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Short Communication

Highly Sensitive Electrochemical Sensing Platform for Hydrazine Detection

*Jianmian Deng**, *Shujun Deng and Yingbo Liu*

School of Environment and Municipal Engineering, North China University of Water Conservancy and Electric Power, Zhengzhou 450011, China
*E-mail: dengdengjd_power@163.com

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In the present study, the *Plectranthus amboinicus* leaf extract was employed for the biosynthesis of ZnO nanoparticles (NPs). Then, a novel electrochemical sensor was fabricated based on the ZnO NP-coated glassy carbon electrode (GCE) and used for the detection of the organic pollutant hydrazine. Our proposed sensor showed high electrocatalytic activity, selectivity, sensitivity, and stability towards the determination of hydrazine. The factors for the high activity sensor include an optimal electronic property, a high charge transfer rate, a high electroactive surface area, along with its nanocrystalline nature.

Keywords: Hydrazine; Biosynthesis; ZnO NPs; Electrochemical determination; Sensor

1. INTRODUCTION

In recent years, hydrazine has been extensively used in aerospace, military, pharmacological, agricultural, and industrial applications and thus has gained considerable interest [1]. In addition to the application in rocket systems as a fuel, hydrazine has many other utilities, including photographic chemicals, metal film manufacturing, pharmaceutical intermediates, and pesticides. [2, 3]. On the other hand, hydrazine also shows certain toxicity levels and poses harm to the human health, including the irreversible deterioration of the nervous system, creation of blood abnormalities, and brain, liver, and DNA damage [4-6]. For the determination of the hydrazine concentration, many different routes have been reported, such as spectrophotometry [7], fluorimetry [8], potentiometry [9] and chemiluminescence [10]. The electrochemical strategies have been accepted as promising substitutes for hydrazine analysis, which consider the facile and low-cost operating procedures, portability, rapid methodologies, high selectivity, etc. [11]. However, analytical applications still cannot be satisfied by the direct oxidation of hydrazine using a bare electrode because of the high overpotentials and sluggish electrode kinetics [12]. Therefore, many different chemically modified electrodes (CMEs) have been reported and used for the detection of hydrazine [3, 13-20], where the oxidation current response can be enhanced and the overpotentials lowered. Despite the desirable catalytic activity of most modifiers to the electro-oxidation of hydrazine, a relatively narrow linear range is usually obtained. Thus, highly conductive modifying material and highly precise and sensitive analytical techniques must be developed for the effective detection of hydrazine [21-24].

Compared with the bulk, semiconductor nanoparticles (NPs) are characterized by distinct electronic, photo-electrochemical, chemical, and optical features; thus, their synthesis has been attracting large numbers of researchers in the material science field over the past two decades [25]. One semiconductor, zinc oxide, has a large exciton binding energy of 60 meV and a band gap energy of 3.37 eV. Nanosized ZnO shows distinct electrical and optical properties and has been considered a favourable multitasking metal oxide [26, 27]. Many different applications have been proposed for ZnO, including photocatalysts, photodetectors, photodiodes, piezoelectric transducers, solar cells, UV-light emitting diodes, memory devices, and sensors. [28-31]. The common synthesis methods of ZnO nanoparticles (ZnO NPs) are as follows: a wet chemical method [32], a vapour phase process [33], a hydrothermal technique [34], and precipitation and sonochemical routes [35, 36]. Unfortunately, these techniques require the use of complex process control, high-cost devices and even toxic chemicals, which necessitates the development of an eco-friendly and facile strategy for the synthesis of ZnO NPs.

A green method for metal or metal oxide NPs formation is characterized by the application of materials such as bacterial, fungi, and plant extracts, which pose no harm to the environment [37]. Sangeetha et al. [38] proposed the use of the leaf extract of *Aloe barbadensis miller* to synthesize ZnO NPs, where the ZnO NPs showed an average size of 25 - 40 nm and a polydispersed property. Jayaseelan et al. [39] used the *Aeromonas hydrophila* (a reproducible bacteria) as a green reducing and capping agent for the synthesis of ZnO NPs. The results showed that the obtained ZnO NPs had an oval, spherical shape, and the average size was 57.72 nm. In addition, Vanathi et al. [40] presented the synthesis of ZnO NPs using a reducing agent of *Eichhornia crassipes* (an aquatic weed). Therefore, the use of a natural product for the synthesis of metal oxide nanoparticles is a wise choice, not only to produce large numbers of nanoparticles but also to eliminate the environmental impact.

