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A Facile synthesis of ultra-small cerium oxide nanoparticles for enhanced Electrochemical Detection of Nitrobenzene in water samples

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The ultra-small cerium oxide nanoparticles (CeO_2 NPs) have been synthesized by the hydrothermal process. The structure and morphology of as-prepared nanoparticle were studied by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX). The results confirm that the morphology of CeO_2 NPs was obtained uniform and spherical structure with the size ranging from approximately 2-5 nm. The obtained CeO_2 NPs was evaluated by the electrochemical sensing of nitrobenzene (NB). In order to, the sensor based on the modified SPCE exhibits good electrocatalytic activity and the sensitivity was about 1.1166 $\mu A\ \mu M^{-1}\ cm^{-1}$. Remarkably, the CeO_2 NPs modified electrode showed the excellent lowest detection limit 0.092 µM over the linear range from 0.1 to 520 µM. Moreover, the ultra-small CeO_2 NPs was established good recoveries towards the determine the NB in tap water and river water samples.

Keywords: Cerium oxide; Hydrothermal; Nitrobenzene; Tap water; Mineral water.

1. INTRODUCTION

Nitrobenzene (NB) is an important aromatic nitro compound, which suspected as carcinogenic and has been extensively used as an intermediate or precursor in chemical syntheses such as various azo dyes, aniline, pesticides, explosives, herbicides and pharmaceutical synthesis [1,2]. Since, it was used in the preparation of shoe polishing materials, the production of pyroxylin materials, soap, and used as a solvent [3]. As a result, the bulk amount of NB is released in soil and water source. However, it was treated as a high-risk chemical and the stability of NB makes a dangerous one for aquatic microorganism and toxicity to the human health [4,5]. Therefore, many developing and developed countries have registered NB as priority pollutants and founded controls in its production, usage, and disposal [6]. Therefore, it is essential to the development of an effective and simple method for rapid detection of NB from water resource is most demanded.

In the past decades, a number of techniques have been accepted for the determination of aromatic nitro compounds, including practical samples analyses such as UV-vis spectrophotometry, fluorescence, high-performance liquid chromatography and capillary electrophoresis [6-9]. However, these methods are relatively expensive, large time consuming, high cost requires an instrument. Remarkably, the electrochemical method has received considerable attention in the determination of NB because of several advantages such as low cost, cheap instruments, time-saving, simple operation, good sensitivity and real time detection of NB [10-11].

The size-dependent (3-50 nm) nanoparticles have been increasing attention in worldwide due to the unique physical and chemical properties compared to bulk materials [12]. Ultra-small cerium oxide (CeO_2) has been widely studied in a verity of application including catalysis, sensor, UV blocker, energy storage, solid fuel cells and biological application due to unique chemical and physical properties [13]. Since, the CeO_2 have shown an interesting property such as large surface area, electrical conductivity, redox properties, nontoxicity, biocompatibility and chemical inertness that can be used to construct electrochemical biosensor [14-15]. Herein, we reported the as-prepared ultra-small (2-5 nm) cerium oxide nanoparticles (CeO_2 NPs) were obtained by a hydrothermal method in the presence polyvinyl pyrrolidinone (PVP). PVP can assist as a surface stabilizer and reducing agent. The prepared CeO_2 NPs were also characterized by structure and morphological properties. As synthesized nanoparticles used as a catalyst for the electrochemical nanomolar detection of NB was an exhibit. Which shows good sensitivity and low detection limit. The CeO_2 NPs/SPCE was successfully applied to the detection of NB in real samples and observed good recoveries. The developed CeO_2 NPs/SPCE shows good NB sensor electrode was compared with the other composites.

2. EXPERIMENTAL

2.1 Chemicals and Apparatus

Ammonium cerium (IV) sulfate ($Ce(NH_4)_4(SO_4)_4.\ 2H_2O$), polyvinylpyrrolidone (PVP), potassium nitrate (KNO_3)**,** nitrobenzene (NB) were occurred from Sigma-Aldrich and all other solution was prepared with deionized water (18.25 MΩ cm, Milli-Q). The supporting electrolytes 0.05 M phosphate buffer solution (PBS) was prepared by mixing of 0.05 M Na_2HPO_4 and NaH_2PO_4 and the pH of the PBS was varied by adding H_2SO_4/NaOH. All the chemicals were used in analytical grade and used as purchased.

