



Fabrication of palladium modified zinc oxide nanorods (Pd-ZnO NRs) for electrochemical detection of mebendazole

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Developing an efficient electrocatalyst for mebendazole (MEBDZ) sensing has been crucial for enhancing the construction of biosensors. Herein, palladium modified zinc oxide nanorods (Pd-ZnO NRs) have been synthesized by facile hydrothermal method for MEBDZ sensing. The FE-SEM and HR-TEM measurements have shown that Pd is dispersed on ZnO rods. The crystal structures of the Pd-ZnO have been revealed by powder X-ray diffraction (XRD). The strategy of modifying ZnO rods by Pd is promising, for fabricating towards MEBDZ sensors applications with its electrocatalytic activities. The differential pulse voltammetry has been used, method for the electroanalytical determination of MEBDZ. Under the optimal conditions, the Pd-ZnO NRs modified electrode has shown a wide linear response to the concentration of MEBDZ with a low noticeable detection limit. The as-prepared samples have shown an excellent electrochemical activity towards the electro-oxidation of MEBDZ leading to a significant improvement in sensitivity as compared to the bare glassy carbon electrode.

Keywords: Electrocatalyst, Hydrothermal method, Mebendazole sensor, Pd-ZnO nanorods

Mebendazole (5-benzoyl-2-benzimidazole carbamic acid methyl ester, MEBDZ) is a broad-spectrum anthelmintic drug, producing high cure rates in infestation by ascaris, threadworms, hookworms and whipworms and can be administered orally as a tablet formulation and suspension¹. MEBDZ is an anthelmintic drug widely used in worldwide deworming program in developing countries. In terms of quantitative analytical applications, CV and DPV is still an emerging technology and its feasibility for polymorph determination has only been briefly explored, with few examples in the literature²⁻⁵. It is worth mentioning that the more polymorphs of MEBDZ in pharmaceutical, the more difficult their quantification and a more efficient quality control method will be required. The potential evaluation of MEBDZ quantification, the polymorphism of MEBDZ in pharmaceutical raw materials using differential scanning calorimetry (DSC), dissolution, solubility and X-ray diffraction pattern (XRDP) methods have been demonstrated⁶ and the electroanalytical methods have been demonstrated by Narayanan *et al.*⁷.

Parasitic disease hits over a billion of people living in this planet. We need to have a commendable strategy to tackle this global burden, by keeping in

mind of multi-disciplinary approach and collaboration for better outcomes, is the need of this hour. Variety of parasitic gastrointestinal infestations in human is being treated with Mebendazole, broad-spectrum benzimidazole, more than 40 years because of its low price and limited toxicity profile⁸. MEBDZ is a drug claiming credits in approved therapies as cells resistant. MEBDZ exhibits cytotoxic activity, stimulating antitumor immune response for the treatment of brain tumours in animal models⁹. MEBDZ acts by inhibiting glucose uptake, reproductive and digestive capacities of parasites. MEBDZ is poorly absorbed in the digestive tract, making it an effective medication for managing intestinal helminthic infections with very few side effects¹⁰. Metabolism of MEBDZ is largely and primarily in liver. Higher plasma levels of MEBDZ, excretion occurs mostly in urine, which impairs liver function in patients owing to its half-life of 3 to 6 hours after oral administration. MEBDZ accompanies the most common adverse effects like loss of appetite, abdominal pain, diarrhea, flatulence, nausea, vomiting, headache, tinnitus, and elevated liver enzymes¹¹. Treatment failure incidence are also increasing in treating hookworm infections with MEBDZ, higher dosages or prolonged treatment

course than usually recommended, post serious side effects in patients. The common toxicity of MEBDZ narrowed down to gastrointestinal irritation. There is a huge challenge and opportunities for exploring electroanalytical sensing methods for MEBDZ¹²⁻¹⁶.

Infections caused by parasitic worms in human, characterized as one of the most important health problems in the world. Helminths parasitic causes severe and hard to treat illnesses in humans, animals, agriculture and aquaculture. MEBDZ depletes the glycogen stores in the parasitic worms by selective and irreversible inhibition of glucose and other nutrients uptake. MEBDZ accumulation pursuant to its huge consumption has been raised environmental pollution and water stream contamination problems. Considering its vast usage, development of an effective and sensitive method for its analysis in biological fluids and other real samples are highly demanded^{17,18}.

