and POA-AgNPs nanocomposite are shown in Fig. 1 (a) & (b). The XRD pattern of POA (Fig. 1a) shows a medium broad peak centred at $2\theta \sim 12.5^\circ$ and 25.3° , which is a characteristic of the semicrystalline nature of polymer. POA-AgNPs (Fig. 1b) exhibits the presence of peaks corresponding to both poly (o-anisidine) ($2\theta \sim 12.5^\circ$ and 25.3°) and silver ($2\theta \sim 38.2^\circ$, 44.4° and 64.6°). The XRD peaks of AgNPs are in good agreement with the JCPDS card no. 04-0783. The preponderant (111) reflection is indicative of the oriented growth of the silver nanoparticles in FCC structure. The XRD results match well with the reports previously available [7, 9]. The average crystallite size of ~ 8 nm was estimated using Scherrer's formula.

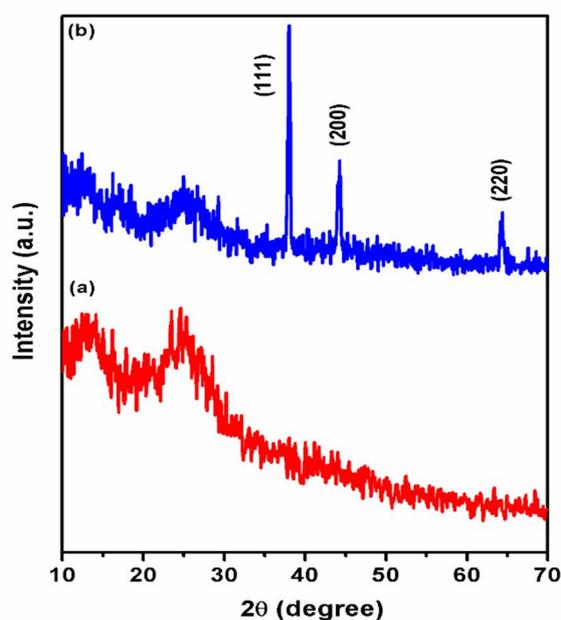


Fig. 1. XRD patterns of (a) pure POA and (b) POA-AgNPs nanocomposite.

3.2 Morphology Studies

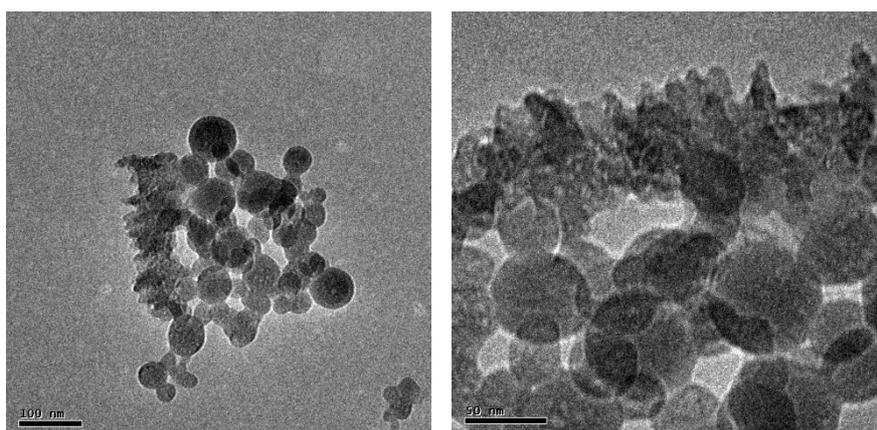


Fig. 2. HRTEM micrographs of POA-AgNPs nanocomposite.

The morphology of POA-AgNPs was studied using HRTEM (Fig. 2). The obtained images revealed the embedment of silver nanoparticles in the polymer matrix. The silver nanoparticles are found to be in spherical shape. The average particle size as measured from the HRTEM image was estimated to be ~ 45 nm. Fig.2 clearly shows the POA matrix in which the silver nanoparticles are embedded (black particles). The studies suggest that the reduction in agglomeration of silver nanoparticles has been efficiently prevented by the presence of polymer matrix in the nanocomposite system.

3.3 Electrochemical sensing of dopamine (DA):

3.3.1 Cyclic Voltammetry

Cyclic voltammograms of dopamine (DA) at the surface of bare GCE and POA-AgNPs/GCE were recorded from the solution of 1.0 mM DA in 0.1 M PBS (pH 7.0) as shown in Fig. 3.

