



Synthesis and Characterization of Metal Oxide Nanocomposites; Application in Electrochemical Detection of Neurotransmitter

S. R. Kiran Kumar¹, K. Yogesh Kumar², H. B. Muralidhara³, M S Raghu⁴, G. P. Mamatha⁵

¹Centre for Nanosciences, Department of Chemistry, K.S. Institute of Technology, Bangalore, India.

²Department of Chemistry, School of Engineering and Technology, Jain University, Jain global campus, Jakkasandra Post, Kanakpura Taluk, Ramanagara, India

³Centre for incubation, innovation, research & consultancy. Jyothy Institute of Technology. Bangalore, India.
Department of Chemistry

⁴New Horizon College of Engineering, Department of Chemistry, Outer Ring Road, Bangalore, India

⁵Centre for incubation, innovation, research & consultancy. Jyothy Institute of Technology. Bangalore, India.

ABSTRACT

ZnO-NiO nanocomposite(NC) has been synthesized by co-precipitation method. This ZnO-NiO composite has been characterized by using, x-ray diffraction (XRD), scanning electron microscope, (SEM). The synthesized composite exhibited a good sensing property and applied for the electrochemical detection of a neurotransmitter, dopamine (DA). ZnO-NiO modified carbon paste electrode (MCPE) showed good catalytic property towards the oxidation of DA. The developed nanocomposite sensor offered high catalytic activity in sensing the dopamine MCPE application in the development of biosensors. The electrochemical responses of 5×10^{-5} M DA and recorded voltammogram at the potential range of -0.2 to 0.6 v vs. SCE in the 0.2 M phosphate buffer of pH 7.2 by Cyclovoltametric technique for both bare carbon paste electrode (BCPE) and MCPE. A good linearity has been observed between scan rate (v) and redox peak current for ZnO-NiO composite MCPE with correlation coefficients of $R = 0.97811$. These results indicated that electron transfer reaction is adsorption controlled. Therefore, ZnO-NiO nanocomposite could serve as an alternative material as sensor material for the electrochemical detection of dopamine.

Keywords : Dopamine, Nanocomposites, Modified Carbon Paste Electrode, Cyclic voltammetry.

I. INTRODUCTION

The scenario at present across the globe is paying much attention for sensitive detection of the neurotransmitters. There has been considerable interest in developing electrochemical techniques have been proven to be significantly advantageous to biosensors and sensing the electrochemical detection of biomolecules [1-6]. Among different semiconductor metal oxide materials as the nanocomposite sensor

offered high catalytic activity and blended oxide permit the possibility of tuning their materials properties according to the necessity for novel application [7-12]. Numerous mixed metal oxide nanoparticles, among that mixed ZnO and NiO nanocomposites (ZnO-NiO'NCs) got extraordinary interests because of its lower expense, higher selectivity, high catalytic activity and the modification of an electrode with ZnO-NiO' NCs can shift voltametric peaks in an analytically useful manner [13-20]. Dopamine (DA) belongs to a member of the

catecholamine family it is a neurotransmitter plays an important role in the functions of the central nervous system and neurological disorders [21, 22]. The amount of dopamine decrease in the brains of patients causes Parkinson's disease and DA played an important role like neurotransmission involves the conversion of an electrical impulse to a chemical event [23, 24]. The developed mixed oxide ZnO-NiO nanocomposites by precipitation method are used for MCPE to study voltametric detection of DA.

II. EXPERIMENTAL

A. Materials and Methods

The sodium hydroxide, NaH_2PO_4 , Na_2HPO_4 , triton X-10, Dopamine hydrochloride, graphite powder, silicone oil, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from SD Fine chemicals, Mumbai, India. The stock solution of 25 mM of dopamine was prepared in 0.1 M perchloric acid, phosphate buffer of pH 7.2 prepared in double distilled water.

B. Preparation of ZnO-NiO nanocomposite

Co-precipitation method has been followed for the preparation of ZnO-NiO nanocomposite. To the cleaned beaker 0.1 molL^{-1} of 1:1 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in water about 40 molL^{-1} triton X-100 was added as capping agent. The NaOH (precipitant) was added slowly to the stirring solution until precipitate appears. The resultant was centrifuged, dried and then powder was further heated to 140°C .