Plectranthus amboinicus, a tender fleshy perennial plant with an oregano-like flavour and odour, belongs to the *Lamiaceae* family. Its biogenic synthesis behaviour was studied by Ajitha et al. [41], where the leaf extract of this plant was used as a reducing agent for the synthesis of Ag NPs. The obtained Ag NPs were found to be highly antimicrobial. The present study reported the state-of-the-art biosynthesis of ZnO NPs with the leaf extract *Plectranthus amboinicus* as the reducing agent. Then, a series of measurements were carried out for the as-prepared ZnO NPs. In addition, a sensing platform that was constructed based on the ZnO NPs was used for the ultrasensitive detection of hydrazine.

2. EXPERIMENTS

2.1 Materials

Plectranthus amboinicus plants were purchased from a local nursery in Zhejiang province, China and have been taxonomically identified and authenticated by the botanical survey of the

Hangzhou botanical garden. Initially, the *plectranthus amboinicus* leaves were cleaned using doubly distilled water. Following this, 5 g of leaves were washed with water and cut into small pieces. After boiling in water (30 mL) for 15 min, these leaves were left to cool. Afterwards, the collected extract was filtered through a filter paper (Whatman No. 1). Before use, these leaf samples were stored in a refrigerator. Alternatively, methyl red (MR) and zinc nitrate hexahydrate ($Zn(NO_3)_2$•$6H_2O$) were commercially available in Sigma-Aldrich. All other test reagents were of analytical grade and used without further purification.

2.2 Biosynthesis of the ZnO NPs

An aqueous solution of zinc nitrate (0.1 M) was synthesized with 30 mL water. This step was followed by the addition of the *plectranthus amboinicus* leaf extract (10 mL). The obtained mixture was continuously stirred for 240 min at 80°C. After centrifugation, a precipitate with a pale white colour was yielded. The obtained precipitate was then washed using ethanol and water. After annealing in a furnace for 60 min at 200°C, the resulting product (ZnO NPs) was collected.

2.3 Electrochemical Measurements

All electrochemical experiments were carried out using a CHI 660D electrochemical workstation in a conventional three-electrode assembly at ambient temperature. A 3.0-mm-diameter glassy carbon electrode (GCE) was polished using alumina slurries (0.5 μm), followed by successive sonication in water, ethanol, and water. The test catalyst ink was synthesized using ethanol, ZnO NPs, and Nafion (5 %). The working electrode was prepared by depositing a certain volume of the obtained ink onto the as-cleaned GCE (loading: 1.27 mg/cm^2). Additionally, the reference and counter electrodes were a Ag/AgCl (in saturated KCl) electrode and a Pt coil, respectively. In addition, the test electrolyte was 0.1 m KOH.

3. RESULTS AND DISCUSSION

Visual observations have confirmed the generation of ZnO NPs during the biosynthesis process. In brief, the colourless $ZnNO_3$ solution was converted into a pale white solution within ~ 60 min after adding the leaf extract. The reaction lasted for almost 240 min at 80°C, which is a lower value than those reported previously [39, 42, 43]. A UV-vis spectrum (UVS) also provided evidence for the generation of ZnO NPs (Figure 1). A significant typical absorption peak was observed at 375 nm, corresponding to the biosynthesized ZnO NPs. It can be seen that the formed ZnO NPs showed a slight redshift in the absorption band possible due to the presence of surface biomolecules from the *plectranthus amboinicus* leaf extract [44-47].

