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# Large interlayer spacing Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> (MXene) promotes the ultrasensitive electrochemical detection of Pb<sup>2+</sup> on glassy carbon electrodes†

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A Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> (MXene)-modified glassy carbon electrode was used for the electrochemical detection of Pb<sup>2+</sup> ions in aqueous media. The sensing platform was evaluated by anodic stripping analysis after optimizing the influencing factors such as pH, deposition potential, and time. The large interlayer spacing, high *c* lattice parameter and higher conductivity of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> compared to other MXenes enhance the electrochemical detection of Pb<sup>2+</sup>. The developed sensor can reach a detection limit of 12 nM at a potential  $\sim -0.6$  V. Additionally, the developed sensor showed promising selectivity in the presence of Cu<sup>2+</sup> and Cd<sup>2+</sup>, and stability for at least 5 cycles of continuous measurements with good repeatability. This work demonstrates the potential applications of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> towards the development of effective electrochemical sensors.

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## Introduction

Lead (Pb) is a common heavy metal, used in a variety of industrial processes and anthropogenic activities.<sup>1</sup> Pb<sup>2+</sup> ions are known for their extremely harmful biological toxicity through enzyme inhibition and induction of oxidative stress and can cause chronic damage to several human body systems, including kidneys, gastrointestinal system, nervous system, and reproductive system.<sup>2–4</sup> Moreover, Pb contamination poses a serious health and environmental hazard due to its high accumulation and low clearance rate at contaminated sites.<sup>5,6</sup> The maximum level of Pb<sup>2+</sup> in drinking water set by the United States Environmental Protection Agency (EPA) is 15  $\mu\text{g L}^{-1}$  (72 nM),<sup>7</sup> while the World Health Organization (WHO) limit for the blood Pb<sup>2+</sup> level is 100  $\mu\text{g L}^{-1}$  (483 nM).<sup>5,8</sup>

Various techniques are used for the detection of Pb<sup>2+</sup> in water including atomic absorption/fluorescence spectrometry, optical emission spectrometry, inductively coupled plasma mass spectrometry, and chemical or optical sensors.<sup>9–11</sup> Despite their reliability, the operations and maintenance associated with these methods are tedious, costly, and not suitable for on-site monitoring. Electrochemical techniques are inexpensive, selective, highly sensitive and effective alternative for the

detection of various toxic substances and heavy metals.<sup>12–14</sup> Moreover, electrochemical methods are characterized by their portability, easy operation, quick analysis time, and low maintenance and instrumentation costs.<sup>8,15</sup> Stripping voltammetry (especially anodic stripping) have been used as the sensitive and powerful electrochemical technique for the detection of heavy metal ions.<sup>1,9</sup> Different carbon nanomaterials such as carbon nanotubes, graphene, and its composite materials have been used as the sensing platform for sensitive Pb<sup>2+</sup> detection.<sup>16–20</sup>

The 2D transition metal carbides and carbonitrides (MXenes) have attracted broad attention with unique physico-chemical properties.<sup>21–24</sup> The large lateral size with few nanometer thickness, embedded with good hydrophilicity, and activated metallic hydroxide sites render MXenes as promising materials for environmental remediation applications.<sup>25–28</sup> MXene surfaces is negatively charged due to its surface functional groups, which facilitate the adsorption of several toxic heavy metals and emerging contaminants.<sup>27,29</sup> In addition, MXenes nanosheets having strong trapping power to small cations, due to less inter planner distance ( $< 2$  Å).<sup>30</sup> It was reported that Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> which is the most studied MXene, is an efficient adsorbent for the gold, lead and chromium cations.<sup>30</sup> In addition, the intercalation of different cations with various sizes and charges are possible between Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> layers.<sup>30</sup> After alkalization intercalation of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, alk-MXene (Ti<sub>3</sub>C<sub>2</sub>(OH/ONa)<sub>x</sub>F<sub>2–x</sub>) exhibits superior sorption behavior for Pb<sup>2+</sup> in presence of high levels of interfering cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup>.<sup>31</sup> Recently, alkalization-intercalated Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> modified electrode displayed enhanced electrochemical response towards the detection of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>.<sup>32</sup> The alkalization process increases the *c* lattice parameter of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>

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from 19.741 Å to 26.187 Å and the alkalization process results in unique morphology and alteration in surface chemistry. This leads to enhanced electrochemical responses for alkalization-intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$  towards the heavy metal detection in comparison with the  $\text{Ti}_3\text{C}_2\text{T}_x$ .

$\text{Nb}_4\text{C}_3\text{T}_x$  is another member of the MXenes family, prepared by etching of Al from the  $\text{Nb}_4\text{AlC}_3$  MAX phase.<sup>33,34</sup> Recently,  $\text{Nb}_4\text{C}_3\text{T}_x$  have been explored in a number of applications, including dye adsorption,<sup>35</sup> energy storage devices,<sup>23,36–38</sup> hematopoietic recovery,<sup>33</sup> photothermal tumor eradication,<sup>22</sup> supercapacitors,<sup>39</sup> and photocatalytic hydrogen production.<sup>40</sup> Even though, the electrochemical performance of  $\text{Nb}_4\text{C}_3\text{T}_x$  has not been widely explored towards sensing applications.

