**Supporting information**

**Insight into lanthanides REVO$_4$ (RE= Ce, Pr, Nd): a comparative study on RE–site variants in electrochemical detection of metronidazole in environmental samples**

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## *Chemicals and reagents*

Cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), praseodymium(III) nitrate hexahydrate ($Pr(NO_3)_3 \cdot 6H_2O$), neodymium(III) nitrate hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$), sodium orthovanadate ($Na_3VO_4$), cetyltrimethylammonium bromide (CTAB), ethylene glycol ($(CH_2OH)_2$), metronidazole ($C_6H_9N_3O_3$), $[Fe(CN_6)]^{3-/4-}$, potassium chloride (KCl), sodium dihydrogen phosphate ($NaH_2PO_4$), sodium phosphate dibasic ($Na_2HPO_4$: ≥99.0%) and ethanol were produced. Ultrapure fresh water is obtained from a millipore water purification system (Milli-Q, specific resistivity > 18 MΩcm, S.A.; Molsheim, France) and is used in all the experiments. $Na_2HPO_4$ and $NaH_2PO_4$ are utilized to prepare 0.1 M (pH 7) PB (phosphate buffer). All the electrochemical experiments are carried out using 0.1 M PB (pH 7) as the supporting electrolyte.

## *Instrumentation and methods*

Phase configuration is identified using X-ray diffraction analysis (XRD) (Bruker (XRD, 2D Phaser)) instrument and crystal structure by using VESTA software. FTIR spectrum of the as-prepared catalyst was documented by using 'Perkin-Elmer RX1 FTIR' spectrometer. The samples surface morphology and the elemental composition are studied utilizing high resolution (HR) transmission electron microscopy (TEM) (JEM–2100F (HR), JEOL LTD) and energy dispersive X-ray spectroscopy by using JOEL Serive Advanced Technology. By utilizing these characterization methods, the physical properties of the as-prepared samples are investigated. The electrochemical properties are explored using