C. Instrumentation

CH Instruments, Austin, USA (CHI 660D) was used for the measurements of cyclic voltammogram. A conventional three electrode system was employed, which consists of a ZnO-NiO modified carbon paste electrode as the working electrode; a saturated calomel electrode (SCE) (reference electrode) and platinum wires (auxiliary electrode) to measure current. XRD patterns were obtained on a Bruker D2Phaser XRD system. SEM was studied using scanning electron microscope (JEOL JSM 840).

D. Preparation of BCPE and ZnO-NiO'ncs MCPE

The bare carbon paste electrode (BCPE) was prepared by addition of appropriate amount of silicon oil and graphite powder and mixed in a mortar to develop a homogenous mixture. The paste was then packed to teflon tube and then smoothed on a emery paper. The copper wire was pierced in to it, dried and used. In the same way ZnO-NiO composite was added appropriately and fabricated ZnO-NiO modified carbon paste electrode.

III. RESULTS AND DISCUSSION

A. Characterization of ZnO-NiO'NCs

The prepared ZnO-NiO'NCs has been subjected for XRD studies, and the XRD pattern is shown in Figure.1. The diffraction peaks like 31.7, 34.4, 36.2, 47.4 are the peaks attributed to ZnO (JCPDS file 80-0075) nanoparticles. On the other hand, it is clear from the diffraction peaks at 43.2, 62.8, 75.1 for NiO (JCPDS -78-0429). The dominance of ZnO over NiO is clearly seen. XRD also shows that ZnO-NiO'NCs is a mixture of two phases: a ZnO-based wurtzite phase and a NiO-based cubic phase with the rock salt structure this confirms the formation of ZnO-NiO'NCs [25]. The sharp diffraction peak in the XRD pattern indicates the crystalline nature and the average crystallite size were found to be 14 nm. Figure.2. shows the SEM micrographs of ZnO-NiO. It demonstrates the interconnected ultrafine particles with nano-sized dimension with agglomeration.

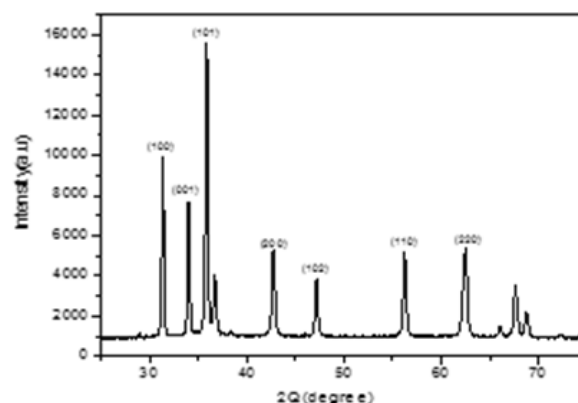


Figure 1. XRD pattern of ZnO-NiO'NCs

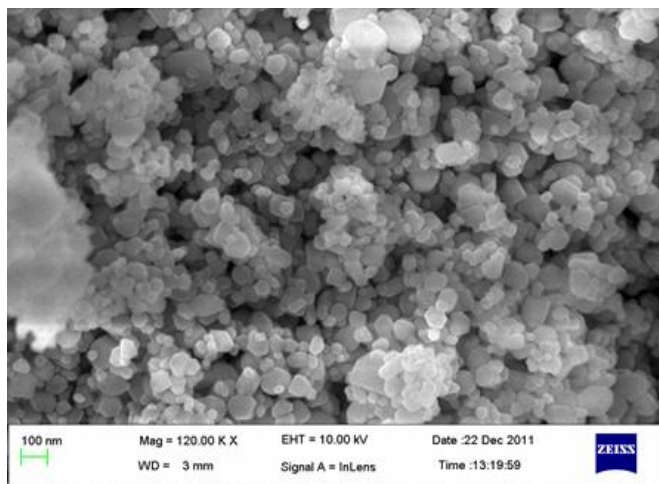


Figure 2. SEM micrographs of ZnO-NiO NC

The chemical composition of ZnO-NiO'NCs was studied by EDX examination. Figure.3. shows EDX spectrum of ZnO-NiO NCs with the insight of wt% of the elements. The compound investigation of the arranged nanocomposites measured by EDX examination demonstrates that just Zn, Ni and oxygen signs have been distinguished, which demonstrated that the nanocomposites are for sure comprised of Zn, Ni and oxygen.