In this paper, we evaluate the electrochemical performance of  $\text{Nb}_2\text{CT}_x$  and  $\text{Nb}_4\text{C}_3\text{T}_x$  on the glassy carbon electrode (GCE) and their application as sensing platform for the detection of  $\text{Pb}^{2+}$  in the aqueous media. To the best of our knowledge, this is the first report discusses the application of  $\text{Nb}_4\text{C}_3\text{T}_x$  as electrochemical sensor for heavy metals.

## Experimental

### Materials

Phosphate buffer (PB) solution, NaOH,  $\text{H}_2\text{SO}_4$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , sodium acetate, acetic acid, lead nitrate, copper sulfate and cadmium acetate were purchased from Sigma Aldrich. The MAX phases of  $\text{Nb}_2\text{CT}_x$  and  $\text{Nb}_4\text{C}_3\text{T}_x$  ( $\text{Nb}_2\text{AlC}$  and  $\text{Nb}_4\text{AlC}_3$  respectively) were prepared by mixing powders of niobium (Alfa Aesar, 99.98%, –325 mesh), aluminum (Alfa Aesar, 99.9%, –325 mesh), and carbon (Alfa Aesar, 99%, 7–11 micron) at different ratios, followed by heating under an argon (Ar) flow. The detailed procedure is given in the ESI† and in the ref. 34 and 37.

### Synthesis of $\text{Nb}_2\text{CT}_x$ and $\text{Nb}_4\text{C}_3\text{T}_x$

The synthesis of multilayered  $\text{Nb}_2\text{CT}_x$  (ML- $\text{Nb}_2\text{CT}_x$ ) and  $\text{Nb}_4\text{C}_3\text{T}_x$  (ML- $\text{Nb}_4\text{C}_3\text{T}_x$ ) MXenes were done by hydrofluoric acid (HF) etching of Al layers from MAX phases  $\text{Nb}_2\text{AlC}$  and  $\text{Nb}_4\text{AlC}_3$  respectively. The  $\text{Nb}_2\text{AlC}$  or  $\text{Nb}_4\text{AlC}_3$  powders were stirred for 96 h at 40 °C after immersing in 50% HF aqueous solution. The resulting reaction mixture were washed 5 to 6 times using DI water and centrifuged at 3500 rpm to separate the ML-MXenes as settled powders from the supernatants. The resulting ML-MXenes were washed using ethanol, and dried at 30 °C under flow of argon. The delaminated  $\text{Nb}_2\text{CT}_x$  (DL- $\text{Nb}_2\text{CT}_x$ ) and  $\text{Nb}_4\text{C}_3\text{T}_x$  MXenes (DL- $\text{Nb}_4\text{C}_3\text{T}_x$ ) flakes were prepared by probe sonication (Cole Parmer, Ultrasonic Processor, 60% amplitude, 750 watt) of ML- $\text{Nb}_2\text{CT}_x$  and ML- $\text{Nb}_4\text{C}_3\text{T}_x$  MXenes (100 mg) in 5 mL of degassed DI water at 20 °C, under a flow of Ar gas for 1 h, followed by freeze-drying.

### Characterization

The morphology of prepared DL- $\text{Nb}_2\text{CT}_x$  and DL- $\text{Nb}_4\text{C}_3\text{T}_x$  MXenes were characterized by scanning electron microscopy (SEM), using a FEI Quanta 650 FEG. The transmission electronic microscopy (TEM) was performed by using FEI Talos

F200×. The ethanol dispersions of DL- $\text{Nb}_2\text{CT}_x$  and DL- $\text{Nb}_4\text{C}_3\text{T}_x$  were mounted on a lacey Formvar carbon-coated Cu grid for TEM analysis. Bruker D8 Advance X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54056 \text{ Å}$ ) was used to record X-ray diffractograms.

### Fabrication of DL- $\text{Nb}_2\text{CT}_x$ and DL- $\text{Nb}_4\text{C}_3\text{T}_x$ modified electrodes and electrochemical analysis

Prior to experiments, GCE was polished with alumina powder followed by sonication in a copious amount of ethanol and distilled water. 0.2 mg of  $\text{Nb}_2\text{CT}_x/\text{Nb}_4\text{C}_3\text{T}_x$  was dissolved in 1 mL of distilled water and homogeneous suspension was made by sonication for 1 min. Then, 6  $\mu\text{L}$  of this suspension was deposited onto GCE and dried at room temperature for overnight under inert atmosphere. CHI760E electrochemical workstation (CHI, Texas, USA) was used to conduct all electrochemical measurements with a three electrode system. The three electrode system consist of a modified GCE as the working electrode, Pt wire as the counter electrode, and Ag/AgCl in saturated KCl as the reference electrode. Cyclic voltammetry (CV) were performed at a scan rate of  $100 \text{ mV s}^{-1}$  in the 0.1 M PB solution (pH 7) and in the solution of 0.1 M KCl with 10 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ . Electrochemical impedance spectroscopy (EIS) measurements were performed at a potential of 10 mV in the 100 kHz to 0.1 Hz frequency range.

