



Onion based zinc oxide nanoparticles ability as electrochemical sensor

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This work describes the preparation of zinc oxide nanoparticles (ZnO NP) from onion extract through a combination of microwave irradiation and muffle furnace in less than 2 h. Characterization with UV-visible, FTIR, and XRD has confirmed successful formation of nanoparticles. TEM analysis displays the nanoparticles to be spherical shaped with an average size of 6.4 nm. The developed ZnO NP film displays good sensing capability of dopamine and had an oxidation potential of + 0.3 V. Under optimized conditions (pH and scan rate), the ZnO NP-GCE is stable even at 500 rpm, showed good linearity in sensing dopamine within the tested range of 3.9-250 μ M, has a limit of detection of 3.53 μ M and stable electrocatalytic activity even after 30 cycles. The newly developed electrode can distinguish dopamine in a satisfactory way in presence of ascorbic acid and glucose and with 94.9 % of detection in human urine. This study also highlighted the potential of IO Rodeostat (an open source electrochemical workstation) as a feasible option in low resource laboratories to perform sensing studies.

Keywords: Onion extract, Zinc Oxide nanoparticles, Glassy carbon electrode, Dopamine, IO Rodeostat

In recent years, nanomaterials are the major interest for researchers due to their immense advantages across various fields¹⁻³. There are various strategies such as chemical process, plant extracts etc. that can be employed to prepare a nanomaterial. In view of sensor development, nanomaterials using chemical approach are only exploited. However, the limitation lies in the practical preparation process i.e. it is not simple. Hence there is a need for easy preparation of nanomaterials and at the same time display sensitivity and selectivity for target biomolecules in presence of interfering components.

To this end, nanomaterials (gold silver, zinc, copper etc.) prepared using plant extracts (apart from fungal, microbial systems) as reactive species is a process that is simple, economical and straightforward to pursue⁴⁻⁶. They were mostly studied for their antimicrobial properties, environmental applications etc.⁷. Surprisingly, materials prepared from these sources were not exploited in biosensor development. This motivated us to explore their potential as working electrode.

As a proof-of-concept, in this study, we choose zinc Oxide (ZnO) as nanomaterial due to its prominent properties such as biocompatibility, antibacterial, etc.^{8,9} and onion extract due to its ease of availability, economical and presence of secondary metabolites that act as reactive species for nanoparticle synthesis¹⁰. As a target molecule, dopamine (DA), a widely known

neurotransmitter was chosen. In literature, DA was detected using chemical approach prepared nanomaterials such as carbon derivatives¹¹⁻¹³, metal-carbon derivative composites¹⁴⁻²⁰, metal-polymer composites^{18, 21, 22}, polymer-carbon derivatives^{20, 23, 24}, metals themselves or in combination²⁵⁻²⁸ etc. In all these studies, electrochemical sensing experiments were conducted using electrochemical workstations that are expensive and not affordable by research labs with low resource settings. Currently, there are two open source potentiostats (IO Rodeostat and cheapstat), which according to the manufacturers could serve as alternatives. In this work, we studied the potential of IO Rodeostat as electrochemical workstation for DA sensing.

The prepared ZnO nanoparticles (NP) from onion extract were characterized and casted as a film on glassy carbon electrode (GCE). Fig. 1 provides the overview of this study i.e. ZnO NP formation, and DA sensing using ZnO NP film with the help of IO Rodeostat. To the best of our knowledge, this is the first report that used a nanomaterial prepared from plant extract as working electrode and IO Rodeostat as electrochemical workstation.

Materials and Methods

Reagents and instrumentation

Zinc nitrate, dopamine (DA), ascorbic acid (AA), glucose (Glu), sodium monobasic, sodium dibasic,