Transition metal doping in semiconductor nanoparticles are studied widely because of their photo-electrochemical, electrochemical and optical properties owing to its band gap modification. This could be possible for the reason that, the choice and ease of preparation to spotlight the materials of interest¹⁹. Many nanomaterials, especially metal oxide nanoparticles, semiconductor nanoparticles show great demand due to their high surface free energy and large specific surface to volume area, can adsorb biomolecules strongly and play a vital role in biosensor construction and show outstanding catalytic properties. They decrease the applied potential, of many analytically important analyte as sensors, in the electrochemical reactions. Electron transfer between electrodes and the analyte of interest are enhanced, is a key process in the construction of electrode modification materials, by these nanoparticles owing to the action as a bridge to electron transfer between the biomolecule and the electrode^{20,21}. Among the various semiconductor metal oxide materials, ZnO is drawing extensive attention due to its amicable properties such as nontoxicity, biocompatibility, antibacterial and low cost, high abundance. Further, the unique properties such as direct wide band gap, good conductivity, piezoelectricity, and large specific surface area, low probability of interference against the major available pharmaceuticals have widened the sensing applications of ZnO. The potential application and use in the area of biomedical is not new²².

ZnO nanomaterials can accept a massive number of structural geometries with an electronic structure that exhibit semiconductor properties. ZnO nanoparticles

exhibit excellent physical and chemical properties due to its assortment size and surface sites. In scientific research, ZnO used in the fabrication of sensors, DSSC and catalytic devices, fuel cells and coatings for the passivation of surfaces against corrosion and as photocatalysts²³⁻²⁶. Commonly, carbon based working electrodes are used for voltammetric analyses. Modified carbon based electrodes are employed mostly, due to lack of sensitivity and high over-voltage of electrochemical processes on the surface of bare carbon electrodes. Therefore, the development of a procedure employing reproducible and repeatable modified electrode applicable for the analyte as well as the desired pH determination, will be very fruitful in electroanalytical measurements. Metal modified ZnO semiconductor is highly requisite, excellence in particle size, such as photocatalysis, sensors and DSSC application. However, the metal modified ZnO nanoparticles in quantities are sufficient to advance ZnO semiconductors and its particle sizes. Further, it has been used as electrodes in electrocatalyst, as cathode in counter electrode show electrocatalytic properties. It has been prepared by various methods such as, template-directed approach, gas-phase deposition, wet chemical method, hydrothermal technique, thermal oxidation and many chemical methods^{27,28}.

In this present study, we have reported the preparation of Pd modified ZnO nanorods, using hydrothermal method. The prepared material is used to modify the glassy carbon electrode (GCE). The modified GCE electrode by Pd-ZnO NRs shows better catalytic activity for the electrochemical oxidation of MEBDZ. This study has demonstrated the quantitative analysis of MEBDZ at modified glassy carbon working electrode using differential pulse voltammetry (DPV).

Experimental Section

Synthesis of Pd modified ZnO NRs (Pd-ZnO NRs)

To synthesis palladium modified ZnO (Pd-ZnO), the $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, NaOH and PdCl_2 were used as precursor. Pd content and ZnO with molar ratio was obtained by varying the PdCl_2 and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ weight accordingly in 40 mL DD water. Then mixture was magnetically stirred for 20 min and transferred into a 100 mL Teflon lined stainless steel autoclave. It was then sealed and maintained at 180°C for 2 h in a muffle furnace. After cooling, solid powders were obtained by

centrifugation and washed with distilled water and absolute ethanol. The powders were finally calcined at 200°C for 2 h.