electrochemical impedance spectroscopy (EIS) through Autolab (PGSTAT101). CHI 1211c electrocatalytic workstation is functional to carry out the electrochemical measurements like cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a conventional three electrode cell. Here, the modified GCE (surface area = 0.072 $cm^2$), saturated Ag|AgCl and Pt wire are active as working, reference and counter electrodes, respectively.
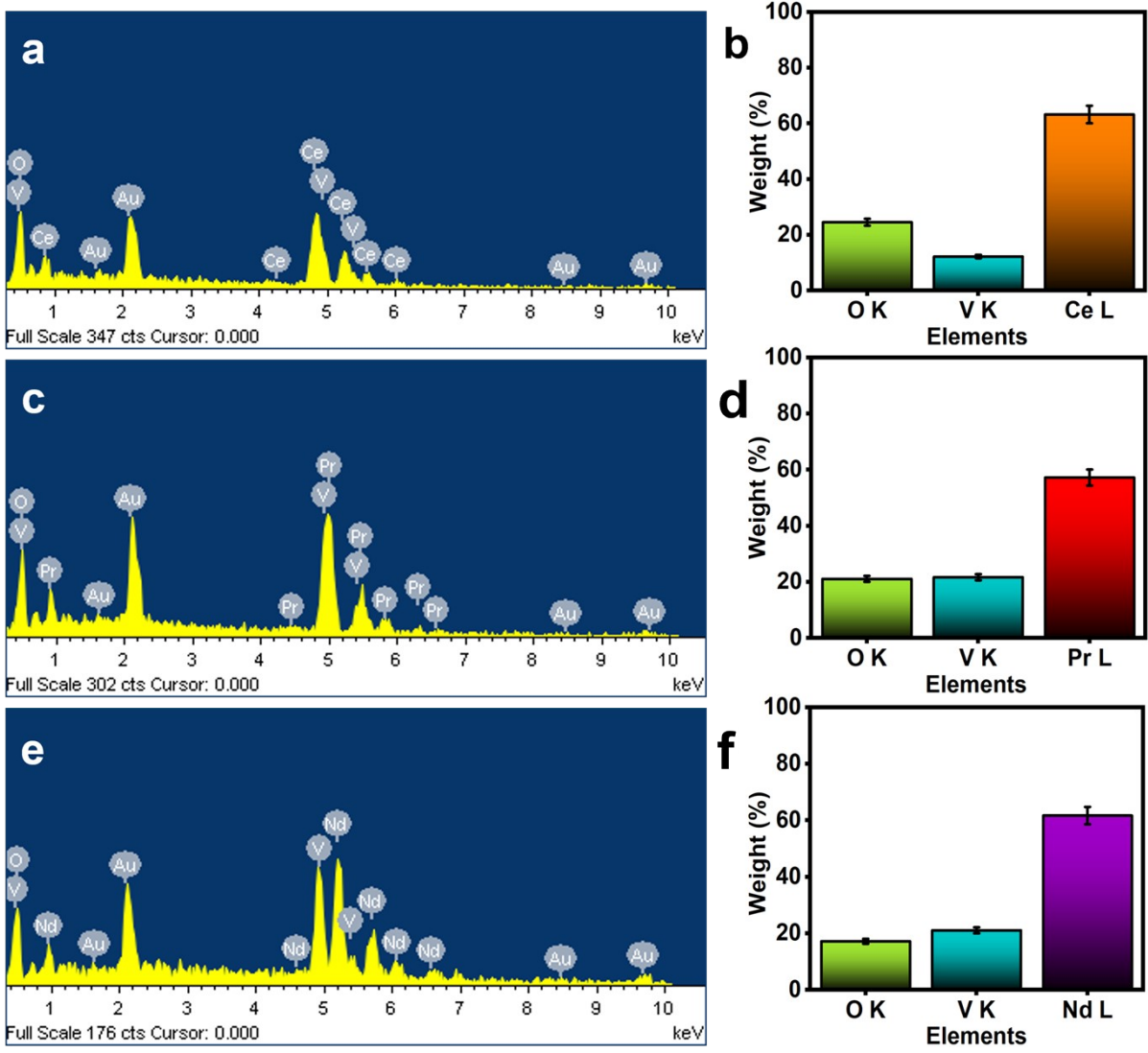
**Figure S1.** EDX spectra with weight% bar diagram of **(a, b)** CeVO$_4$, **(c, d)** PrVO$_4$, and **(e, f)** NdVO$_4$.
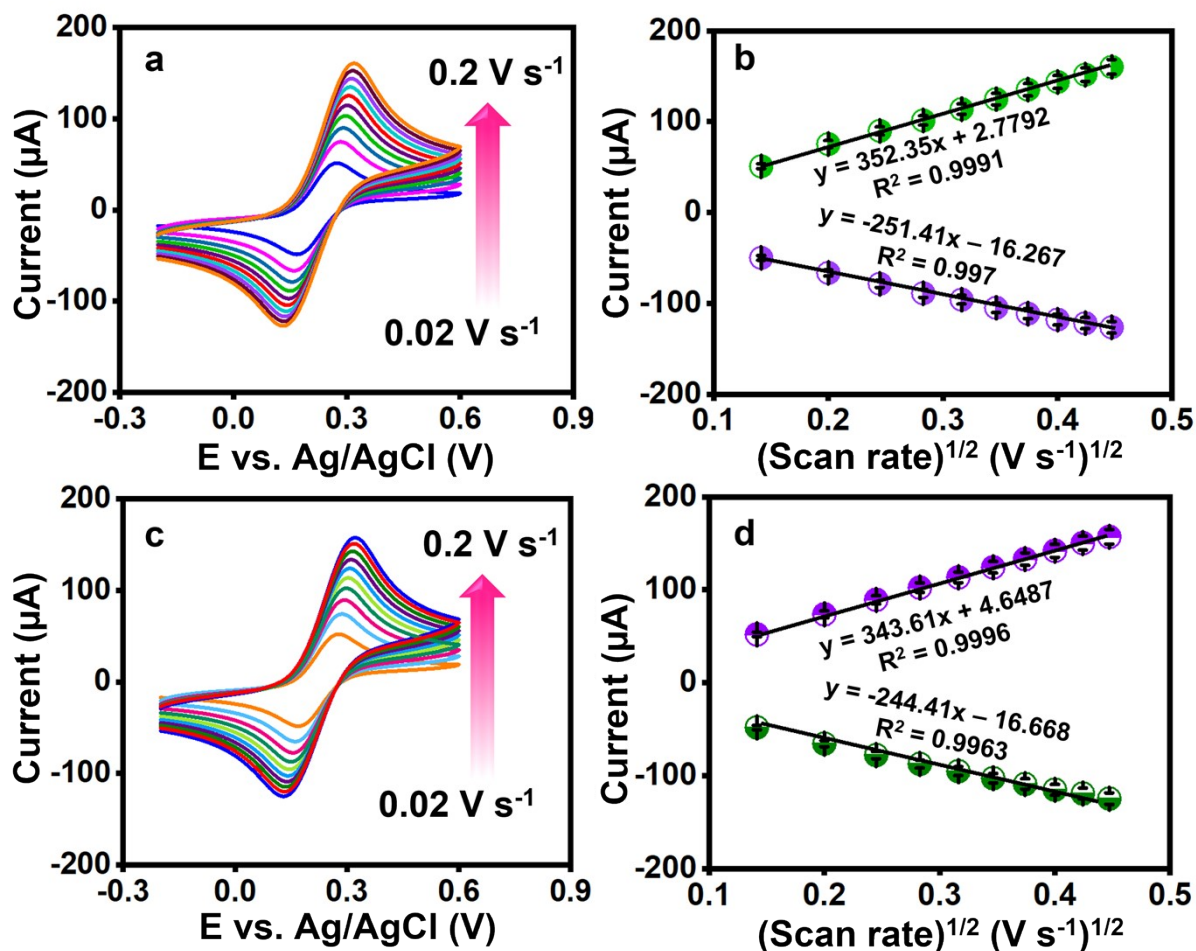
**Figure S2. (a and b)** CV curves of $PrVO_4$/GCE by increasing scan rate from 0.02 to 0.2 V s$^{-1}$ and linear plot of current vs square root of scan rate. **(c and d)** CV curves of $NdVO_4$/GCE by increasing scan rate from 0.02 to 0.2 V s$^{-1}$ and linear plot of current vs square root of scan rate.