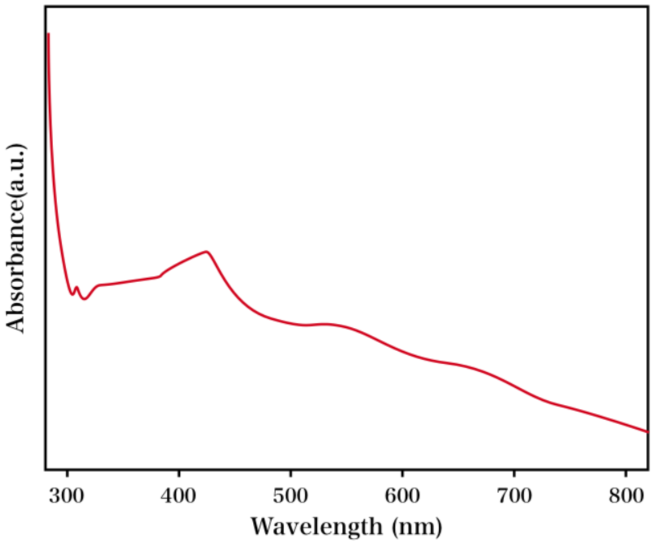

Figure 1. UVS recorded for the obtained ZnO NPs.

An EDX spectrum was recorded for the obtained ZnO NPs (Figure 2A) with corresponding elemental zinc and oxygen signals. In addition to a high intense peak, P showed a minute weak peak, associated with the binding of biomolecules to the obtained ZnO NPs. Additionally, weight percentages of 23.55% and 75.12% were estimated for the oxygen and zinc, respectively. The result indicated that the formed ZnO NPs had a high purity.

The obtained ZnO NPs were also characterized via XRD, as shown in Figure 2B. It can be seen that the as-prepared ZnO NPs exhibited high purity and a crystalline structure. The peaks observed at 31.77°, 34.41°, 36.22°, 47.985°, 56.54°, 63.12° 67.95° and 69.01° were associated with the (100), (002), (101), (102), (110), (103), (112) and (201) reflection lines of hexagonal wurtzite ZnO (JCPDS 36-1451), respectively. No impurity related diffraction peaks were observed, which suggested that the highly pure ZnO NPs could be generated using our developed preparation route. Therefore, the biosynthesis of ZnO NPs using *plectranthus amboinicus* leaf extract as a reducing agent could be considered a green chemical method compared with other routes [48-52].

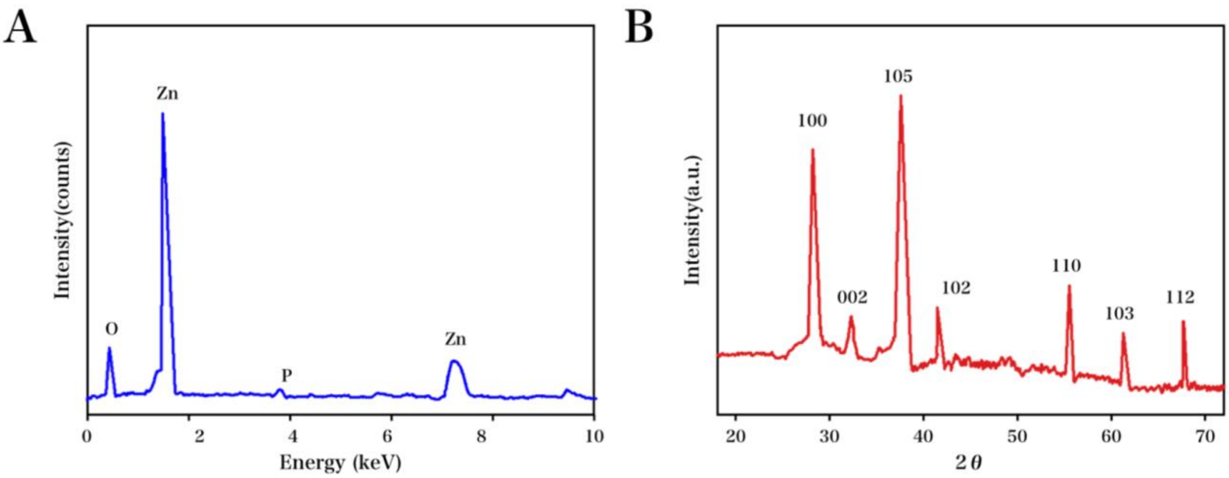

Figure 2. (A) EDX spectrum and (B) XRD profile for the obtained ZnO NPs.