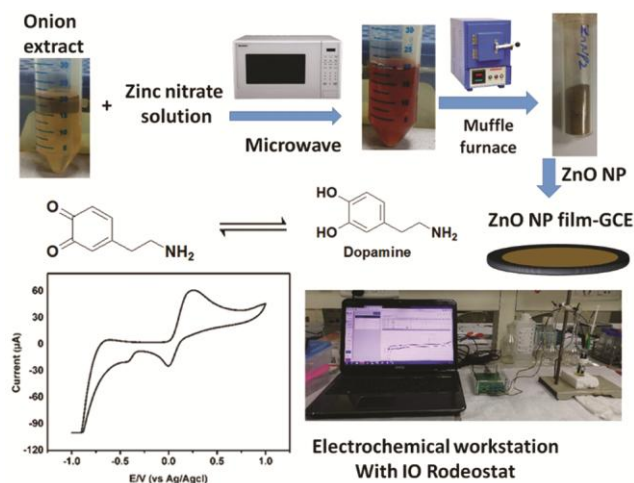


Fig. 1 — Schematic overview of dopamine sensing on ZnO NP film-GCE

ethanol, and Whatman filter paper were all purchased from Sigma Aldrich (Bangalore, India). Milli Q water was used in all experiments to prepare buffer solutions and washing of the electrode.

Characterization of the prepared Zinc Oxide (ZnO) NP was carried out using UV-visible spectroscopy (Beckman coulter DU-730, USA), Fourier transform infra red (FTIR) spectrometry (Shimadzu IR-Affinity 1, Shimadzu scientific, Japan), transmission electron microscope (TEM; Tecnai, G² 20 Twin, FEI company, USA), powder X-Ray Diffraction (XRD; D8 advance, Bruker, Germany) and BET (Brunauer–Emmett–Teller) nitrogen (N₂) sorption (Autosorb IQ, Quantachrome instruments, USA). Electrochemical based studies were performed with IO Rodeostat (an open source potentiostat) workstation connected to the three electrode systems: glassy carbon electrode ($\varnothing = 3$ mm) as working electrode, Ag/AgCl electrode (model no. CHI111) as reference electrode and platinum electrode (model no. CHI102; $\varnothing = 2$ mm) as counter electrode. Fig. S1 depicts the schematic image of our electrochemical workstation.

Onion extract preparation

Onions were purchased from local vegetable market. 500 g of skin peeled onions were chopped into small pieces and made into a paste using a blender. To this onion paste in a 1000 mL plastic beaker, 300 mL of milli Q water was added and mixed well to obtain a slurry, which was transferred to a 1000 mL round bottom flask. Subsequently, the slurry was refluxed at 65–75 °C for 90 min. Once the slurry temperature reached to 25–30 °C it was centrifuged at 5000 rpm (temperature: 20 °C) for

15 min. The resulting extract was re-filtered using Whatman filter paper in a separation funnel and stored in refrigerator until further use.

Zinc Oxide NP preparation and characterization

Onions are rich with many secondary metabolites such as flavonoids, polyphenols, etc. that act both as reducing and capping agents during ZnO NP preparation. Apart from being with less water content, the ease of extracting the secondary metabolites efficiently into aqueous stream make it preferable to work for NP preparation. 3 g of zinc nitrate aqueous solution (15 mL) was added slowly to a 28 mL solution of aqueous onion extract with constant mixing. The mixture was then subjected to heating in microwave oven at 360 W for 5 min 30 sec. Subsequently, the obtained solution was subjected for heating in a muffle furnace at 200 °C for 90 min, which resulted in ZnO NP as brown coloured powder. ZnO NPs were characterized using various analytical techniques (UV-visible, FTIR, XRD, TEM and BET analysis) as mentioned in literature^{29–31}.

Preparation of electrode

Prior to preparation, the electrode was polished using 0.05 μm alumina powder followed by rinsing with milli Q water and dried with a hair dryer. In parallel to this a finely powdered 6 mg of ZnO NPs were suspended in 1 mL of ethanol solution and sonicated for 3 h. From this, a 5 μL solution was added on the electrode and left it to dry in room temperature. Once the solution was evaporated, the electrode was heated with hair dryer to evaporate any remaining traces of ethanol. The resulting ZnO NP film was studied for its electrochemical sensing ability of dopamine.