### Stripping voltammetry analysis

Square wave anodic stripping voltammetry (SWASV) measurements were used to detect  $\text{Pb}^{2+}$  in acetate buffer solution (0.1 M, pH 5.0) containing different concentration  $\text{Pb}^{2+}$ . The pre concentration step was performed at –1.2 V for 150 s while stirring the electrolyte solution. SWASV voltammograms were recorded after an equilibration period of 15 s, in the potential range from –0.8 V to 0 V with square wave potential scan having 4 mV increment potential, 25 mV amplitude and 50 Hz frequency. After each anodic stripping measurement, a desorption step was performed at a potential of 0.8 V for 100 s under stirring to remove the residual heavy metal ions on the electrode surface. For interference measurements, the pre concentration step was carried out at the potential of –1.2 V for 150 s while string the electrolyte solution containing  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  (5 times concentration than  $\text{Pb}^{2+}$ ) followed by recording SWASV voltammograms in the potential range from –1.2 V to 0 V. Error bars shows the standard deviation for three repetitive measurements in each experiment.

## Results and discussion

### Material characterization

DL- $\text{Nb}_2\text{CT}_x$  and DL- $\text{Nb}_4\text{C}_3\text{T}_x$  MXenes nanosheets were prepared by acid etching of Al layer using HF aqueous solution from their corresponding MAX phases as described in the Experimental section, followed by sonication and freeze drying. SEM images in (Fig. 1(a and c)) describe the typical accordion-like structure in both multi-layered (ML)- $\text{Nb}_2\text{CT}_x$  and ML- $\text{Nb}_4\text{C}_3\text{T}_x$  (Fig. 1(a and c)). After probe sonication, DL- $\text{Nb}_2\text{CT}_x$  and DL- $\text{Nb}_4\text{C}_3\text{T}_x$



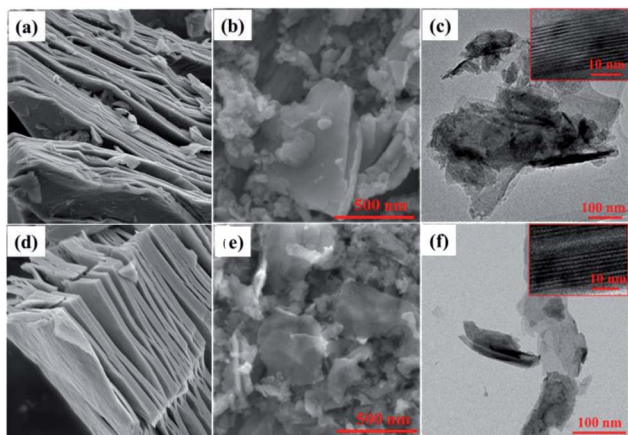
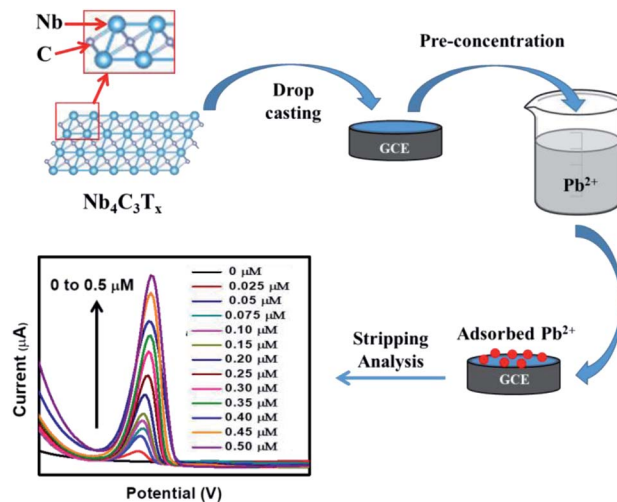


Fig. 1 SEM image of (a) ML-Nb<sub>2</sub>CT<sub>x</sub> (b) DL-Nb<sub>2</sub>CT<sub>x</sub> (d) ML-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> and (e) DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>. TEM image of (c) DL-Nb<sub>2</sub>CT<sub>x</sub> and (f) DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>. HR-TEM image of DL-Nb<sub>2</sub>CT<sub>x</sub> and DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> are shown in the inset of (c) and (f) respectively.