2.2 Preparation of ultra-small CeO_2 NPs

The CeO_2 was prepared by the hydrothermal process [16]. Thereby, the 0.2g of $Ce(NH_4)_4(SO_4)_4.\ 2H_2O$ and 0.6g of PVP were dissolved in 80 mL water and sonicated for 15 min.

Additionally, 10 mL solution of 1 M KNO_3 and 10 mL of 1 M NH_3OH was added and stirred for 1 h at room temperature. Then the mixture of solution transferred to the Teflon-lined stainless-steel autoclave of 150 mL capacity. Then, the sample was washed three times with deionized water and ethanol to remove the unreacted compounds. Finally allowed to dried in an oven at 50 ^{o}C for 6 h.

2.3 Preparation of modified SPCE

Typically, 5 mg of ultra-small CeO_2 NPs was dispersed in 1 mL of water followed by sonication. Then, 8 µL of prepared solution was drop casted into pre-cleaned SPCE and allowed to dried.

3. RESULTS AND DISCUSSION

3.1 Characterization of CeO_2 NPs

We synthesized CeO_2 NPs by reacting $Ce(NH_4)_4(SO_4)_4$. $2H_2O$ with PVP in closed autoclave at 150 ˚C for 6 h. The structure and morphology of CeO_2 NPs were characterized by HR-TEM. As shown in Fig. 2(A), the size of CeO_2 NPs was homogeneous. In Fig. 2(B), obviously shows the size of nanoparticles was about 2-5 nm and the shape of CeO_2 NPs was spherical. A typical EDX spectrum as shown in Fig. 2(C), which indicate the purity and the presence of Ce and O element in the as-prepared CeO_2 NPs.

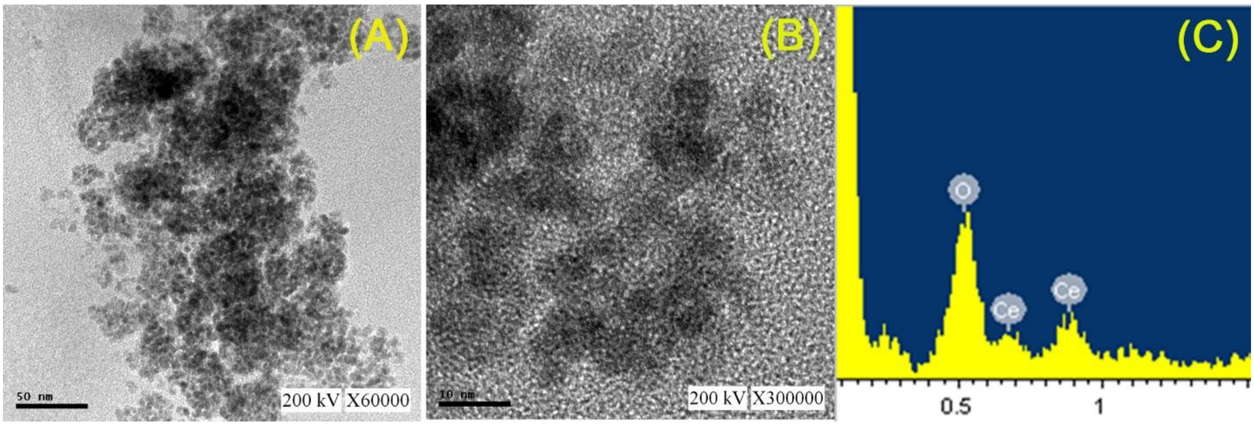


Figure 1. TEM images of CeO_2 NPs at different magnification (A and B) and EDX spectra of CeO_2 NPs (C).

3.2 Electro-catalysis behavior of NB at CeO_2 NPs/SPCE

The electrochemical performance of NB was studied at the different modified electrode, such as (a) bare SPCE and (b) CeO_2 NPs/SPCE was investigated by CVs in 0.05M PBS (pH 7.0) containing 200 µM NB at a scan rate (50 mV/s). Figure 2, A bare SPCE, the irreversible reduction peak current is appeared in cathodic peak potential (-0.73 V) was observed. The CeO_2/SPCE in presence of NB revealed three different peaks were observed in electrode.