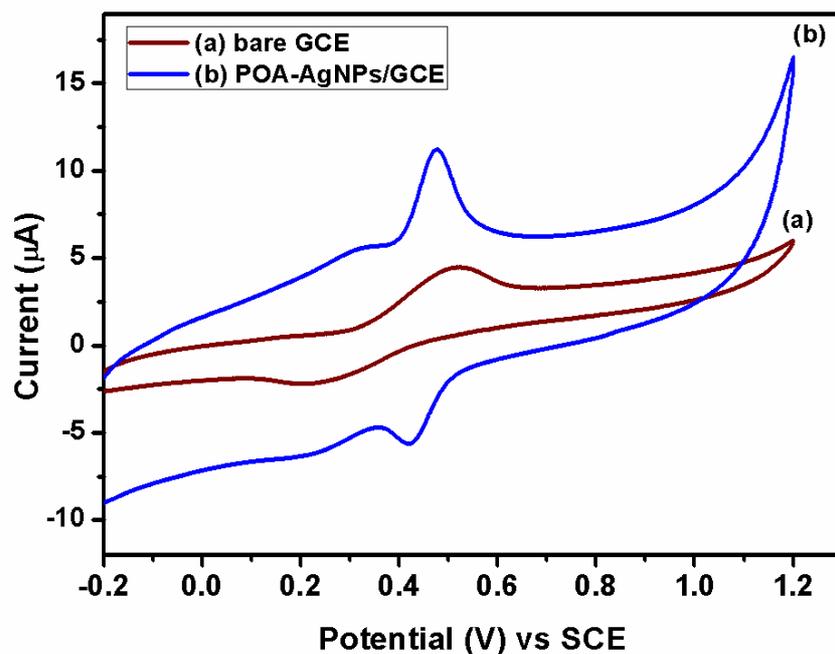


Fig. 3. Cyclic voltammograms of (a) bare GCE/DA and (b) POA-AgNPs/GCE/DA ($[DA] = 1\text{ mM}$; 0.1 M PBS , $\text{pH } 7.0$).

At the surface of bare GCE (Fig. 3, a), DA exhibited a broad and ill-defined reversible peaks with the oxidation and reduction potentials of $E_{pa}=0.522\text{ V}$ and $E_{pc}=0.218\text{ V}$, respectively together with the redox peak currents of $I_{pa}=4.64\text{ }\mu\text{A}$ and $I_{pc}=-2.310\text{ }\mu\text{A}$, respectively. The redox peak currents and the redox potentials of POA-AgNPs/GCE (Fig. 3b) were found to be $I_{pa}=+11.4\text{ }\mu\text{A}$; $I_{pc}=-5.77\text{ }\mu\text{A}$ and $E_{pa}=+0.47\text{ V}$; $E_{pc}=0.415\text{ V}$.

The observed increment in the catalytic response suggests the synergistic effects of POA and AgNPs toward the redox reaction of DA. The obtained results clearly signifies the large surface area, subtle electronic properties of AgNPs and the appreciable ion-exchange characters of POA. The modified POA-AgNPs/GCE not only improved the redox peak currents but also enabled the redox reaction of DA more reversible. This strongly suggests that the hybrid composite of POA and AgNPs have tuned the electron transfer significantly and results in improved response towards the detection of DA while compared to bare GCE.

3.3.2 Differential Pulse Voltammetry

DA. Inset: Calibration plot of concentration of DA vs peak current.

Differential pulse voltammograms (DPV) of POA-AgNPs/GCE in PBS ($\text{pH } 7.0$) was determined with different concentrations of DA and the results are shown in Fig. 4. It is observed that with the addition of DA, a peak around $+0.45\text{ V}$ has emerged. With the increase of DA concentrations, the anodic peak current of DA was apparently increased. From the inset of Fig. 4, linear regression equation of DA detection was found to be $I_{pa} = 1.8963C_{DA}\text{ }\mu\text{M} + 9.63$ with a correlation coefficient of 0.9832 ($n=14$) and the range of linearity was from 10.0 to $140.0\text{ }\mu\text{M}$ with a sensitivity of $6.72\text{ }\mu\text{A}\mu\text{M}^{-1}$. The limit of detection (LOD) of DA at the POA-AgNPs/GCE in 0.1 M PBS ($\text{pH } 7.0$) was $0.2\text{ }\mu\text{M}$ ($S/N=3$). High performance in the detection of DA indicates that POA-AgNPs nanocomposite has significantly improved the electron transfer between DA and GCE.