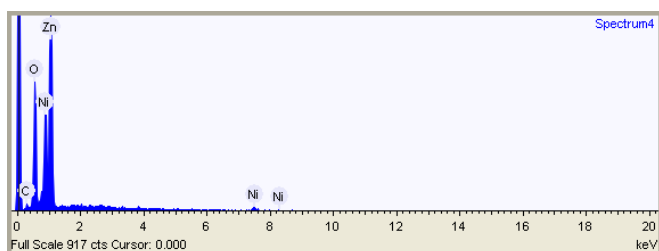


Figure 3. EDX pattern of ZnO-NiO NCs

B. Electrochemical study of DA at BCPE and ZnO-NiO NCs MCPE

The CV studies of 5×10^{-5} M DA in the potential range of -0.2 to 0.6 V in the 0.2 M PBS of pH 7.2 were measured at ZnO-NiO'NCsMCPE. The comparable peak potential differences ΔE_p 0.1136 V for the ZnO-NiO'NCs MCPE are shown in Figure 4. At the BCPE the E_{pa} 0.1046 V and the anodic peak currents significantly increased at the ZnO-NiO'NCs MCPE with the anodic peak potential 0.1100 V respectively.

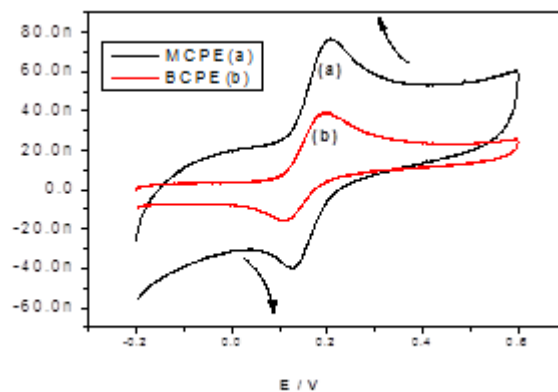
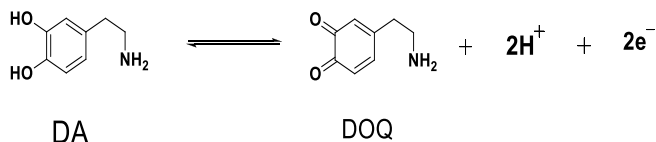


Figure 4. CVs in 0.2 M PBS, pH 7.2 at BCPE and ZnO-NiO'NCs MCPE of DA with scan rate 50 mV s^{-1} .

The result indicates ZnO-NiO'NCs exhibit good electrocatalytic activity than BCPE. Based on the Table .1 results from this study, it is very clear the metal oxide can be effectively used as alternative MCPE for electrochemical sensor for the detection of dopamine and DA undergoes oxidation to form dopaquinone as shown in scheme 1.

Table 1. Comparison of the corresponding peak potential differences ΔE_p of different modified electrodes of various metal oxides synthesized

Electrode	Synthesis method	ΔE_p , V	Technique	References
CuO/MCPE	Hydrothermal	0.1405	CV	26
TiO ₂ /MCPE	Precipitation	0.0487	CV	27
ZnO-CuO/MCPE	Hydrothermal	0.0473	CV	28
NiO/MCPE	Hydrothermal	0.1145	CV	29
GO-CuONCS/MCPE	Modified Hummers	0.0802	CV	30
ZnO/MCPE	Hydrothermal	0.0816	CV	31
ZnO-NiO/MCPE	Precipitation	0.1136	CV	Present work



Scheme 1: Plausible mechanism of oxidation of dopamine

C. Effect of scan rate

The result of scan rate influence on the CV studies for peak current of DA in PBS at pH 7.2 at ZnO-NiO'NCs MCPE. Figure. 5 show an increase in the redox peak current I_{pa} 4.8 A at a scan rate of 0.005–0.250 V s⁻¹ for ZnO-NiO'NCsMCPE. The graph obtained exhibited good linearity between the scan rate and the redox peak current (Figure. 7) for the ZnO-NiO'NCsMCPE with correlation coefficients of R^2 0.978, which indicates that the electron transfer reaction was adsorption -controlled process.

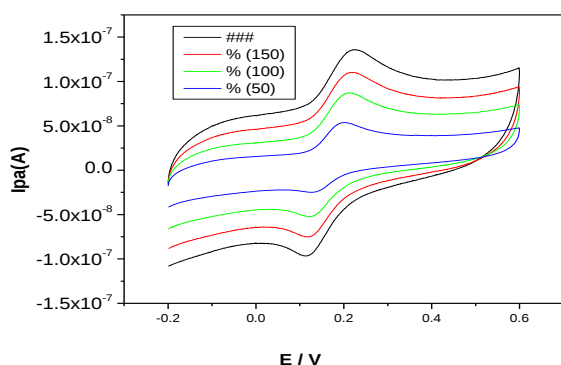


Figure 5. CVs of MCPE in 0.2 M PBS containing 5×10^{-5} M DA at different scan rates.