Characterization

The surface morphology of the prepared sample was analyzed by FE-SEM using a HITACHI SU6600 field emission-scanning electron microscopy and TEM using a PHILIPS CM200 transmission electron microscopy respectively. To analyse the sample structure a Rich Siefert 3000 diffractometer with Cu-K α 1 radiation ($\lambda=1.5406 \text{ \AA}$) was used. A CHI 600A electrochemical instrument using as-prepared sample coated glassy carbon electrode (GCE) and bare GCE as working, where the electrocatalytic experiments were performed. The electrocatalytic experiments were carried out using a platinum wire and the saturated calomel electrode (SCE) as the counter electrode and as reference electrodes respectively.

Results and Discussion

Characterization

Crystallite nature of as-prepared Pd-ZnO NR samples were analysed through XRD analysis and the patterns are shown in the Fig. 1. The peak diffractions at 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 66.4°, 68.0°, 69.1° can be indexed to the planes of standard patterns for hexagonal phase wurtzite structure ZnO (JCPDS Card File No. 36-1451). All the peaks agree well with ZnO crystal phases and no other characteristic peaks were observed, indicating high purity of as-prepared samples. The Pd diffraction peaks were not observed in this XRD pattern, which

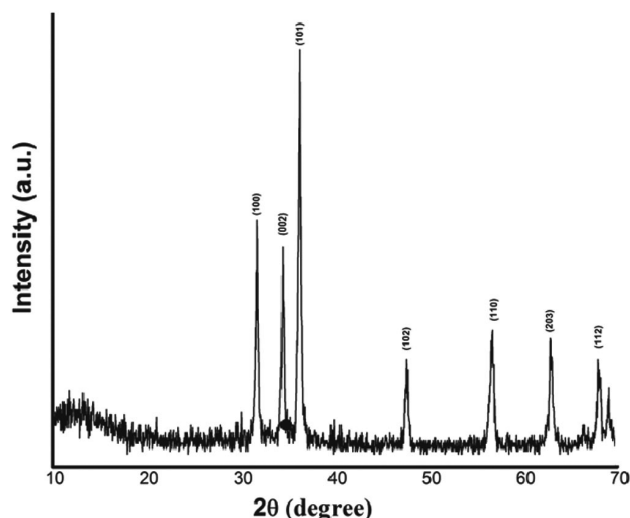


Fig. 1 — XRD patterns for Pd-ZnO NRs.

can be explained by considering that the quantity of Pd was much smaller than that of ZnO. The come out suggests that the prepared sample is ZnO NRs²⁹.

The room temperature photoluminescence spectrum for colloidal solution of the sample at 340 nm of excitation energy is shown in Fig. 2. As can be seen in the figure, the peak at 386 nm is attributed due to the radiative recombination of electron and hole as concluded earlier²⁸. Optical absorption spectra of as-prepared Pd modified ZnO NR samples were studied through DRS-UV spectra and is shown in the Fig. 3. The study showed prominent excitonic absorption peak at 344 nm at room temperature, may be attributed due to the quantum size effects in nanocrystals. The variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for the synthesized sample is plotted in

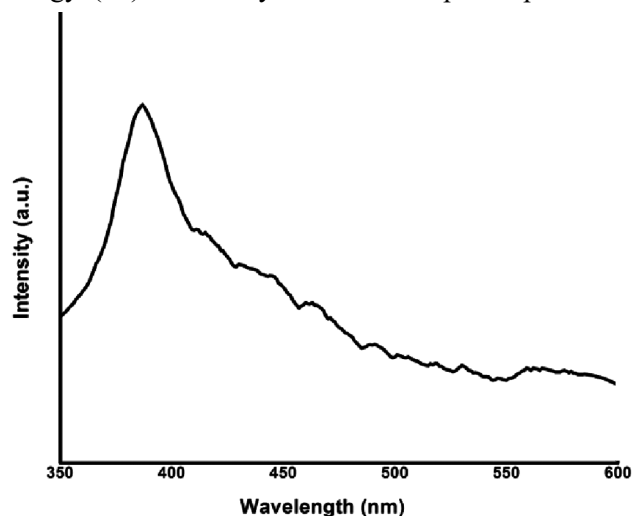


Fig. 2 — PL spectrum of Pd-ZnO NRs.