Electrochemical studies

All electrochemical experiments were performed in a 10 mL glass cell using Ag/AgCl as counter electrode, platinum electrode as reference electrode and ZnO NP film as working electrode. Cyclic voltammetry (CV) measurements were performed with IO Rodeostat (an open source potentiostat) as electrochemical workstation. 0.1 M phosphate buffer (PB) with pH 7 was the chosen buffer with a scan rate of 0.5 V/s and voltage range of -1 to +1 respectively. In case of pH influence studies, citrate buffer was used for pH 3 only whereas for pH's 5, 6, 7, 8 and 9, 0.1 M PB was used. Concentration experiments were done in the range of 0.25 to 0.002 mM i.e. 250–2 μM , and different scan rate experiments were performed in the

range of 0.5-0.05 V/s. Hydrodynamic CV experiments were done under optimized conditions and stirring 0.25 mM DA solution at different RPMs (100, 200, 300, 400 and 500). Selectivity experiments were done using two interfering molecules (ascorbic acid and glucose) in presence of DA. In case of biological sample i.e. urine, 1 mL of urine was mixed with 9 mL of 0.1 M buffer. To this solution 39 μ M DA was spiked to study determine DA detection recovery.

Results and Discussion

Zinc Oxide nanoparticle preparation and characterization

In recent years, synthesis of metal oxide NPs³²⁻³⁴ are performed using microwave irradiation over thermal process because of its minimal equipment requirement and preparation time. In this work, we employed a two-step process i.e. microwave irradiation followed by muffle furnace heating to prepare ZnO NP from pre-prepared aqueous onion extract. After microwave irradiation for 5 min 30 sec, the colour of the solution turned dark brown (Fig. S1A). However, in absence of zinc nitrate solution the colour stayed pale brown even after microwave irradiation (Fig. S1B). Subsequent muffle furnace heating has resulted in a dark brownish powder, which was analysed further with UV-visible, FTIR,

XRD and TEM. Fig. 1 depicts the obtained graphs with these analytical techniques. Using the same protocol, two more batches of ZnO NP were prepared and characterized with FTIR, and XRD as well (Fig. S3-S4).

Fig. 2a depicts the UV-visible spectra of both onion extract itself and ZnO NP in water. From this image, it is clear that onion extract has maximum absorbance at 425 nm only. Reaction of onion extract with zinc nitrate under microwave irradiation and muffle furnace heating has resulted in two wavelengths (295 nm and 305 nm). These values are within the range of literature reported values of 230-370 nm^{29-31, 35} and confirm that ZnO NPs are formed. The reason for observing two close UV-peaks in our approach could be the ability of ZnO to display different band energies with varying temperatures³⁶. Here in this work, the solution containing both onion extract and zinc nitrate was first subjected to microwave irradiation followed by muffle furnace treatment. These are two different temperature treatments. Hence we hypothesize that the ZnO NPs prepared in our approach had displayed two peaks in the absorption spectrum. Fig. 2b depicts the FTIR spectral comparison of onion extract vs ZnO NP. Onion extract (black colour line) displayed major