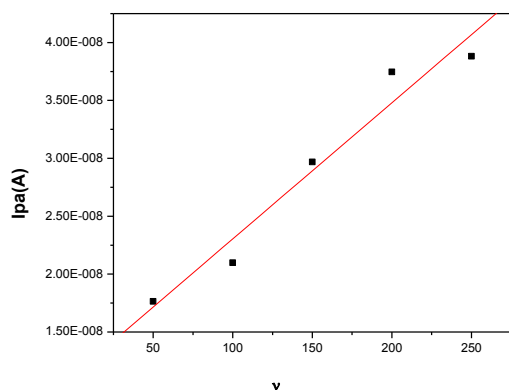


Figure 6. Graph shows the linear correlation between the I_{pa} and scan rate.

D. Interference study

The determine of several extraneous species as interfering compounds with the study of DA in DHI solution was investigated and allowance limit is defined as the upper limit concentration of interfering species that cause an estimated relative error of $\pm 5\%$ for the finding of DA. After the CV studies, we found no major disturbance for the finding of DA in the chosen compounds CaCl_2 4000 μM , NaCl 4000 μM and KCl 5000 μM . Electrochemical response as the peaks remains unchanged after successive 20 cyclic voltammetric scans, confirms ZnO-NiO /MCPE has good stability.

IV. CONCLUSIONS

Simple co-precipitation method has been used for the synthesis of ZnO-NiO metal oxide nanocomposite and characterized by different analytical techniques. This nanocomposite has been used as modified carbon paste electrode for the electrochemical detection of dopamine. ZnO-NiO nanocomposite exhibited enhanced sensing property compared to ZnO nanoparticle alone. The composite exhibited no interference in tables during dopamine sensing. It is expected that it's good electro catalytic behavior the ZnO-NiO'NCsMCPE application in the development of biosensors and electro analytical chemistry. Due to the high stability and repeatability of the ZnO-NiO'NCsMCPE, it has the potential for the future development of nano sensors for clinical research.

V. ACKNOWLEDGEMENTS

The authors wish to thank Dr. B.E. Kumaraswamy, Department of Industrial Chemistry, Kuvempu University, for his invaluable suggestions and moral support. The authors are also thankful to K.S. Institute of Technology, Bangalore for providing lab facility. MSR thank management of New Horizon College of Engineering for support and facilities.