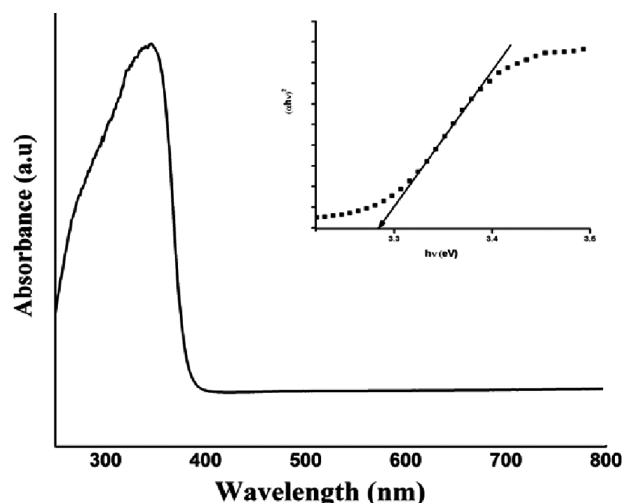


Fig. 3 — DRS UV-Visible spectrum. Inset Fig: Plots of $(\alpha h\nu)^2$ vs photon energy ($h\nu$)

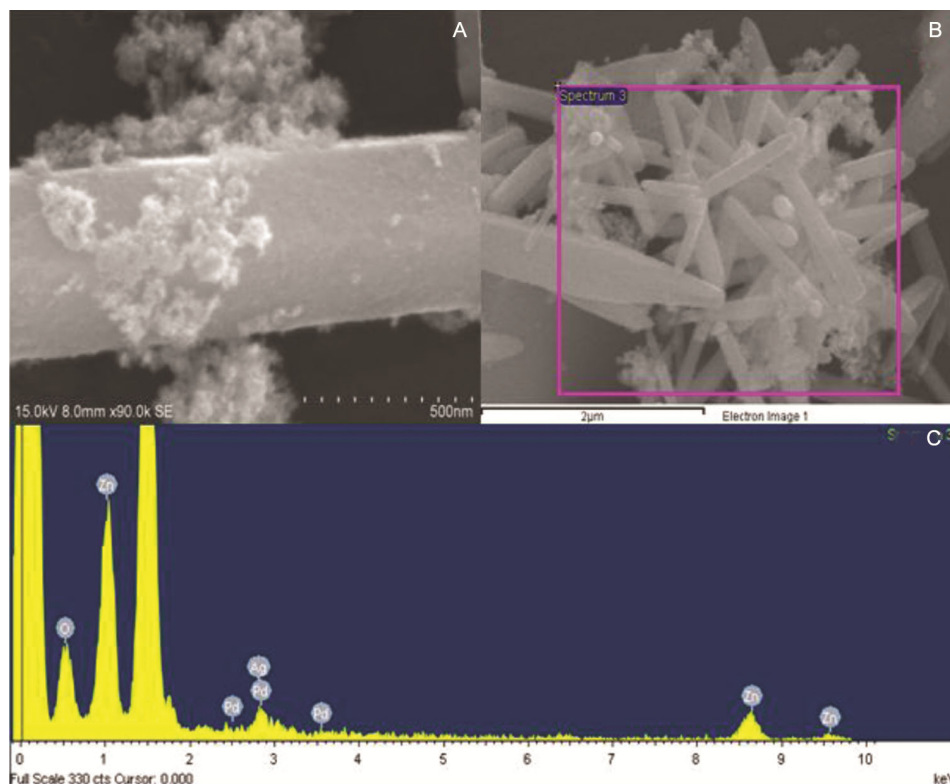


Fig. 4 — (A), (B) FE-SEM images and (C) EDAX spectrum of Pd-ZnO NRs.

Fig. 3 inset. The band gap (E_g) was estimated through the extrapolation method. The band gap value was found to be 3.26 eV.

FESEM and HRTEM images are shown in Fig. 4 (A & B) and Fig. 5(A), respectively. Large number of straight and smooth homogenous solid rods in the images evidenced the regular rod like arrangements with hexagonal structure. They demonstrated the rod like morphology of ZnO and also the distribution of palladium particles on the ZnO rods. Figure 4 (C) depicted EDX spectrum of the sample that confirms the presence of Pd, Zn and O elements as well as the purity of the sample. In Fig. 5(B), the selected area electron diffraction (SAED) pattern is shown and demonstrated the crystalline nature of the sample. This is ascribed due to the synthesis method. The distribution of palladium particles on the ZnO rods in nanoscale was explicated through the characterization techniques.