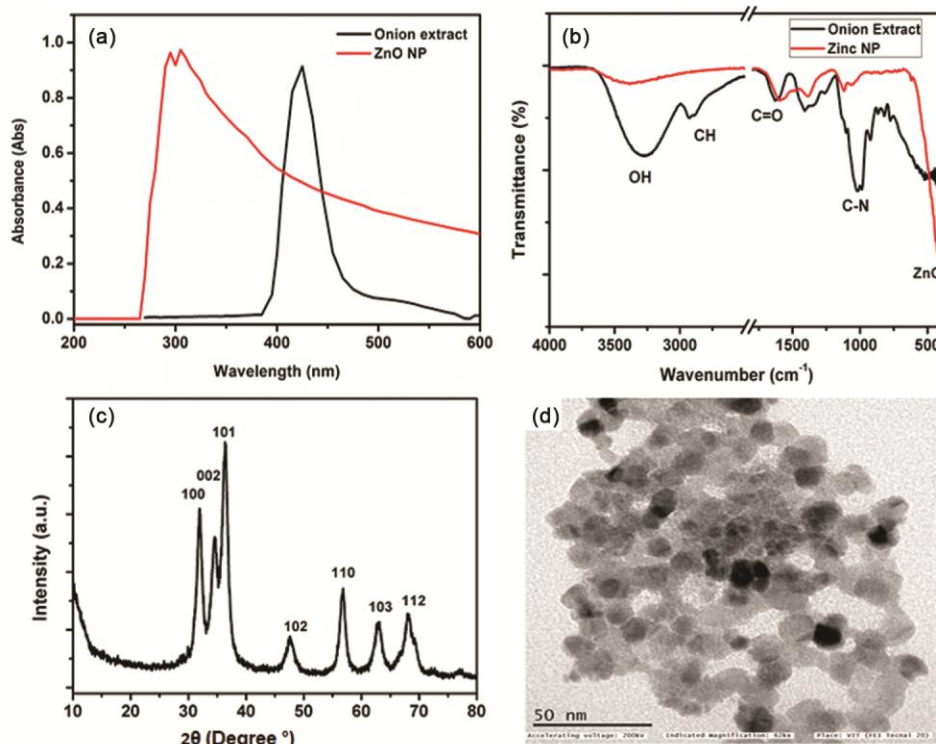


Fig. 2 — (a) UV-visible spectra, (b) FTIR spectra, (c) XRD and (d) TEM image of ZnO NPs prepared from onion extract.

peaks at $3700\text{-}3000\text{ cm}^{-1}$, $3000\text{-}2800\text{ cm}^{-1}$, 1610 cm^{-1} , $1450\text{ - }1200\text{ cm}^{-1}$, $1100\text{ - }800\text{ cm}^{-1}$ corresponding to stretching bands of various functional groups such as -OH , -CH , C=O , -NH , and -C-N , respectively. These functional groups are major chemical moieties present in secondary metabolites like alkaloids, flavonoids, polyphenols etc. In case of ZnO NP, similar peaks were observed (red colour line) but with slight shift and low intensity. The reason for slight shift in IR peaks is that the molecules are not anymore free and also internal ordering can happen during bonding on ZnO NP surface. Higher temperatures above $150\text{ }^{\circ}\text{C}$ leads to decrease in flavonoids and polyphenols content in the onion extract³⁷. Here ZnO NPs are prepared at high temperatures ($200\text{ }^{\circ}\text{C}$). We hypothesize that the available secondary metabolites are low in amount at this temperature due to which only small available amount of metabolites were capped on ZnO NPs. Apart from these peaks, a major peak with high intensity in the wavenumber range of $480\text{ - }400\text{ cm}^{-1}$ was observed, which corresponds to metal-oxygen stretching i.e. Zn-O. Next was to confirm the phase and crystallinity of prepared ZnO NP. Fig. 2c shows the XRD data of ZnO NP. The obtained peaks (100), (002), (101), (102), (110), (103), (112) and (202) at 2θ values of 31.9, 34.5, 36.4, 47.6, 56.8, 63.02, 68.1, and 77.01, respectively are in accordance with JCPDS data of 89-1397, which indicates the ZnO NP possess hexagonal phase. Using Debye-Scherrer equation³⁸, the average crystallite size from XRD data was found to be 4.5 nm. Both FTIR spectral data and XRD data is in agreement with literature^{29,31}. Structural and surface morphology of ZnO NP was studied using TEM (Fig. 2d, Fig. S5A and S5B) and the obtained image along with histogram prepared using Image J software (Fig. S5C). The average size of the NPs was 6.4 nm with a polydispersity index of 27 % and are in spherical shape with few agglomerates of particles. EDAX analysis (Fig. S5D) show a strong and major signal of Zinc atoms followed by presence of both carbon and oxygen atoms, which is similar to Jayaseelan et. al.³⁵. ZnO NP displayed a surface area of $7.006\text{ m}^2/\text{g}$ (pore volume of 0.022 cc/g ; Fig. S6 depicts surface area data obtained using BET method).

Sensing of dopamine via cyclic voltammetry: optimization studies

The prepared ZnO NP from onion extract was drop casted as a film on bare glassy carbon electrode (GCE) and studied for its ability to detect dopamine.