VI. REFERENCES

- [1]. C. Y. Hsu, V. S. Vasantha, P. Y. Chen, and K. C. Ho, *Sensors and Actuators B*, 137, 313 (2009). doi:10.1016/j.snb.2008.11.014.
- [2]. Sathish Reddy, B. E. Kumara Swamy, and H. Jayadevappa, *Electrochimica Acta*, 61, 78 (2012). doi:10.1016/j.electacta.2011.11.091.
- [3]. T. Thomas, R. J. Mascarenhas, C. Nethravathi, M. Rajamathi, and B. E. Kumara Swamy, *J. Electroanal. Chem.*, 659, 113 (2011). doi:10.1016/j.jelechem.2011.05.011.
- [4]. R. Chand, T. Wateri, K. Inoue, H. Kawakita, H. N. Luitel, D. Parajuli, T. Torikai and M. Yada, *Mineral Eng*, 22, 1277 (2009). doi:10.1016/j.mineng.2009.07.007 1277.
- [5]. T. Motsi, N. A. Rowson, and M. J. H. Simmons, *Int J Mineral Process.* 92, 42 (2009). doi:10.1016/j.minpro.2009.02.005 42.
- [6]. C. Y. Chen, C. L. Chiang and C. R. Chen, *Sep Purif Technol.* 54, 396 (2007). doi:10.1016/j.seppur.2006.10.020.
- [7]. C. Tasdelen, S. Aktas, E. Acma and Y. Guvenilir, *Hydrometallurgy*, 96, 253 (2009). Doi:10.1016/j.hydromet.2008.10.006.
- [8]. L. Ai and Y. Zeng, *Chem Eng J*, 215, (2013).doi:10.1016/j.cej.2012.10.059.
- [9]. H. Karimi Maleh, P. Biparva, and M. Hatami, *Biosens. Bioelect.* 48, 270 (2013). doi:10.1016/j.bios.2013.04.029.
- [10]. A.A. Kovalenko, A.N. Baranov and G.N. Panin, *Russ. J. Inor. Chem.*, 53, 1546 (2008). doi:
- [11]. H. Ohta, M. Hirano, K. Nakahara, H. Maruta, T. Tanabe, M. Kamiya, T. Kamiya and H. Hosono, *Appl. Phys. Lett.*, 83, 1029 (2003). doi:10.1063/1.1598624.
- [12]. J. Wang, C. Lee, Y. Chen, C. Chen, Y. Chen, C. Lin and Y. Chen, *Appl. Phys. Lett.*, 95, 131117 (2009). doi:10.1063/1.3232244.
- [13]. R. K. Gupta, K. Ghosh and K. Kahol, *Physica E*, 41, 617 (2009). doi:10.1016/j.physe.2008.10.013.
- [14]. Z. Zhang, C. Shao, X. Li, C. Wang, M. Zhang and Y. Liu, *ACS Appl. Mat. Interf.*, 2, 2915 (2010). doi:
- [15]. D. Han, H. Yang and F. Wang, *Nanosci.*, 11, 146 (2006). doi:.
- [16]. S. Ulubay and Z. Dursun, *Talanta*, 80, 1461 (2010). doi: 10.1016/j.talanta.2009.09.054.
- [17]. S. Alwarappan, G. Liu and C. Z. Li, *Nano Med. Nano. Techno.*, 6, 52 (2010). doi:
- [18]. E. Frackowiak, *Phys. Chem. Chem. Phys.*, 9, 1774 (2007). doi: 10.1039/B618139M.
- [19]. C.C. Hu, W.C. Chen and K.H. Chang, *J. Electrochem. Soc.*, 151, A281 (2004). doi: 10.1149/1.1639020.
- [20]. K. W. Nam, K. H. Kim, E. S. Lee, W.S. Yoon, X.Q. Yang and K. B. Kim, *J. Power Sources*, 182, 642 (2008). doi: 10.1016/j.jpowsour.2008.03.090 642.
- [21]. Grace and B. Bunney, *Dopamine. In Neurotransmitter Actions in the Vertebrate Nervous System*; (Rogawski, M.; Barker, J., Eds.; Plenum Press: New York), 285 (1985). doi: .
- [22]. N. Volkow, G. Wang, L. Maynard, M. Jayne, J. Fowler, W. Zhu, J. Logan, J. Gatley, Y. Ding, D. Wong and N. Pappas, *J. Eating Disorders*, 33, 136 (2003). doi: 10.1002/eat.10118.
- [23]. P. Phillips, G. Stuber, M. Heien, R. Wightman and R. Carelli, *Nature*, 422, 614 (2003). doi:
- [24]. N. Sharma, and E. Richman, *Parkinson's disease and the family: A new Guide*. (Harvard University Press), 2005. doi:
- [25]. K. Y. Kumar, H. B. Muralidhara and Y. Arthoba Nayaka, *J Chem Pharma Res*, 12, 5005 (2012). doi: 10.1109/ICANMEET.2013.6609244.
- [26]. S.R. Kiran Kumar, G.P Mamatha, K. Yogesh Kumar, H.B. Muralidhara, *Springer- Surface Engineering and Applied Electrochemistry*, 52, 469 (2016). doi:
- [27]. S.R. Kiran Kumar, G.P Mamatha, K. Yogesh Kumar, H.B. Muralidhara, *Analytical & Bioanalytical Electrochemistry*, 7, 175 (2015). doi:

- [28]. S.R. Kiran Kumar, G.P Mamatha, K. Yogesh Kumar, H.B. Muralidhara, Journal of Chemical, Biological and Physical Sciences Section-A, (Chemical Sciences), 6, 821 (2016). doi:
- [29]. S.R. Kiran Kumar, G.P Mamatha, K. Yogesh Kumar, H.B. Muralidhara, Journal of Chemical and Pharmaceutical Research, 8, 633 (2016). doi:.
- [30]. S.R. Kiran Kumar, G.P Mamatha, K. Yogesh Kumar, H.B. Muralidhara, Journal of science: Advanced Materials and Devices, 2, 493 (2017). doi: 10.1016/j.jsamd.2017.08.003
- [31]. S.R. Kiran Kumar, G.P Mamatha, K. Yogesh Kumar, H.B. Muralidhara, Journal of Chemical, Biological and Physical Sciences Section-A, (Chemical Sciences), 8, 28 (2017).