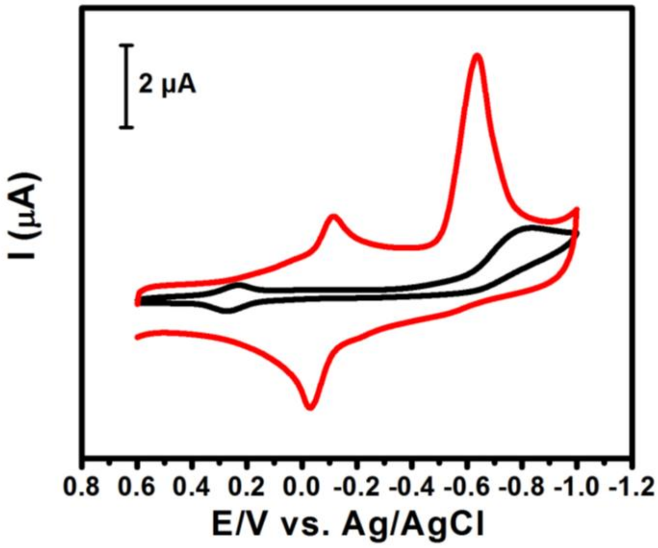
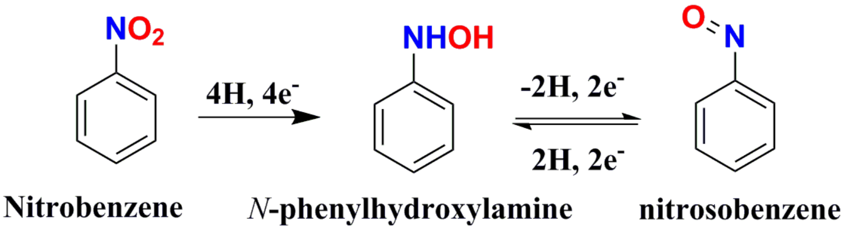


Figure 2. CVs response of bare SPCE (a), CeO_2 NPs/SPCE (b) in 200 μM NB containing PBS (pH 7) at a scan rate of 50 mV s^{-1}.

This result obviously indicates that the CeO_2 modified SPCE shows highly enhanced reduction peak current and potential response for NB reduction compared to the bare SPCE. The cathodic peak (-0.63 V) are attributed to the reduction of NB to phenylhydroxylamine. On the reverse anodic segment, no oxidation peak was detected corresponding to reduction peak, signifying that the reduction peak is irreversible. However, an anodic peak potential appeared at -0.026 V with reduction peak at -0.109 V during the cathodic segment. The observed CV curve respect to the oxidation of phenylhydroxylamine to nitrosobenzene (Scheme 1) [3, 17]. Therefore, CeO_2/SPCE has the better sensitive electrochemical detection for NB.



Scheme 1. A plausible mechanism of electrochemical reduction process.

3.3 Effect of scan rate

Figure 3, displays the various scan rate on the electro-catalytic reduction performance of CeO_2 NPs modified SPCE for determination of 200 μm NB in 0.05 M pH 7 (PBS) with different scan rate (20 – 200 mV/s). From the CV curves observed clearly explain, the cathodic peak currents are gradually increased as the increase scan rate results in slightly shift of cathodic peak potential towards negative value. Figure 3B, the linear plot of the cathodic peak current vs. square root of scan rate, which may indicate the linear regression equation I (μA) = 0.0463 + 7.7408, R^2 = 0.999. The results are clearly confirming that the surface-confined process is a diffusion-controlled process (Figure 3B) [18].