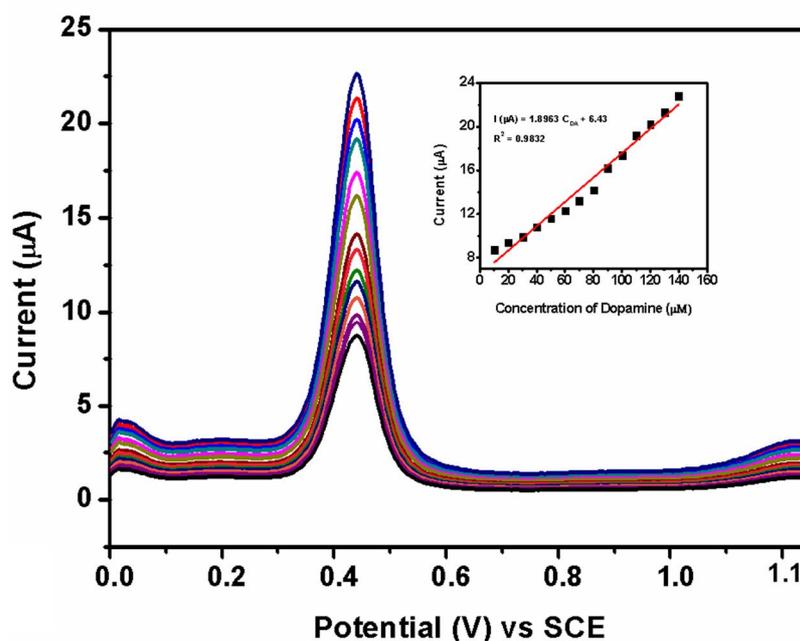


Fig. 4. Differential pulse voltammograms of POA-AgNPs/GCE in 10.0 to 140.0 μM concentration.

Summary. Poly (o-anisidine) and silver (POA-AgNPs) nanocomposite prepared via insitu polymerization method was successfully employed for the detection of dopamine (DA). XRD studies revealed the face centred cubic structure of silver and the semi-crystalline nature of poly (o-anisidine). The embedment of silver nanoparticles in the polymer matrix was evident from HRTEM. The synthesized POA-AgNPs nanocomposite was found to exhibit electrocatalytic activity towards the detection of DA at a potential of +0.45 V. The modified electrode showed enhanced catalytic current and a linear response in the concentration range of 10.0-140.0 μM with a detection limit of 0.2 μM (S/N=3).

Acknowledgement: The author DS thanks DST INSPIRE for the financial support. The authors thank NCNSNT, University of Madras.

References

- [1] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)_x, J. Chem. Soc., Chem. Commun. 1977, 578– 580.
- [2] P.A. Savale, M.D. Shirsat, Synthesis of Poly (o-anisidine)/H₂SO₄ Film for the Development of Glucose Biosensor, Applied Biochemistry and Biotechnology, 159, 2009, 299-309.
- [3] B. Angaleeswari, R.M. Dura Amirtham, T. Jeevithaa, V. Vaishnavi, T. Eevera, S. Berchmans, V. Yegnaraman, Poly (o-anisidine)-anion composite films as sensing platform for biological molecules, Sensors and Actuators B: Chemical, 129, 2008, 558-565.
- [4] D. Sangamithirai, S. Munusamy, V. Narayanan, A. Stephen, Fabrication of neurotransmitter dopamine electrochemical sensor based on poly (o-anisidine)/CNTs nanocomposite, Surfaces and Interfaces, 4, 2016, 27-34.
- [5] J.S. Kim, E. Kuk, K.N. Yu, J.H. Kim, S.J. Park, H.J. Lee, S.H. Kim, Y.K. Park, Y.H. Park, C.-Y. Hwang, Y.K. Kim, Y.S. Lee, D.H. Jeong, M.-H. Cho, Antimicrobial effects of silver nanoparticles, Nanomedicine: Nanotechnology, Biology and Medicine, 3, 2007, 95-101.

- [6] S. Lee, Y.-S. Nam, H.-J. Lee, Y. Lee, K.-B. Lee, Highly selective colorimetric detection of Zn (II) ions using label-free silver nanoparticles, *Sensors and Actuators B: Chemical*, 237, 2016, 643-651.
- [7] E.A.K. Nivethaa, V. Narayanan, A. Stephen, Synthesis and spectral characterization of silver embedded chitosan matrix nanocomposite for the selective colorimetric sensing of toxic mercury, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 143, 2015, 242-250
- [8] C. Zhao, Z. Jiang, X. Cai, L. Lin, X. Lin, S. Weng, Ultrasensitive and reliable dopamine sensor based on polythionine/AuNPs composites, *Journal of Electroanalytical Chemistry*, 748, 2015, 16-22.
- [9] D. Patil, Y.K. Seo, Y.K. Hwang, J.-S. Chang, P. Patil, Humidity sensing properties of poly (o-anisidine)/WO₃ composites, *Sensors and Actuators B: Chemical*, 128, 2008, 374-382.

Cite the paper

D. Sangamithirai, V. Narayanan, A. Stephen (2017). [Electrochemical Detection of Dopamine at Poly \(o-anisidine\)/Silver Nanocomposite Modified Glassy Carbon Electrode](#). *Mechanics, Materials Science & Engineering*, Vol 9. doi:[10.2412/mmse.91.86.223](#)