Electrocatalytic detection of mebendazole (MEBDZ) by Pd-ZnO NRs

Cyclic voltammogram of MEBDZ at Pd-ZnO NRs/ GCE

The superimposed cyclic voltammogram, an electrochemical behaviour, of (a) bare GCE in the absence of MEBDZ and (b) bare GCE, (c) ZnO/GCE,

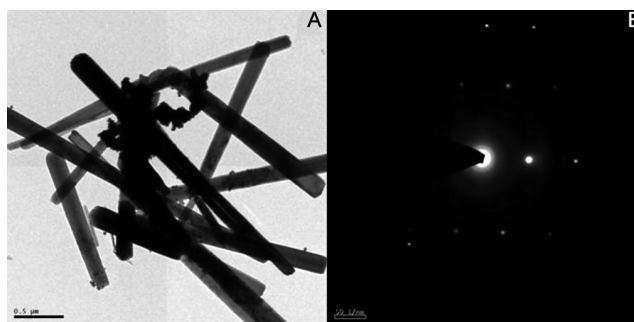


Fig. 5 — (A) HR-TEM image and (B) SAED pattern of Pd-ZnO NRs.

(d) Pd/ZnO/GCE in the presence of 1×10^{-7} M MEBDZ in 0.1 M PBS (pH 4) with the scan rate of 50 mVs^{-1} are shown in Fig. 6(A to D). As can be seen in the figure the MEBDZ oxidation peak potential is lower with higher current for MEBDZ in PBS (pH4) for Pd- ZnO NRs modified GCE than at other electrodes, indicated that the modified electrode is electroactive in the potential window of 0.4 to 1.5 V at PBS (pH 4). The anodic peak currents were $3.63 \mu\text{A}$ (at 1.06 V) and $2.26 \mu\text{A}$ (at 1.20 V) for Pd-ZnO/GCE and bare GCE respectively. The CVs of MEBDZ at a bare GC electrode and Pd-ZnO/GCE modified electrode as can be seen in the Fig. 6, at the bare GC electrode the MEBDZ has no obvious

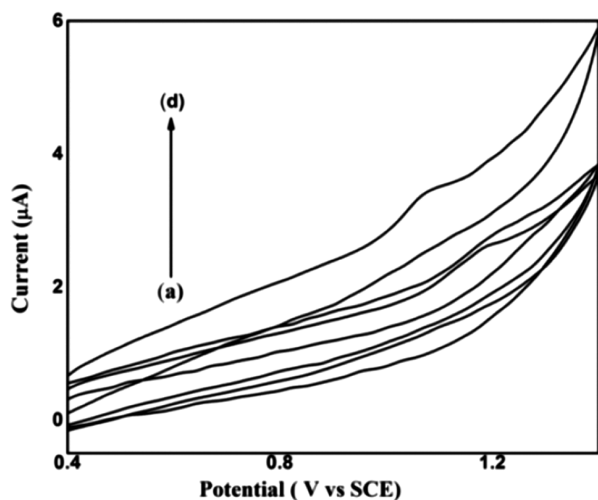


Fig. 6 — Superimposed CVs of MEBDZ at (A) bare GCE in the absence of MEBDZ, (B) bare GCE in the presence of MEBDZ, (C) ZnO/GCE and (D) Pd-ZnO NRs/GCE in PBS (pH 4) solution at 50 mV/s scan rate.