***DPV analysis:*** For comparison, **Fig. S3a-d** displays the corresponding DPV measurement responses for $PrVO_4$ and $NdVO_4$. The calculated LODs and sensitivity of $PrVO_4$/GCE is 6.1 nM and 1.2 $\mu A \cdot \mu M^{-1} \cdot cm^2$, respectively. Similarly, the calculated LOD and sensitivity of $NdVO_4$/GCE is 6.9 nM and 0.85 $\mu A \cdot \mu M^{-1} \cdot cm^2$, respectively. When compared to $CeVO_4$/GCE exhibit high sensitivity and lower LOD than those other two modified electrodes. Due to the high electroactive surface area, and numerous active sites, which enhanced rapid electron transfer between electrode and electrolyte solution the $CeVO_4$ exhibits superior electrochemical activity when compared to other electrodes.
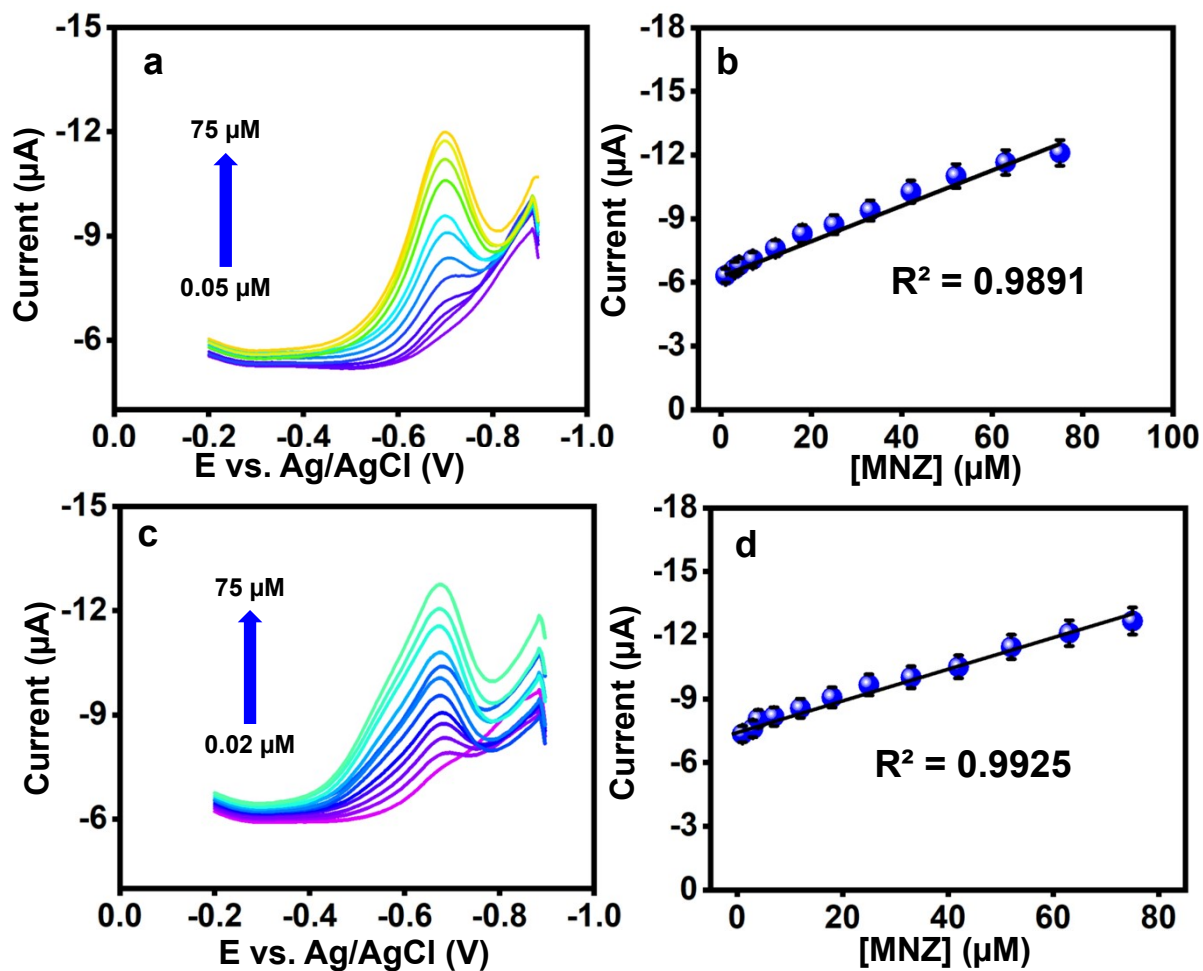
**Figure S3.** DPV analysis of MNZ at **(a)** NdVO$_4$ and **(c)** PrVO$_4$ with a sequential concentration of **(b)** NdVO$_4$= 0.05–75 μM and **(d)** PrVO$_4$= 0.02–75 μM in 0.1 M PB and its calibration plot of reduction peak current versus concentration of MNZ.