Detailed information was presented on the electrochemical oxidation of hydrazine using the ZnO NPs/GCE. CVs were recorded for hydrazine in a 0.1 M pH 7 PBS solution using the bare GCE and the ZnO NPs/GCE (scan rate: 50 mV/s), as shown in Figure 3. When using the ZnO NPs/GCE, a sharp and well-defined oxidation peak was observed for the hydrazine. In contrast, an insignificant current response was observed for hydrazine oxidation when using the bare GCE. The ZnO NPs/GCE showed an ~ 11 times higher oxidation peak current than that of the bare GCE. The undesirable voltammetric response observed using the bare GCE can be explained by the slow charge transfer kinetics. The presence of biomolecules from the *Plectranthus amboinicus* extract absorbed on the formed ZnO NPs could be used for hydrazine absorption during the electrochemical determination. Therefore, the ZnO NP-modified GCE could effectively enhance the charge transfer rate between the electrode and the analyte. In addition, it can be presumed that the ZnO NPs have the potential use as an effective electrocatalyst for the oxidation of hydrazine.

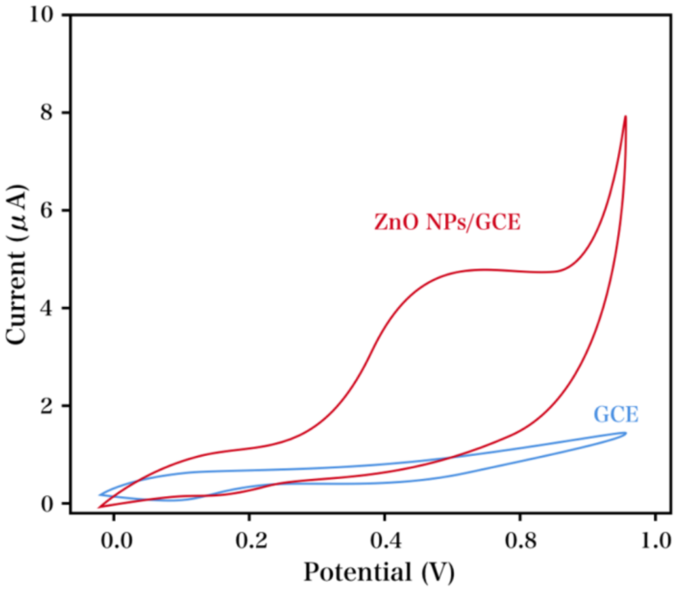

Figure 3. CV response recorded for hydrazine (100 μM) in a 0.1 M pH 7 PBS solution using the bare GCE and ZnO NPs/GCE. Scan rate: 50 mV/s.

The electrocatalytic oxidation of hydrazine at the ZnO NPs/GCE was performed using chronoamperometry in 0.1 M pH 7 PBS. Figure 4A shows the chronoamperograms of the ZnO NPs/GCE towards 50 μM hydrazine at varying potentials. In addition, at the applied potential of 0.78 V, the current response reached the maximum value. As shown in the chronoamperometry of Figure 4B, the current response was sharply increased with an increase in the hydrazine concentration in the electrochemical cell (0.78 V). In addition, the current response recorded at the ZnO NPs/GCE was found to be linearly related to the hydrazine concentration over a range of 20 nM – 4000 μM with a detection limit of 0.14 nM. Therefore, for the electrocatalytic oxidation of hydrazine, the ZnO NPs/GCE could be considered an excellent electrode material. The ZnO NPs/GCE sensor is more sensitive and has lower detection limit towards hydrazine than other materials previously reported for hydrazine detection, as given in the Table 1.