appreciable electrochemical response and a well-defined irreversible wave of MEBDZ was observed at the activated modified electrode suggesting that the observations were significant for the modified electrode against MEBDZ. This MEBDZ oxidation potential was comparable and we reported that the electrochemical oxidation process of MEBDZ at Pd-ZnO/GCE as significant. It must be indicated that the irreversible sites were available for the oxidation of MEBDZ at the sample modified GCE. This unusual electrochemical sensing behaviour was mainly attributed to the presence of electron transfer sites in Pd-ZnO NRs, play vital role in the electrocatalytic oxidation of MEBDZ. This can be ascribed due to the electron transfer owing to the conductive nature between Pd and ZnO support in Pd-ZnO NRs, which ultimately increases the sensing signal in the form of current towards MEBDZ. The CV schemes of the modified electrode are sensible, differently associated to those of two other electrodes. Surely, distinct anodic peaks canister represented at 1.06 V for the Pd-ZnO modified electrode. This peak instigated from the faradaic behavior of Pd-ZnO NRs as suggested by Singha *et al.*³⁰. It is worth stating that the electrochemical responding ability of the analyte that assimilated on the electrode, also stimulates the catalytic activity of the modified electrode.

Preparation and electrode activation of Pd-ZnO/GCE modified electrode was done by taking one milligram of as prepared catalyst, was disseminated with the aid of ultrasonic nervousness in 10 mL of

ethanol to stretch 0.1 mg mL⁻¹ suspension. The glassy carbon electrode was polished with 0.3 µm alumina slurry and then washed ultrasonically in distilled water and then, finally washed with ethanol for sufficient minutes, respectively. The GC electrode was modified by 5 µL of suspension of the sample (0.1 mg mL⁻¹) in ethanol and dehydrated under air circumstance. These investigates specify the activating potential range, has an inordinate influence on the electrochemical response of MEBDZ at the Pd-ZnO NRs/GCE modified electrode. At the potential range, from +0.4 to +1.5 V, the best response of MEBDZ was achieved at all the stages, beyond this potential range, the rejoinder of MEBDZ became poorer again. The electrode was thoroughly washed with triply distilled water and put in water before use. The upstairs activating condition was enhanced for our determination.

Effect of pH

The influence of pH on the peak potential of MEBDZ (1 × 10⁻⁷ M) oxidation at the modified Pd-ZnO NRs/GCE electrode was studied. The recorded CVs under each pH, were superimposed for MEBDZ (1 × 10⁻⁷ M) at Pd-ZnO/GCE with the scan rate 50 mVs⁻¹ in the PBS solution over the pH ranges from 3 to 7. The response of MEBDZ is obedient in 0.1 M phosphate buffer solution in the range of pH 3 to 7. At pH-4, a well-defined and stable CV of MEBDZ was obtained at an activation potential, at a scan rate 50 mVs⁻¹. Consequently, 0.1 M phosphate buffer solution (pH 4) was preferred for our experiments, in view of the fact that best irreversibility of MEBDZ was realized and shorter activating potential could result in insufficient (high current was obtained) activation. The influence of pH exhibits a linear relationship between anodic peak potentials. The linear regression equations is found to be as:

$$E_{pa} \text{ (V)} = -0.0100 \text{ pH} + 1.237 \text{ (R}^2 = 0.994\text{)}, [\text{Pd-ZnO/GCE}] \dots (1)$$

The electrocatalytic oxidation peak current of MEBDZ was influenced within the investigated pH range. The highest peak current was obtained at pH 4 with the PBS solution. The pH study revealed that pH 4 could be the best supporting electrolyte for MEBDZ at Pd-ZnO/GCE.

Effect of scan rate

Different scanning rates were used to examine the dynamic property of Pd-ZnO/GCE. Figure 7 displays

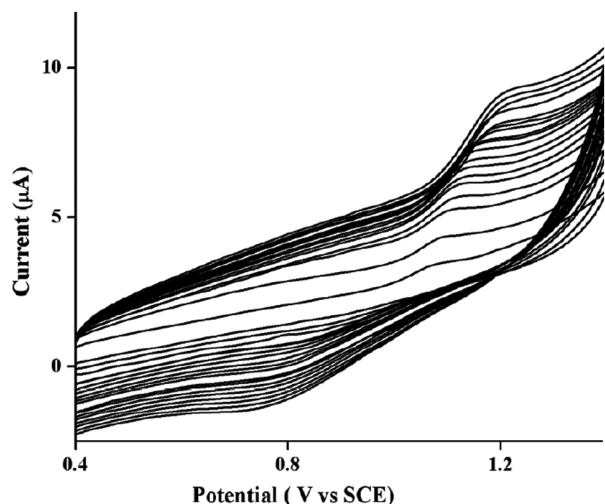


Fig. 7 — CV analysis of 1×10^{-7} M MEBDZ at Pd- ZnO NRs/ GCE in the PBS solution (pH 4) at (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, (f) 300, (g) 350, (h) 400, (i) 450, (j) 500, (k) 550, (l) 600, (m) 650 and (n) 700 mV/s scan rates.