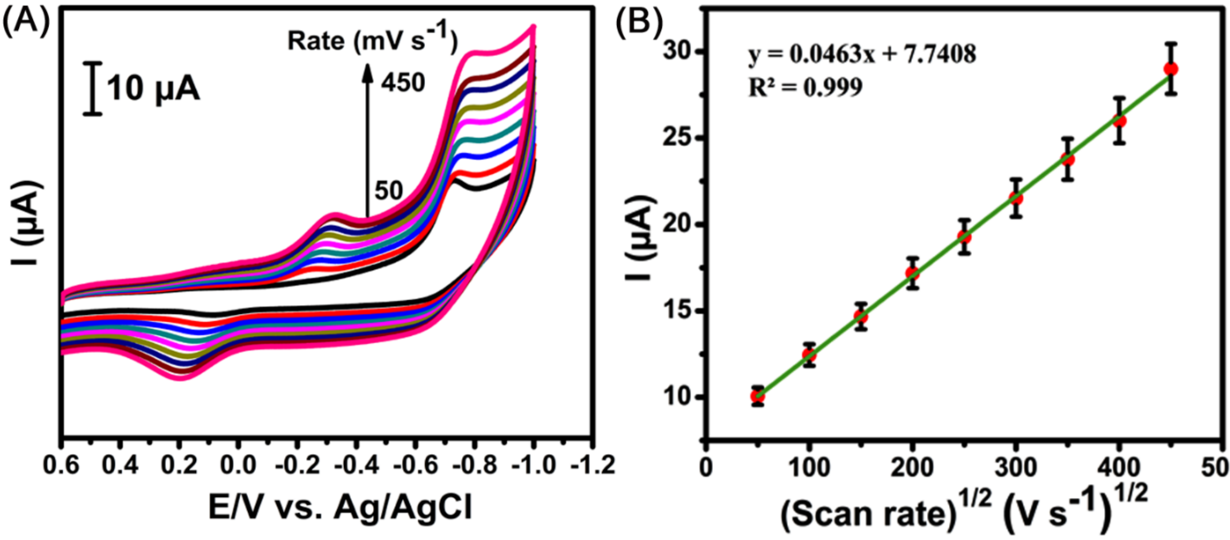


Figure 3. (A) CVs obtained at CeO_2 NPs/SPCE for 500 μM NB with PBS (pH 7) at varying scan rate from 50 to 450 mV s^{-1}. (B) The liner calibration plot of the current vs. square root of scan rates.

3.4 Effect of concentration

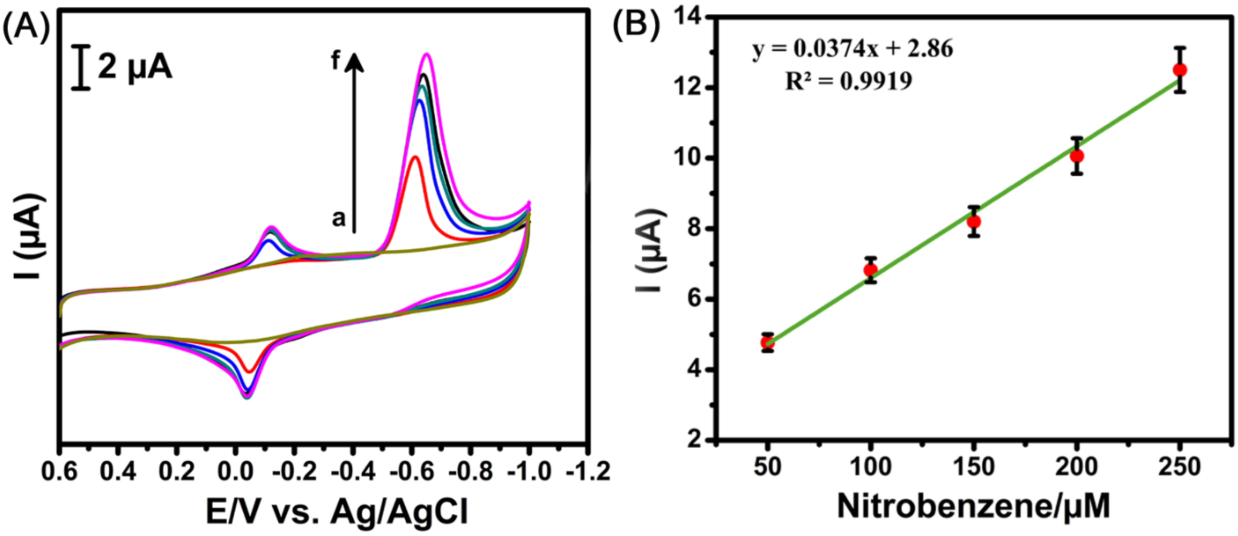


Figure 4. (A) CVs obtained CeO_2 NPs/SPCE towards different concentration of NB (a-f) in 0.05 M PBS (pH 7) at scan rate = 50 mV s^{-1}. (B)The calibration plot: current vs. nitrobenzene (μA).