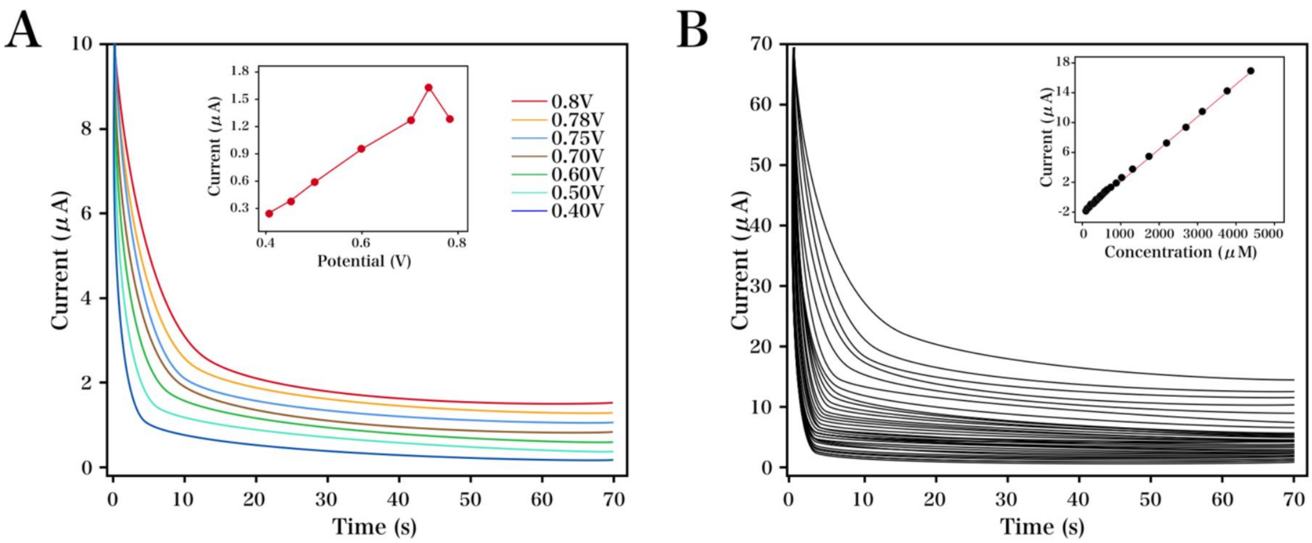

Figure 4. (A) Effect of potential on the chronoamperogram of 50 μM hydrazine in 0.1 M pH 7 PBS using the ZnO NPs/GCE. (B) Chronoamperograms recorded for hydrazine (20 nM – 4000 μM) in 0.1 M pH 7 PBS using the ZnO NPs/GCE.

We further investigated the sensor reproducibility and stability. The reproducibility was studied by fabricating five ZnO NPs/GCEs and recording their current response towards 10 μM hydrazine. For hydrazine, the relative standard deviation (RSD) was calculated to be 2.2%, which suggested a high reproducibility for our developed construction technique. To study the long-term stability, the sensitivity of the sensor to 20 μM hydrazine was investigated for 20 days. The as-prepared sensor was stored in refrigerator, with its sensitivity was analysed at an interval of 0.13 days. For the same hydrazine concentration, the electrode showed almost the same chronoamperometry response with an RSD of 4.7%. Therefore, it can be seen that the developed sensor was highly stable. The sensor selectivity to the electrochemical detection of hydrazine was studied by chronoamperometry experiments with varying interferents. We also tested hydrazine in the tap water. GC-MS was used as a comparison method. The results are presented in Table 2. It can be seen that the proposed ZnO NPs/GCE can be effectively used for determination of hydrazine in water samples.

Table 1. Comparison of the analytical performance for hydrazine detection using various nanomaterials or nanocomposites by electrochemical approaches.

Electrode	LOD	Reference	Electrode	LOD	Reference
MWCNT/Chlorogenic acid	8 nM	[53]	Hierarchical micro/nano architectures/ZnO	0.25 nM	[54]
CNT powder microelectrode	-	[55]	Pristine ZnO NRs array	0.2 nM	[56]
Ag-ZnO Nanoellipsoids	0.07 nM	[57]	ZnO NPs/GCE	0.14 nM	This work

Table 2. Detection of hydrazine in tap water using the proposed electrochemical method and GC-MS.

Sample	Added (µM)	GC-MS (µM)	ZnO NPs/GCE (µM)	RSD (%)
1	10	9.98	9.92	4.32
2	50	50.22	48.87	3.66
3	100	103.54	102.44	4.21

4. CONCLUSIONS

This report presented the *Plectranthus amboinicus* involved preparation of ZnO NPs in 300 min at 80°C. Our developed synthesis technique is simple, economically viable, and could be scaled up; therefore, it has an edge on those reported previously. In addition, the results in this study provided some insight into the preparation of metal oxide nanoparticles using *Plectranthus amboinicus*. Additionally, our proposed ZnO NPs/GCE was employed for the detection of the organic pollutant hydrazine and was found to be highly electrocatalytic, sensitive, selective and stable towards the analysis of hydrazine.