the influence of scan rate on the electrochemical response of 1×10^{-7} M MEBDZ at Pd-ZnO /GCE at the scan rate ranges from 50 mVs^{-1} to 700 mVs^{-1} in PBS (pH 4) solution. When increasing the scan rate, the oxidation peak potential moved positively and the oxidation current is also increased, evidences the dynamic property, owing to the electrocatalytic interaction between the electrode surface and MEBDZ. As the scan rate was varied, the shape of the CV curves continued nearly indistinguishable. In addition, the voltammetric current is proportional to the scan rate, consistent to an electric diffusion control behavior. Very less cathodic peaks, as can be seen in the CV curves, which designate that faradaic redox reactions lead to the charge shifting mechanism. However, it is fairly problematic to allocate the redox peaks due to the porosity of the sample and it is suggested that the charging mechanism of the material ascended from the combination of electrical donor–acceptor creation in faradic reactions. Therefore, the electrocatalytic activity of the material censoriously depends on its morphological characteristics such as rods of ZnO support and the presence of Pd metal nanoparticles on it. The charge transfer is directly related to the surface properties of the electrode, on the electrochemically active surface area of the modified electrode materials. The oxidation peak current was linearly related to the scan rate in the range 50 to 700 mV s^{-1} . The obtained linear regression equation is:

$$E_{pa} \text{ (V)} = 0.1194 \ln v + 0.8534 \text{ (R}^2 = 0.98), [\text{Pd-ZnO}$$

$$\text{NRs /GCE}] \quad \dots (2)$$

It exhibits that the electrode reaction corresponds to a diffusion-controlled process. Further, the plot between scan rate (mV/s) versus current shows that the electrode process is diffusion-controlled process. Quantificational relationship, between the logarithm of oxidation peak current and logarithm of the scan rate is:

$$\log I_{pa} = 0.2636 \log v + 0.1649 \text{ (R}^2 = 0.987), [\text{Pd-ZnO NRs /GCE}] \quad \dots(3)$$

The number of electrons involved in the overall reaction was obtained. The total number of electrons involved in the oxidation process of MEBDZ is 2. The findings are consistent, on the oxidation process of MEBDZ at Pd-ZnO /GCE. We ensure that the electrochemically active sites of Pd-ZnO NRs /GCE, which is in direct contact with the electrolytes and analyte by maintaining scan rate stability, are the key parameters. The charge transfer between Pd and ZnO NRs support is directly related to the surface properties of the electrode, that, the electrochemically active surface area of the electrode materials. It designates the strong electrochemical sensing behaviour of the modified electrodes, were heightened and was chiefly accredited towards (i) The incidence of Pd-ZnO NRs evidenced by XRD analysis, enhances the conductivity in Pd-ZnO NRs, such as donor-acceptor characters of the material (ii) owing to larger electroactive superficial sites of hexagonal rod shape of Pd-ZnO NRs in nm dimension on the modified GCE, as figured out in FESEM and HRTEM analysis (iii) The Pd-ZnO NRs /GCE play the energetic character as the electrocatalyst, involving electrostatic interaction of MEBDZ with the modified electrode and stands as described earlier that the electrochemical oxidation via $2e^-$ and $2H^+$ process³⁰.