showed similar wrinkled sheet-like structure (Fig. 1(b and d)). Energy-dispersive spectroscopy (EDS) confirmed the presence of fluorine, oxygen, carbon and niobium elements in both MXenes (Fig. S1†). The TEM images revealed electron transparent single or few sheets with an average of 200–400 nm sheet size (Fig. 1(c and f)). In addition, the high resolution TEM (HR-TEM) images of DL-Nb<sub>2</sub>CT<sub>x</sub> and DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> shown in the inset shows the *d*-spacing  $\sim 11.5$  Å and  $\sim 15$  Å, respectively.<sup>36</sup> The XRD patterns of ML-Nb<sub>2</sub>CT<sub>x</sub>, DL-Nb<sub>2</sub>CT<sub>x</sub>, ML-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> and DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> are given in Fig. S2.† After delamination the intensity of (002) peaks were increased while intensity of other peaks decreased. The strong characteristic peak (002) in both DL-Nb<sub>2</sub>CT<sub>x</sub> (at 2theta of 7.87°) and DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> (at 2theta of 5.94°) confirmed the successful delamination and preparation of DL-MXenes.<sup>23,35</sup> DL-Nb<sub>2</sub>CT<sub>x</sub> has a smaller *c* lattice parameter (*c*-LP) of 22.44 Å as compared to 29.70 Å for DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>, as calculated from (002) peak position. The corresponding interlayer distance for DL-Nb<sub>2</sub>CT<sub>x</sub> was 11.22 Å and 14.85 Å for DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>, which is in a good agreement with the TEM results. The interlayer spacing in DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> were higher than that of DL-Nb<sub>2</sub>CT<sub>x</sub>, which could explain the interplanar distance increases with carbide blocks (*n*) in each MXene layer of M<sub>*n*+1</sub>X<sub>*n*</sub>T<sub>x</sub>. A 14.85 Å spacing of DL-Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> is larger than most studied MXenes.<sup>41</sup> As far as the electrochemical performance is concerned, larger interlayer space allows faster adsorption and intercalation of ions, and it enhances ion diffusion and charge transport of the electrolyte.<sup>42</sup>

### Electrochemical characterization of Nb<sub>2</sub>CT<sub>x</sub> and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>

The fabrication of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> modified GCE and the development of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> modified sensor for Pb<sup>2+</sup> detection is given in Scheme 1. CV and EIS analysis were used to investigate the electrochemical behaviour of Nb<sub>2</sub>CT<sub>x</sub> and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> modified electrodes in an aqueous solution containing ferrocyanide/ferricyanide redox couple solution. As observed in Fig. 2(a), well-defined redox peaks were observed for all the electrodes and these peaks can be attributed to the reversible redox



Scheme 1 The electrode fabrication and development of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> modified sensor for Pb<sup>2+</sup> detection.

behaviour of [Fe(CN)<sub>6</sub>]<sup>3−/4−</sup>. The  $\Delta E_p$  values for Nb<sub>2</sub>CT<sub>x</sub>/GCE and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE were 197 mV and 141 mV, respectively and the lowest  $\Delta E_p$  value of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE indicating highest electron transfer kinetics than Nb<sub>2</sub>CT<sub>x</sub>/GCE. In addition, the  $\Delta I_p$  values for Nb<sub>2</sub>CT<sub>x</sub>/GCE and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE were 114.51 mV and 110.10 mV respectively. The higher value of  $\Delta I_p$  again confirmed the highest electron transfer kinetics of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE than Nb<sub>2</sub>CT<sub>x</sub>/GCE. The electrochemical active surface area was calculated by using the Randles–Sevcik equation and it has a value of  $0.574 \times 10^{-3}$  cm<sup>2</sup> and  $0.621 \times 10^{-3}$  cm<sup>2</sup> for Nb<sub>2</sub>CT<sub>x</sub> and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> respectively (see ESI†).<sup>43</sup> The Nyquist plot for Nb<sub>2</sub>CT<sub>x</sub>/GCE and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE is given in Fig. 2(b). The charge transfer resistance (*R*<sub>ct</sub>) parameter was obtained after fitting the Nyquist plot and was used to evaluate the electron-transfer kinetics of the redox couple at the electrode interface.<sup>44</sup> The *R*<sub>ct</sub> values obtained for Nb<sub>2</sub>CT<sub>x</sub>/GCE and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE were (2142 ± 24) Ω and (1732 ± 19) Ω respectively by fitting with R(Q [RW]) Randles equivalent circuit. The resistivity is lowest for Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE and hence Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> is having the highest conductivity than Nb<sub>2</sub>CT<sub>x</sub> which can be justified by the higher '*n*' value of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> (*n* = 3) than Nb<sub>2</sub>CT<sub>x</sub> (*n* = 1).<sup>45</sup> From the CV and EIS analysis, it was found that Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> having highest electrochemical activity.