References

1. C. Wang, L. Zhang, Z. Guo, J. Xu, H. Wang, K. Zhai and X. Zhuo, *Microchim. Acta.*, 169 (2010) 1.
2. B. Fang, C. Zhang, Z. Wei and G. Wang, *Electrochimica Acta*, 55 (2010) 178.
3. E.F. Perez, G.D.O. Neto, A.A. Tanaka and L.T. Kubota, *Electroanalysis*, 10 (2015) 111.
4. J. Li, H. Xie and L. Chen, *Sensors & Actuators B Chemical*, 153 (2011) 239.
5. Q. Yi, F. Niu and W. Yu, *Thin Solid Films*, 519 (2011) 3155.
6. D. Yu, L. Wei, W. Jiang, H. Wang, B. Sun, Q. Zhang, K. Goh, R. Si and Y. Chen, *Nanoscale*, 5 (2013) 3457.
7. A.A. Ensafi and B. Rezaei, *Talanta*, 47 (1998) 645.
8. A. Safavi and A.A. Ensafi, *Anal. Chim. Acta.*, 300 (1995) 307.
9. J.W. Mo, B. Ogorevc, X. Zhang and B. Pihlar, *Electroanalysis*, 12 (2000) 48.
10. K. Ravichandran and R.P. Baldwin, *Anal. Chem.*, 55 (1983) 1782.
11. R. Ojani, J.B. Raoof and B. Norouzi, *Electroanalysis*, 20 (2008) 1378.
12. G. Wang, A. Gu, W. Wang, Y. Wei, J. Wu, G. Wang, X. Zhang and B. Fang, *Electrochemistry Communications*, 11 (2009) 631.
13. X. Luo, J. Pan, K. Pan, Y. Yu, A. Zhong, S. Wei, J. Li, J. Shi and X. Li, *Journal of Electroanalytical Chemistry*, 745 (2015) 80.
14. R. Channon, M. Joseph, E. Bitziou, A. Bristow, A. Ray and J. Macpherson, *Anal. Chem.*, 87 (2015) 10064.
15. C. Chen, L. Jacobse, K. Mckelvey, S. Lai, M. Koper and P. Unwin, *Anal. Chem.*, 87 (2015) 5782.
16. B. Zhou, J. Yang and X. Jiang, *Mater. Lett.*, 159 (2015) 362.
17. Z. Zhao, Y. Sun, P. Li, W. Zhang, K. Lian, J. Hu and Y. Chen, *Talanta*, 158 (2016) 283.
18. S. Wang, X. Xu and X. Zhang, *Chemistry Letters*, 44 (2015) 642.
19. S. Zhao, L. Wang, T. Wang, Q. Han and S. Xu, *Appl. Surf. Sci.*, 369 (2016) 36.