A homogenously dispersed ZnO NPs solution with different ZnO NP concentrations (3 mg/mL, 6 mg/mL and 9 mg/mL in ethanol) were prepared. Fig. 3 depicts CV response of DA (concentration was fixed at 1mM in 0.1M phosphate buffer pH 7) on bare GCE (black colour line), and GCE-ZnO NP films with varying concentrations. As seen from the image, GCE itself gave a redox peak for DA indicating its individual capability to detect DA. Presence of ZnO NP film of 3 mg/mL (film A) and 6 mg/mL on GCE has resulted in a significant increase in current (μA) from 48.03 to 52.48 and 72.01 and shift of positive potential (V) from 0.36 to 0.3. However, when the concentration of ZnO NP film was 9 mg/mL, there was a drastic decrease in the current value which is below than GCE itself indicating that 6 mg/mL concentration is the ideal one for this study. We hypothesize that at 9 mg/mL concentration, ZnO NPs form as a dense and thick film where ZnO NPs aggregate and lower the overall effective surface area which in turn affects its sensing property. This phenomenon is similar to reduction of sensor sensitivity with increasing polymerization rates and cycles of nanoparticle deposition as film on electrodes²². Based on these observations, the concentration of 6 mg/mL of ZnO NP is fixed as film for rest of the study.

Next, we investigated the influence of buffer pH on the redox peaks of DA as the microenvironment effects the performance of DA sensing. For this, scan rate was fixed at 0.5 V/s and DA concentration was fixed at 1 mM. Fig. 4a represents the CV of DA at varying buffer pH i.e. from 3 to 9. A general striking

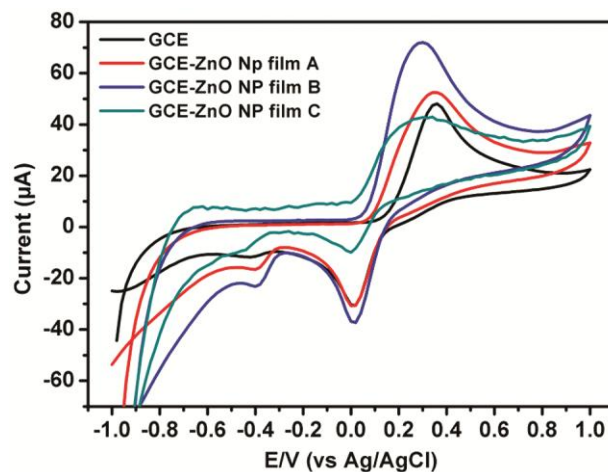


Fig. 3 — Cyclic voltammetry (CV) of dopamine at GCE, ZnO NP film A (3 mg/mL), ZnO NP film B (6 mg/mL) and ZnO NP film C (9 mg/mL) in 0.1 M phosphate buffer (pH 7) at a scan rate of 0.5 V/s.