### Stripping behaviour of Pb<sup>2+</sup> and optimization of experimental parameters

The SWASV response of the bare GCE, Nb<sub>2</sub>CT<sub>x</sub>/GCE and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE were analyzed for the detection of Pb<sup>2+</sup> ions using acetate buffer solution containing 0.5 μM Pb<sup>2+</sup>. Compared with the bare GCE, well defined stripping peaks at around −0.58 V were observed for the Nb<sub>2</sub>CT<sub>x</sub>/GCE and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE and the peak current is highest for Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE than Nb<sub>2</sub>CT<sub>x</sub>/GCE (Fig. 3(a)). The highest response for Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> can be attributed to large interlayer spacing, high *c* lattice parameter value than Nb<sub>2</sub>CT<sub>x</sub> which is evident from TEM and XRD measurements. In addition, it was established that the resistivity of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> is



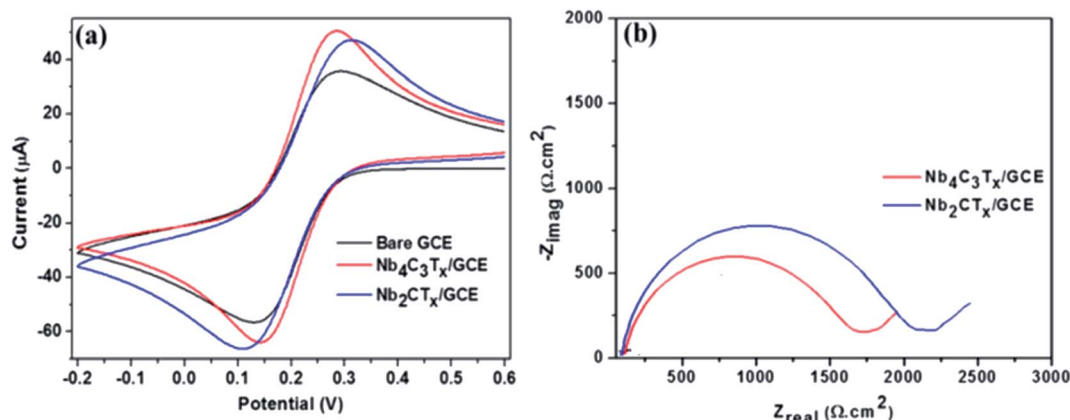


Fig. 2 (a) CVs of bare GCE,  $\text{Nb}_2\text{CT}_x/\text{GCE}$  and  $\text{Nb}_4\text{C}_3\text{T}_x/\text{GCE}$ . (b) Nyquist plots of  $\text{Nb}_2\text{CT}_x/\text{GCE}$  and  $\text{Nb}_4\text{C}_3\text{T}_x/\text{GCE}$ . Frequency range: 0.1 Hz to 10 kHz. The experiments were performed in the solution of 0.1 M KCl with 10 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ .

lower than  $\text{Nb}_2\text{CT}_x$ ,<sup>45</sup> which corresponds to the higher conductivity of  $\text{Nb}_4\text{C}_3\text{T}_x$  as evident from electrochemical analysis (Fig. 2). Hence,  $\text{Nb}_4\text{C}_3\text{T}_x$  has been selected as the sensing platform for the sensitive detection of  $\text{Pb}^{2+}$ .

The optimum conditions for highly sensitive  $\text{Pb}^{2+}$  detection were evaluated by changing the critical parameters such as pH,

deposition time and potential. The impact of pH on the stripping current was studied from 3.0 to 6.0 (Fig. 3(b)). The peak current of  $\text{Pb}^{2+}$  was increased with increasing the pH from 3.0 to 5.0 and then decreased at pH = 6. The presence of  $[\text{Nb}-\text{O}]-\text{H}^+$  groups favours the ion exchange behaviour of  $\text{Nb}_4\text{C}_3\text{T}_x$  and this behaviour increases with the pH which results in the