Differential pulse voltammetry of MEBDZ at Pd-ZnO NRs/GCE

To find the sensitivity and detection limit (DL) of Pd-ZnO NRs/GCE towards MEBDZ, DPV was done in 0.1 M PBS (pH 4). Figure 8 presents the DPV of Pd-ZnO NRs/GCE, upon the addition of 0.05 mL of 1×10^{-7} M MEBDZ in 60 mL of continuously stirred 0.1 M PBS (pH 4), respectively. A successive addition of MEBDZ produces a significant increase in MEBDZ oxidation peak current. The calibration graph for the determination of MEBDZ around 1.0 V, by the Pd-ZnO/GCE is ascribed in the Inset figure of Fig. 8. The linear ranges are found between 0.83×10^{-7}

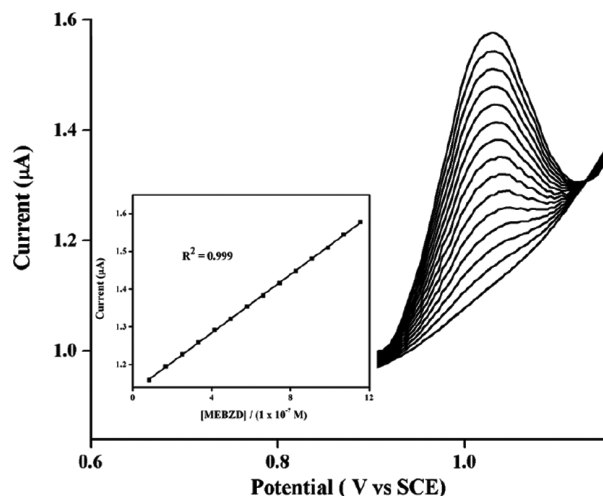


Fig. 8 — DPV analysis of Pd-ZnO NRs/ GCE in the PBS solution (pH 4) with concentration range 0.83×10^{-7} – 11.54×10^{-7} M MEBDZ. [Inset is the current vs concentration calibration plot]

to 11.54×10^{-7} M. The linear regression equations is: $I_a (\mu A) = 0.0387 [\text{MEBDZ}] (1 \times 10^{-7}) + 1.1291$ ($R^2=0.999$), [Pd-ZnO/GCE] ... (4) with the correlation coefficient $R^2=0.999$, respectively.

The obtained sensitivity of the Pd-ZnO/GCE is $0.387 \mu A$, shows that the modified GCE is highly sensitive towards MEBDZ. The estimated DL is $0.1627 \mu M \mu A^{-1}$. The obtained results are commendable in accordance with the earlier work on MEBDZ by the electrochemical reactions^{31,32}.

We had shown that, the sensing mechanism of Pd-ZnO NRs was mainly due to its electron transfer and faradaic behaviour, offered by the donor-accepter mechanism. In Pd-ZnO NRs, the catalytic behaviour improved the sensing ability of the modified electrode, in the case of DPV, it is advantageous to its low concentration ability with much lower detection of MEBDZ, in good agreement with morphology patterns of the material. Since the thickness of modified GCE were equipped very similar, this suggests that the electrochemical behaviour of the sample possibly involving on donor-accepter. As-prepared catalyst (Pd-ZnO NRs) can be exploited as a high sensitive transducer for the electrochemical analysis of MEBDZ.

Conclusion

In this study, we have demonstrated the preparation of Pd modified ZnO NRs by facile hydrothermal method. The results have demonstrated that DPV is useful for quantitative analysis, and reasonable estimates for the concentration versus current have been observed, which enables peak attributions, and

reinforces the distinction between MEBDZ/GCE and Catalyst/MEBDZ/GCE features. The well dispersion of Pd nanoparticles on ZnO NRs support provides strong, metal-support interaction that alleviate sensing ability of the material through high electron transfer efficiency, result in much higher electro-catalytic activity and better stability, evidenced by XRD analysis and enhanced conductivity on the larger electroactive superficial sites of hexagonal rod shape of Pd-ZnO NRs in nm dimension, as figured out in FESEM and HRTEM analysis. This work describes a fast and easy electrochemical analytical method for quantifying MEBDZ in the modified GCE, with wider linear response to the concentration of MEBDZ, with a low detection limit. The as-prepared samples have shown an excellent electrochemical activity towards the electro-oxidation of MEBDZ leading to a significant improvement in sensitivity, can be exploited in pharmaceutical raw material detection towards MEBDZ and in the field of biosensors.

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