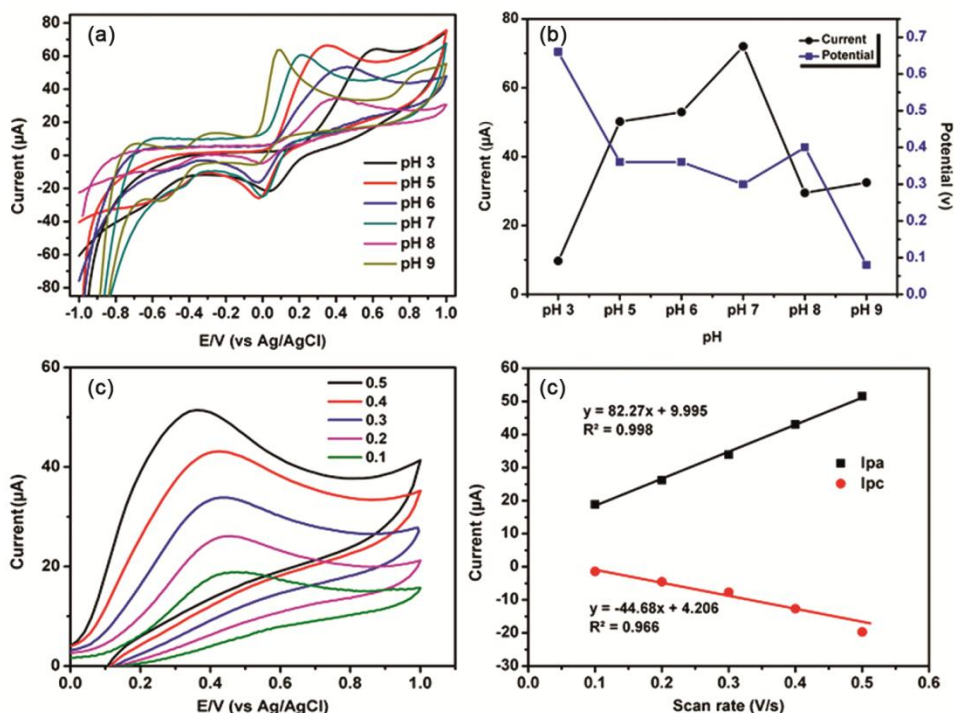


Fig. 4 — (a) CV curves of dopamine at various buffer pH (3, 5, 6, 7, 8 and 9), (b) current and potential differences at different buffer pH, (c) CV curve of DA at different scan rates and (d) plot of anodic and cathodic peak current responses at various scan rates. For a and b the scan rate is fixed at 0.5 V/s.

observation from this image is that, an increase or decrease of buffer pH from 7 results only in decrease of both cathodic and anodic peaks of DA. We have also observed that when the buffer pH was 8 and 9, the colour of the DA solution turned brownish (Fig. S7). Fig. 4b depicts the current (μA) value of oxidation peak at a fixed potential of +0.3 V and it can be observed that the current value increased with increasing pH from 3 to 7 and decreased once the pH changed from 7 to 9. Also a closer look at the maximum oxidation peak potential at each pH (see Fig. 4b; square shape) indicates that there was a significant clear shift in positive peak potentials when the pH was 3 or 9 but for other pH's (5, 6, 7 and 8) there was only a slight shift. This data suggest that pH of the buffer plays a very important role in oxidation and reduction of DA in presence of ZnO NP film. Based on these experiments, pH of the buffer was fixed at 7 for further experiments.

Effect of scan rate is an important parameter that determines the electrocatalytic response of ZnO NP film for DA. For this, scan rates ranging from 0.5 V/s to 0.1 V/s were studied and the obtained results are schematically presented in Fig. 4c with a calibration plot of redox peak currents (I_{pa} and I_{pc}) in Fig. 4d. From Fig. 4c, we can observe a noticeable

shift of peak current towards positive potential with increasing scan rate indicating that there is a quasi-reversible reaction. Also there is a linear correlation for both redox peak currents which suggest that electrooxidation of DA for ZnO NP film is adsorption controlled process and is in agreement with literature^{16, 19}.

Limit of detection (LOD)

Using the optimized conditions, the limit of detection of ZnO NP film was studied using various concentrations of DA. Fig. 5a presents a schematic overview of CV of different concentrations of DA. It can be noted that with decreasing DA concentration, oxidation peak current response decreased gradually while the oxidation potential was not altered and was stable. The obtained calibration plot (Fig. S8) showed a linearity in the measured concentration range of 3.9 to 250 μM with linear regression equation as I (μA) = $0.039x + 3.1761$, $R^2 = 0.9825$. Limit of detection (LOD) for ZnO NP film was studied based on earlier literature³⁹ and found to be 3.53 μM . A comparative data of this LOD with some literature data is presented in Table 1. All the nanomaterials prepared in those articles were by chemical approaches. Looking at the comparative data, the