Figure 4, shows that the CVs responses for the detection of NB with different concentration at CeO_2 NPs modified SPCE in PBS (pH 7) at scanning rate 50 mV s^{-1}. When the without the addition of 4-NA (a), the CeO_2 NPs/SPCE does not show distinct peaks. Whereas a well-defined cathodic peak was observed with 100 µM NB. Additionally, the cathodic peak currents of the NB increases with increase in every addition the concentration from 100 to 500 µm NB (b-f). The result shows that the excellent electrochemical reduction behavior of NB at CeO_2 NPs/SPCE. Figure 4B corresponding to the linear plot between cathodic peak currents and NB concentration. Which shows the linear regression equation and correlation coefficient calculated as I (µA) = 0.0374x + 2.86 and R^2 = 0.9912.

3.5 Electrochemical determination of NB

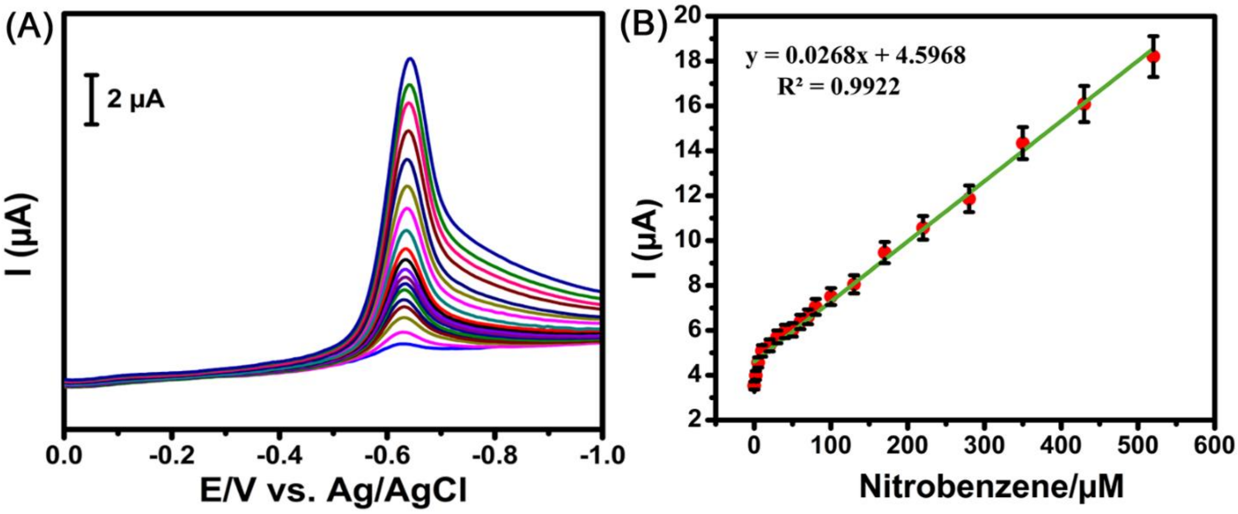


Figure 5. (A) DPVs of the CeO_2NPs/SPCE in N_2 PBS (pH 7) with different concentration of NB (0.1 to 520 µM) at scan rate 10 mV s^{-1}. (B) The calibration plot for concentration [NB] vs. current (µA)