20. M. Wu, *Analytical Letters*, 48 (2015) 1551.
21. Y. Liu, S.S. Chen, A.J. Wang, J.J. Feng, X. Wu and X. Weng, *Electrochimica Acta*, 195 (2016) 68.
22. A. Benvidi, M. Nikmanesh, M.D. Tezerjani, S. Jahanbani, M. Abdollahi, A. Akbari and A. Rezaeipoor-Anari, *Journal of Electroanalytical Chemistry*, 787 (2017) 145.
23. X. Gao, C. Du, C. Zhang and W. Chen, *Chemelectrochem*, 3 (2016) 1266.
24. S. Samanta and R. Srivastava, *Journal of Electroanalytical Chemistry*, 777 (2016) 48.
25. M. Daniel and D. Astruc, *Chemical Reviews*, 104 (2004) 293.
26. A. Al-Ghamdi, O.. Al-Hartomy, M. El Okr, A.M Nawar, S. El-Gazzar, F. El-Tantawy and F. Yakuphanoglu, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 131 (2014) 512.
27. L. Ismail, M. Emara, M. El-Moselhy, N. Maziad and O. Hussein, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 131 (2014) 158.
28. W. Water, S. Chu, Y. Juang and S. Wu, *Mater. Lett.*, 57 (2002) 998.
29. A. Ahmad and J. Walsh, *Journal of Materials Science*, 38 (2003) 4325.
30. M.H. Habibi and M.H. Rahmati, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 137 (2015) 160.
31. R. Saleh and N.F. Djaja, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 130 (2014) 581.
32. H.N. Tien, V.H. Luan, L.T. Hoa, N.T. Khoa, S.H. Hahn, J.S. Chung, E.W. Shin and S.H. Hur, *Chem. Eng. J.*, 229 (2013) 126.
33. L.-C. Chao, P.-C. Chiang, S.-H. Yang, J.-W. Huang, C.-C. Liau, J.-S. Chen and C.-Y. Su, *Applied Physics Letters*, 88 (2006)
34. B. Li, T. Liu, Y. Wang and Z. Wang, *Journal of Colloid and Interface Science*, 377 (2012) 114.
35. S.-H. Hu, Y.-C. Chen, C.-C. Hwang, C.-H. Peng and D.-C. Gong, *J. Alloy. Compd.*, 500 (2010) L17.
36. A.H. Moharram, S.A. Mansour, M.A. Hussein and M. Rashad, *Journal of Nanomaterials*, 2014 (2014) 1.
37. P.R. Rathi Sre, M. Reka, R. Poovazhagi, M. Arul Kumar and K. Murugesan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 135 (2015) 1137.
38. G. Sangeetha, S. Rajeshwari and R. Venckatesh, *Mater. Res. Bull.*, 46 (2011) 2560.
39. C. Jayaseelan, A.A. Rahuman, A.V. Kirthi, S. Marimuthu, T. Santhoshkumar, A. Bagavan, K. Gaurav, L. Karthik and K.V.B. Rao, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 90 (2012) 78.
40. P. Vanathi, P. Rajiv, S. Narendhran, S. Rajeshwari, P.K.S.M. Rahman and R. Venckatesh, *Mater. Lett.*, 134 (2014) 13.
41. B. Ajitha, Y. Ashok Kumar Reddy and P. Sreedhara Reddy, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 128 (2014) 257.
42. H. Abdul Salam, R. Sivaraj and R. Venckatesh, *Mater. Lett.*, 131 (2014) 16.
43. G. Singh, P.K. Babele, A. Kumar, A. Srivastava, R.P. Sinha and M.B. Tyagi, *Journal of Photochemistry and Photobiology. B, Biology*, 138 (2014) 55.
44. L. Fu and Z. Fu, *Ceramics International*, 41 (2015) 2492.
45. L. Fu, Y. Zheng, Q. Ren, A. Wang and B. Deng, *J. Ovonic Res*, 11 (2015) 21.
46. S. Vijayakumar, G. Vinoj, B. Malaikozhundan, S. Shanthi and B. Vaseeharan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 137 (2015) 886.
47. Y.-S. Chen, H.-M. Yu, J.-J. Shie, T.-J.R. Cheng, C.-Y. Wu, J.-M. Fang and C.-H. Wong, *Bioorganic & Medicinal Chemistry*, 22 (2014) 1766.
48. S. Muthulingam, K.B. Bae, R. Khan, I.-H. Lee and P. Uthirakumar, *Journal of Environmental Chemical Engineering*, 4 (2016) 1148.
49. P. Sutradhar and M. Saha, *Journal of Experimental Nanoscience*, 11 (2016) 314.
50. B. Sundarakannan and M. Kottaisamy, *Materials Letters*, 165 (2016) 153.

51. X. Zhang, J. Wu, G. Meng, X. Guo, C. Liu and Z. Liu, *Applied Surface Science*, 366 (2016) 486.
52. A. Di Mauro, M. Zimbone, M.E. Fragalà and G. Impellizzeri, *Materials Science in Semiconductor Processing*, 42 (2016) 98.
53. A. Salimi, L. Miranzadeh and R. Hallaj, *Talanta*, 75 (2008) 147.
54. Y. Ni, J. Zhu, L. Zhang and J. Hong, *CrystEngComm*, 12 (2010) 2213.
55. Y. Zhao, W. Zhang, H. Chen and Q. Luo, *Talanta*, 58 (2002) 529.
56. J. Liu, Y. Li, J. Jiang and X. Huang, *Dalton Transactions*, 39 (2010) 8693.
57. R. Kumar, D. Rana, A. Umar, P. Sharma, S. Chauhan and M.S. Chauhan, *Talanta*, 137 (2015) 204