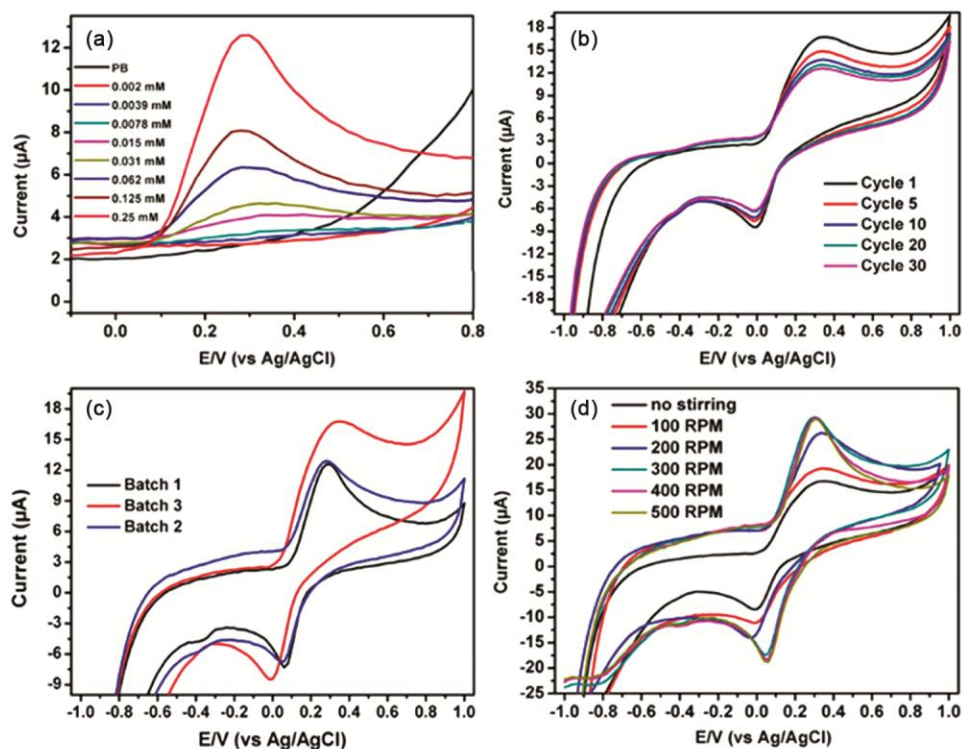


Fig. 5 — CV curve of DA at: (a) different concentration (0.25, 0.125, 0.062, 0.031, 0.015, 0.0078, 0.0039, 0.002 mM), (b) various cycles (1, 5, 10, 20 and 30), (c) three different batch ZnO NP films and (d) hydrodynamic CV curve of DA at different RPMs.

Table 1 — Comparison of various literature on electrochemical based DA sensing. (*LOD = Limit of detection)

Material	Detection method	LOD* (μM)	Ref.
Graphene oxide, MWCNT	DPV	1.5	13
Reduced graphene oxide	DPV	1.4	20
Graphene	CV/DPV	2.64	41
Graphene-AuNP	CV/DPV	1.86	42
NiAl-LDH/graphene	DPV	9.6	43
Ag-Pt bimetallic nanoparticle	DPV	0.11	26
Graphene carbon fiber	DPV	1.36	12
Gold nanoparticles	DPV	0.017	23
Poly(hydroquinone)/Gold nanoparticles	DPV	0.042	22
Cobalt oxide-graphene oxide	Amperometry	0.277	19
Polypyrrole/graphene	Amperometry	2.3	44
ZnO nanoparticles	CV	3.53	This work

obtained LOD for onion based ZnO NP seems promising and reasonable one, if not the best, and highlights that the NPs prepared from plant extract can act as a reliable working electrode besides preparation of NPs using green approach does not require toxic chemicals and reagents. We believe, with further optimization conditions the green approach based NPs with various shapes can be prepared and they would be excellent working electrodes than NPs prepared using chemical approaches.

Reproducibility and stability

We studied the effect of electrocatalytic activity of ZnO NPs prepared in three different batches under the optimized conditions with a fixed concentration of DA at 0.25 mM and the obtained results are shown in Fig. 5b. As seen in the figure, both batch 1 and batch 2 showed similar redox peak profiles but batch 3 showed a slight increase of redox peak profile. The relative standard deviation (RSD) at +0.3 V was 2.01 %, which is an acceptable value. Next, the current reproducibility and stability of the developed

ZnO NP film was investigated for 30 consecutive cycles. Fig. 5c depicts the oxidation peak profiles for cycle 1, 5, 10, 20 and 30, and has an RSD value of 1.48 % and oxidation peak current was 92.81 % at + 0.3 V. This data suggest the reliable reproducibility and stability of ZnO NP film indicating the suitability of ZnO NPs prepared from onion extract as working electrodes.