The electrochemical determination of NB was studied by CeO_2 NPs modified electrode in PBS (pH 7) by using DPV. Figure 5. shows that the DPV response of CeO_2 NPs/SPCE in containing PBS (pH 7) different concentration from NB from 0.1 to 520 µM. here the DPVs curves show, a sharp and stable cathodic reduction peak current for NB. These results confirmed that the CeO_2 NPs modified electrode exhibited an excellent sensitivity (1.1166 µA $µM^{-1}$ cm^{-1}) for NB and with a detection limit (LOD) of 0.092 µM (S/N=3). The obtained sensitivity and LOD of the sensor was compared with previously reported NB sensor and shown in Table 1. The obtained linear regression equation is I (µA) = 0.0268 + 4.5968 [NB]/µM with the correlation coefficient of 0.9922. the sensitivity calculated as 1.2762 µA $µM^{-1}$ cm^{-1} with the limit of detection.

Table 1. Comparison of sensor performance of CeO_2 NPs/SPCE with previously reported chemical modifiers

Electrode modifier	**Linear range /µM**	**Detection limit /µM**	**Sensitivity /µMµM^{-1} cm^{-2}**	**Ref.**
Au/silica microspheres	0.1 – 2500	0.050	0.348	[19]
Au microstructure	0.05 – 038.8	0.01	0.665	[10]
Au MOF-5	1.0	1.0	0.43	[20]
Ag/SiO_2 NPs	5 – 45	0.50	-	[21]
Au NPs	0.1 - 600	0.016	1.01	[22]
Pd-GG-g-PAM-silica	1 –1900	0.026	0.06	[23]
β-CD/GO	0.5–100	0.184	2.291	[24]
RGO–Ag NPs	0.5 – 900	0.261	0.836	[25]
γ -Al2O3	0.5- 145.5	0.15	1.27	[26]
GR-GHI	0.1- 594.6	0.037	1.98	[27]
Ultra-small CeO_2 NPs	0.1 - 520	0.092	1.1166	**This work**

NPs-nanoparticles, GR-CHI- Graphene-Chitin, β-CD- β-Cyclodextrin

3.6 Stability, repeatability and reproducibility

In order to determine the storage stability of the CeO_2 NPs/SPCE, its NB detection of performance was observed every day. During two weeks storage period, the fabricated modified electrode retained 93.45% of initial current response which revealing good storage stability. The CeO_2 NPs/SPCE revealed appreciable repeatability with RSD of 1.98% for five successive repetitive measurements in the single modified electrode. Moreover, the sensor exhibits excellent reproducibility with RSD of 2.2% for four independent measurements carried out at four different CeO_2 NPs/SPCE.

3.7 Real sample analysis

Table 2. Detection of NB at CeO_2 NPs/SPCE in water samples

Sample	**Spiked (µM)**	**Found (µM)**	**Recovery % (mean± RSD) (n=3)**
Tap water	5.0	4.94	98.8 ± 1.4
	10.0	9.53	95.3 ± 2.5
	15.0	14.97	99.8± 1.73
River water	5.0	4.76	95.2± 2.9
	10.0	9.90	99.0± 1.5
	15.0	14.95	9..6± 2.2

* RSD = Relative Standard Deviation of (n=3) three individual measurements.

To examine the Practical feasibility of the CeO_2NPs/SPCE NB sensor, the determination of NB in real water samples were evaluated by DPV. Thus, the CeO_2NPs/SPCE was practical to the detection of NB in tap water and river water samples were determined using spiked recovery method. The attained results were shown in Table 2, the found and recovery values are satisfactory range of RSD values below 2.9%. Hence the CeO_2/SPCE effectively applicable for the real-time application of NB sensor.

4. CONCLUSION

In conclusion, we successfully synthesized the ultra-small CeO_2 NPs by the simple hydrothermal method. The as-prepared CeO_2 NPs was fabricated on SPCE have been effectively employed for the low-level detection of NB. The CeO_2 NPs/SPCE exhibited an acceptable level of linear range, lower LOD (0.092 μM) and high sensitivity (1.1166 $\mu A\ \mu M^{-1}\ cm^{-1}$) for the detection of NB. In addition, the CeO_2 NPs/SPCE modified electrode used for the determination of NB in tab water and river water samples. The NB sensor electrode furnished the good recoveries in real samples. Therefore, the CeO_2 NPs/SPCE an appropriate for the real sensing of NB in a commercial application.

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