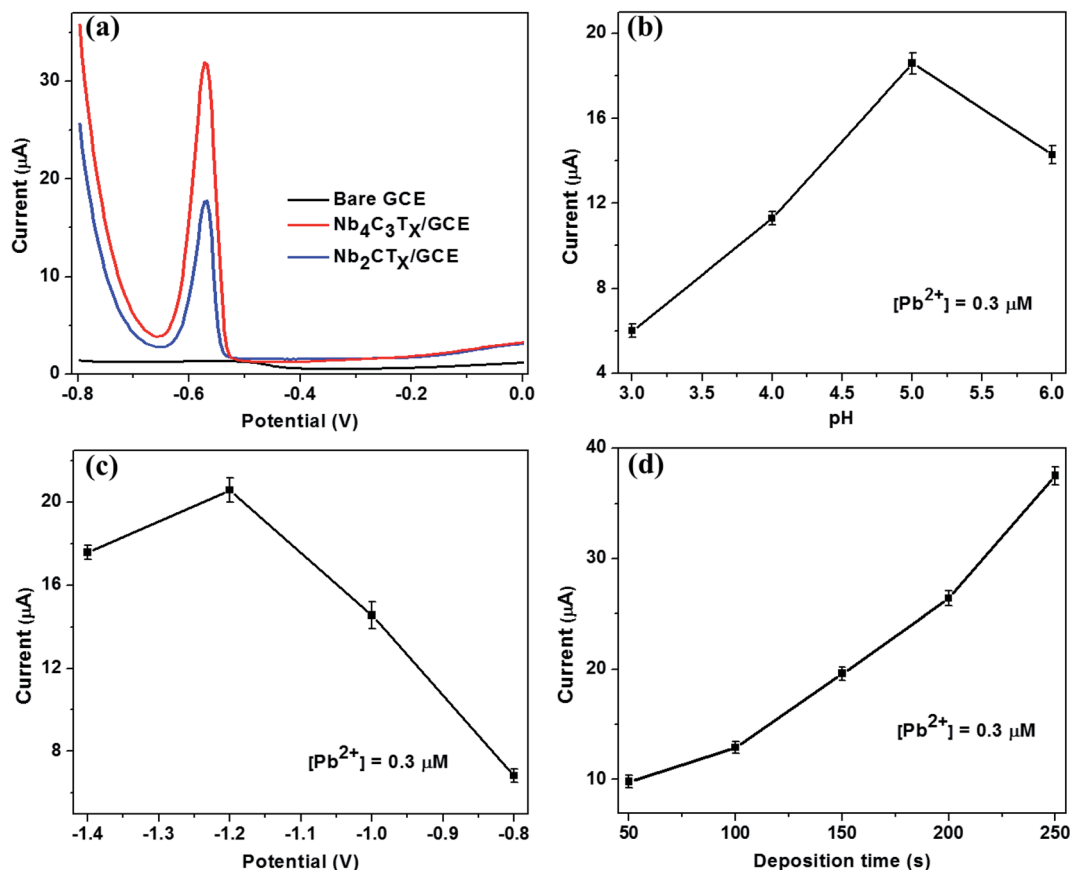


Fig. 3 (a) SWASV responses for bare GCE,  $\text{Nb}_2\text{CT}_x/\text{GCE}$  and  $\text{Nb}_4\text{C}_3\text{T}_x/\text{GCE}$  in presence of  $0.5 \mu\text{M}$  of  $\text{Pb}^{2+}$  in  $0.5 \text{ M}$  acetate buffer at pH 5, deposition potential of  $-1.2 \text{ V}$  and deposition time of  $150 \text{ s}$ . Optimization of experimental parameters. (b) pH, (c) deposition potential, and (d) deposition time towards the stripping current of  $\text{Nb}_4\text{C}_3\text{T}_x/\text{GCE}$ .





strengthening of stripping current.<sup>32</sup> The decrease in peak currents at pH 6 could be attributed to the hydrolysis of cations results in the formation of more  $\text{Pb}(\text{OH})_2$ , which inhibits the further accumulation of  $\text{Pb}^{2+}$ . Considering the maximum observed stripping peak current, pH 5 was selected as optimal for subsequent experiments.

Deposition potential and time are also critical factors for stripping analysis to detect heavy metal ions. The deposition potential was varied from  $-1.4$  to  $-0.8$  V and the resulting stripping currents increases with negative potential until  $-1.2$  V (Fig. 3(c)). A reduction in the current response was observed at deposition potential lower than  $-1.2$  V. This might be due to occurrence of more hydrogen evolution in the acetate buffer. Hence, the deposition potential of  $-1.2$  V was selected as optimal for further experiments. The deposition time was varied from 50 to 250 s and the stripping peak currents response was evaluated (Fig. 3(d)). The stripping peak current have increased linearly with the deposition time increase. A deposition time of 150 s was selected for subsequent experiments considering the concession between short measurement time, high sensitivity and good reproducibility favoured for practical applications.

### Quantitative detection of $\text{Pb}^{2+}$

Under the optimal conditions, the quantitative detection of  $\text{Pb}^{2+}$  was performed by SWASV on  $\text{Nb}_4\text{C}_3\text{T}_x/\text{GCE}$ . Fig. 4(a) shows the SWASV responses at different concentrations from 0 to  $0.5 \mu\text{M}$  of  $\text{Pb}^{2+}$ . The stripping peak currents increases with increasing the  $\text{Pb}^{2+}$  concentration and a good linear relationship was observed in the concentration range from  $0.025 \mu\text{M}$  to  $0.5 \mu\text{M}$ . There was no response for the developed sensor when the  $\text{Pb}^{2+}$  concentration was less than  $0.025 \mu\text{M}$  and this concentration can be regarded as limit of quantification of the sensor. The corresponding calibration plot is given in Fig. 4(b), by plotting the peak current vs.  $\text{Pb}^{2+}$  concentration. The calibration plot equation was represented as  $i (\mu\text{A}) = 58.49[\text{Pb}^{2+}] + 1.13$ , with 0.99688 as correlation coefficient ( $R^2$ ). The limit of detection (LOD) was calculated as  $12 \text{ nM}$  ( $\text{S/N} = 3$ ), which is much lower (or comparable) than the similar kind of sensors for  $\text{Pb}^{2+}$