The experiments conducted so far were done in static CV where the mass transport of DA is *via* diffusion. The influence of mass transport *via* convection was studied by stirring the DA solution at different RPM's as it provides information of sensitivity enhancement at higher RPMs and film stability. The obtained results are depicted in Fig. 5d. As seen in the image, with increasing RPMs a significant increase of current (μA) from 16.7 to 29.2 and a slight change in positive potential (V) from +0.3 to +0.28 was observed and the current value stabilized at 300 RPM with no significant increase. The observed change in current indicates that there is a mass transport *via* convection and most importantly the ZnO NPs are tightly adhered together in the film without any leakage even at 500 rpm.

Interference studies

In a biological fluid like plasma, urine etc. there are many molecules such as glucose (Glu), ascorbic acid (AA) etc. that are present in high or low concentration than DA. Due to this, the electrochemical detection ability of ZnO NP film for those interfering substances was also studied. For this experiment, the solutions were stirred at 300 rpm and the potential of the system was fixed at +0.3 V and the resulting current (μA) was recorded. As can be seen in Fig. 6a, both AA and Glu displayed 6-7 times lower current value (μA) than DA. This result indicates that both AA and Glu will not interfere with ZnO NP film detection of DA.

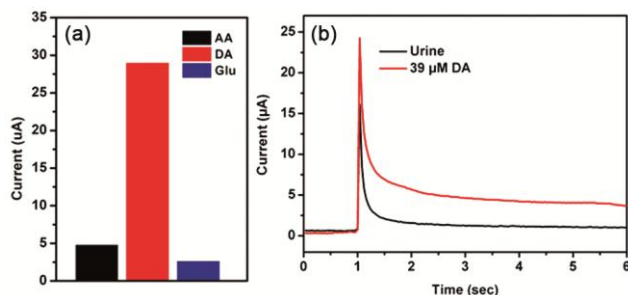


Fig. 6 — (a) Currents from CV curve of Ascorbic acid (AA) vs Dopamine (DA) vs Glucose (Glu) and (b) Chronamperometry of urine and DA spiked urine.

Application with real sample

To test the reliability of the developed ZnO NP film in detecting DA in a biological sample, DA of 39 μM was spiked to a solution of diluted urine sample under constant voltage (chronamperometry). The obtained result is shown in Fig. 6b, which is a graph plotted with time (s) vs current (μA). As seen from the graph, in the duration of zero (0) to 1 sec there was no change in current (i.e. quiet period) because the potential (V) applied is 0. After 1 sec and up to 6 sec (i.e. test period), a potential of +0.3 V was applied to all the samples. It can be noted that the current (μA) value significantly increased when DA was spiked to urine indicating that DA can be detected in urine sample. The recovery % of DA was calculated using the calibration curve (Fig. S8) and is found to be 94.9 % (37.02 μM).

Although the sophisticated electrochemical workstations are less expensive than other analytical instruments such as HPLC, SERS and MS, but still they are not afforded by research labs in developing nations. In recent years, there are few open source electrochemical workstations such as IO Rodeostat and CheapStat available in the market at affordable rates. In this work, we evaluated whether IO Rodeostat (see Fig. S1) can yield reliable results and be used as an instrument in low resource laboratory settings. The above presented data (Fig. 3 to Fig 6) indicate that indeed the IO Rodeostat is a reliable electrochemical workstation with easy user guide to perform cyclic voltammetry and constant voltage.

Conclusions

In this work, we synthesized spherical shaped ZnO NPs with an average particle size of 6.4 nm from onion aqueous extract. The ZnO NP displayed maximum wavelength of 295 nm and 305 nm and possessed a typical hexagonal phase. The developed protocol showed similar properties for ZnO NP prepared from other batch onion extracts as well. Uniform ZnO NP film with good electrocatalytic activity was observed with 6 mg/mL concentration of ZnO NPs. Of all the tested buffer pHs and scan rates, pH 7 and 0.5 V/s were found to result highest oxidation current. The ZnO NP film displayed good sensitivity and satisfactory selectivity for dopamine in presence of ascorbic acid and glucose and ability to detect dopamine in urine sample. The potential of Rodeostat as an electrochemical workstation in low resource laboratories has been demonstrated. We expect these ZnO NPs from

onion extract has also the potential for the sensing other biomolecules⁴⁰.

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Supplementary Data

Supplementary Data associated with this article are available in the electronic form at [http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A\(08\)1100-1107_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(08)1100-1107_SupplData.pdf).

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