**Table S1. Comparison table of various analytical methods for MNZ determination**

| Modified electrode | Detection technique (μM) | LOD (μM) | Linear range (μM) | Ref. |
|---|---|---|---|---|
| PTH/GCE | DPV | 0.96 | 35−500 | 50 |
| Cu-poly (Cys)/GCE | LSV | 0.37 | 0.5-400 | 51 |
| Carbon fiber microdisk electrode | SWASV | 0.5 | 1-22 | 52 |
| Polydopamine/MWCNTs-COOH nanocomposites/GCE | DPV | 0.25 | 5–5000 | 53 |
| p-GR–Ag/GCE | LSV | 0.028 | 0.05−10 10−4500 | 54 |
| Co/GCE | LSV | 0.2 | 0.4–100 | 55 |
| DMIP/CPE | DPV | 0.091 | 0.4−200 | 56 |
| PCHAGCE | DPV | 0.33 | 10−400 | 57 |
| $CeVO_4$/GCE | **DPV** | **0.0045** | **0.02-75** | **This work** |
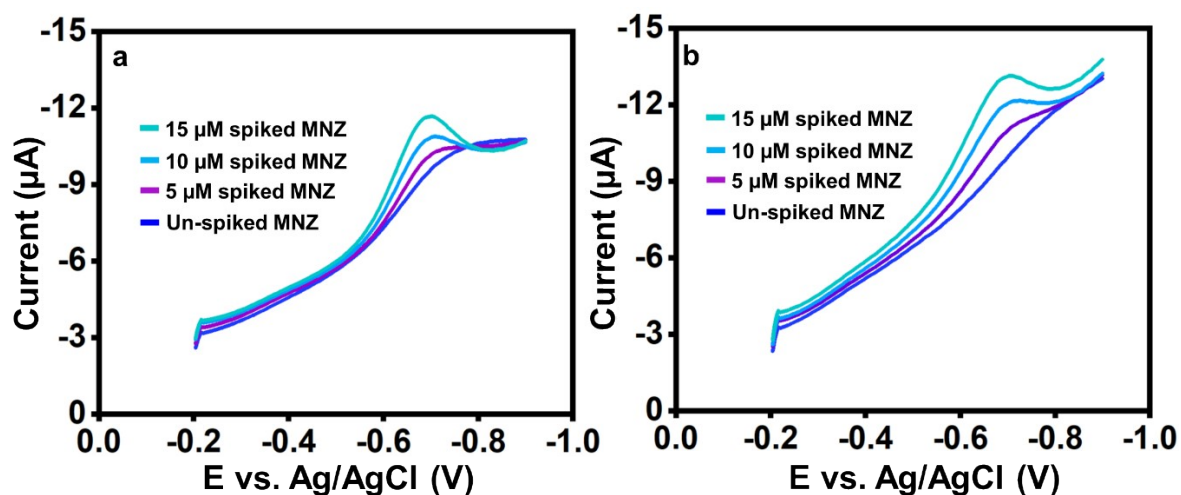
**Figure S4. (a, b)** Real-world samples DPV analysis of spiked and un-spiked MNZ at CeVO$_4$/GCE with a different concentration MNZ in 0.1 M PB (pH-7).

**Table S2.** Determination of MNZ in different water samples using CeVO$_4$/GCE.

| Samples | Added[a] (μM) | Detected[b] (μM) | | Detection rate (%) (mean ± RSD) (n = 3)[c] |
|---|---|---|---|---|
| | | DPV | HPLC | |
| **Tap water** | 0 | – | – | – |
| | 5 | 4.92 | 4.98 | 98.4 ± 0.24 |
| | 10 | 9.86 | 9.91 | 98.6 ± 0.019 |
| | 15 | 14.85 | 14.99 | 99.02 ± 0.021 |
| **River water** | 0 | – | – | – |
| | 5 | 4.82 | 4.93 | 96.58 ± 0.016 |
| | 10 | 9.89 | 9.95 | 98.9 ± 0.022 |
| | 15 | 14.72 | 14.87 | 98.13 ± 0.018 |

[a]Amount of sample added. [b]Average value of three measurements. [c]Relative standard deviation (RSD) of three individual measurements (n = 3).