detection (refer Table 1). In a similar work with alkaline intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene as platform for electrochemical detection of heavy metals, the stripping analysis showed a detection limit of  $32 \text{ nM}$  with linear range of  $0.10$ – $0.55 \mu\text{M}$  and this response is significantly higher than bare  $\text{Ti}_3\text{C}_2\text{T}_x$ . The analytical performance of  $\text{Nb}_4\text{C}_3\text{T}_x$  modified GCE is higher compared to bare  $\text{Ti}_3\text{C}_2\text{T}_x$  as well as alkaline intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$ . The analytical performance of  $\text{Nb}_4\text{C}_3\text{T}_x$  modified GCE was compared with other similar reported electrodes (summarized in Table 1) and it showed that the  $\text{Nb}_4\text{C}_3\text{T}_x$  modified GCE exhibited a wider range, promising detection limit and enhanced sensitivity. The large interlayer spacing and high  $c$  lattice parameter of  $\text{Nb}_4\text{C}_3\text{T}_x$  (in comparison with  $\text{Nb}_2\text{CT}_x$ ) have allowed for the adsorption of larger amount of  $\text{Pb}^{2+}$  between the sheets as well as the higher conductivity of  $\text{Nb}_4\text{C}_3\text{T}_x$  have improved the electrochemical response on the electrode surface. This strategy can be easily implemented into screen printed electrodes for practical and portable applications considering the versatile sensor fabrication by drop-casting  $\text{Nb}_4\text{C}_3\text{T}_x$  on the electrode followed by drying.<sup>46</sup>

### Selectivity, stability and repeatability

The selectivity of the  $\text{Nb}_4\text{C}_3\text{T}_x/\text{GCE}$  was analyzed in the presence of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  as interfering agents in 5 fold excess along with  $\text{Pb}^{2+}$  ion. The SWASV was performed under the optimum conditions. It is found that no or negligible change in the peak current of  $\text{Pb}^{2+}$  in presence of interfering ions. The peak for  $\text{Cu}^{2+}$  at around  $-0.1 \text{ V}$ ,<sup>32</sup> is present in the SWASV curve as shown in Fig. 5(a). The peak for  $\text{Cd}^{2+}$  at around  $-0.8 \text{ V}$ ,<sup>32</sup> is not clearly visible; however, the current response is higher in the particular range where the peak for  $\text{Cd}^{2+}$  normally visible. Fig. 5(b) shows the current response for the individual metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ) and their mixture at  $-0.58 \text{ V}$ . The peak current was almost the same for  $\text{Pb}^{2+}$  alone and in the mixture with other interfering ions. There is no current response at particular potential of  $-0.58 \text{ V}$  for the electrolyte solution containing  $\text{Cd}^{2+}$  or  $\text{Cu}^{2+}$ . These results confirmed the insignificant impact of interfering

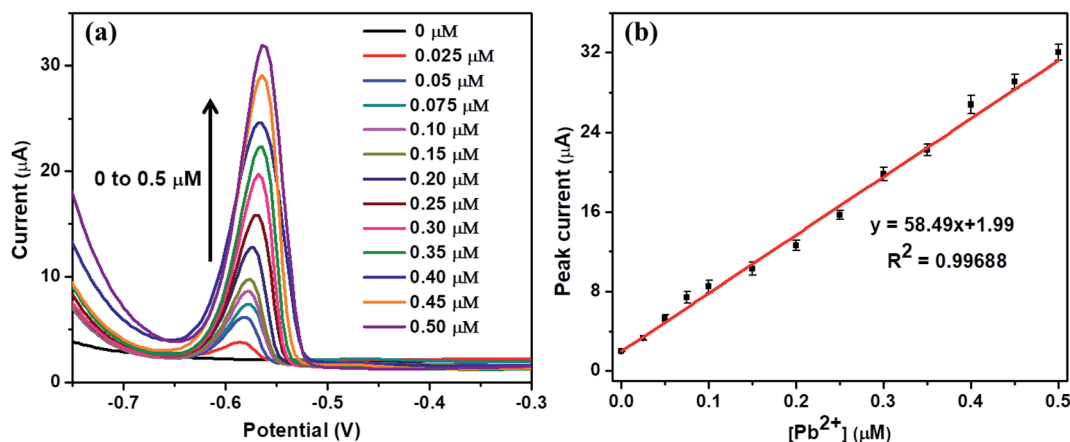


Fig. 4 (a) SWASV response of the  $\text{Nb}_4\text{C}_3\text{T}_x/\text{GCE}$  for in presence of  $\text{Pb}^{2+}$  from 0 to  $0.5 \mu\text{M}$ . (b) The calibration plot of peak current vs.  $\text{Pb}^{2+}$  concentrations.

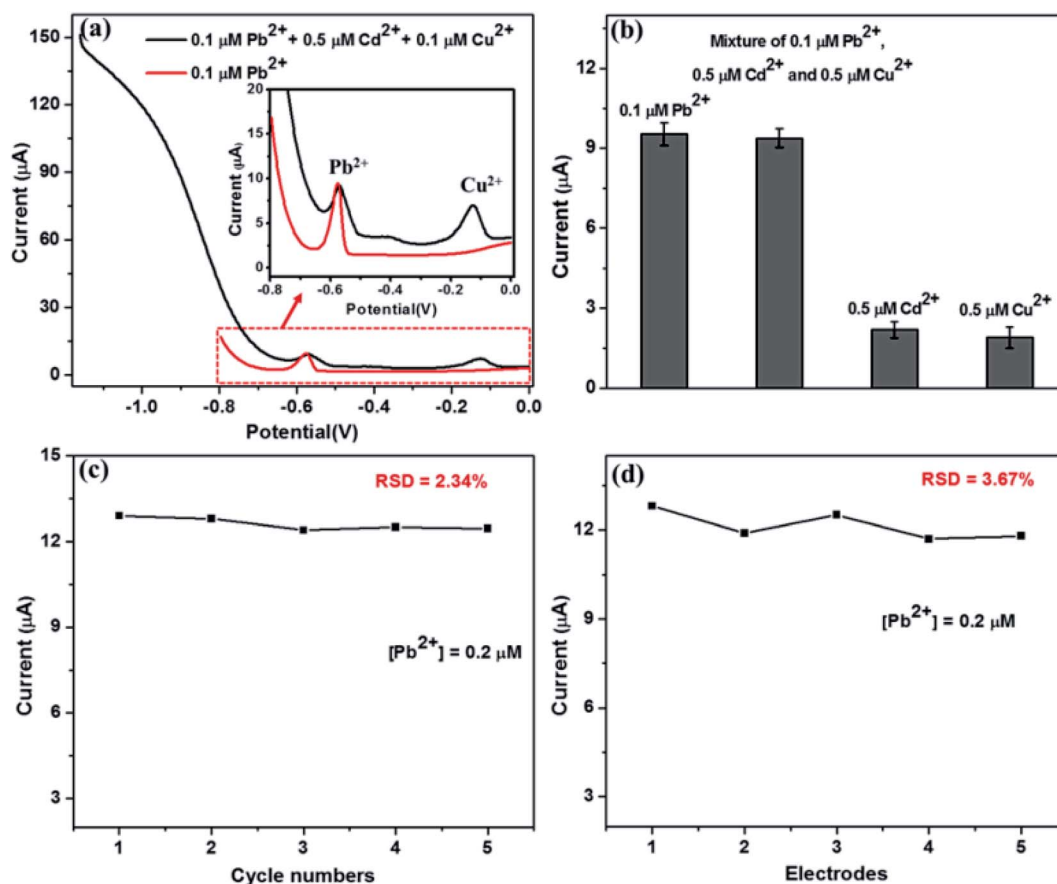
**Table 1** The analytical performance of different 2D materials used for  $\text{Pb}^{2+}$  detection

Electrode	Detection technique	Detection limit	Linear range	Ref.
L-Cys/AuNPs/NG/GCE	SWV	56 nM	1–80 $\mu\text{M}$	1
Bismuth modified exfoliated graphite	SWASV	53 nM	1.0–250 $\mu\text{M}$	9
MWCNT/P1,5-DAN/Pt	SWASV	2.1 $\mu\text{M}$	4 to 150 $\mu\text{M}$	16
MWCNT/5-Br-PADAP/GCE	SWASV	100 nM	0.9 to 114.6 $\mu\text{M}$	17
G/PANI/PS nanoporous fiber/SPCE	SWASV	3.30 $\mu\text{M}$	10–500 $\mu\text{M}$	18
L-Cys-rGO/GCE	DPASV	215 nM	0.4 to 1.2 $\mu\text{M}$	19
Nafion/G/PANI nanocomposite/SPE	SWASV	100 nM	1–300 $\mu\text{M}$	20
Alk- $\text{Ti}_3\text{C}_2$ /GCE	SWASV	32 nM	0.10–0.55 $\mu\text{M}$	32
$\text{Nb}_4\text{C}_3\text{T}_x$ /GCE	SWASV	12 nM	0.025–0.5 $\mu\text{M}$	This work

metal ions and hence the selectivity of the sensor at around  $-0.58$  V.

The stability of the  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE was investigated after 5 repetitive measurements using the same electrode and electrolyte containing  $0.2 \mu\text{M}$   $\text{Pb}^{2+}$ . After every measurement, a desorption step at a potential of  $0.8$  V was performed before the next electrodeposition steps. It is found that the SWASV response was highly reproducible with RSD value of 2.34 (Fig. 5(c)). In addition, the stripping current of  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE for

$\text{Pb}^{2+}$  was measured after keeping the electrode at  $4^\circ\text{C}$  for one week and the stripping current obtained was 94.3% of the initial current with RSD of 3.15. These results confirmed the stability of the  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE electrode towards the detection of  $\text{Pb}^{2+}$ . The reproducibility analysis of the sensor was carried out by using five identical  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE electrodes for the detection of  $\text{Pb}^{2+}$  using similar procedures. The SWASV responses for five different electrodes with  $0.2 \mu\text{M}$   $\text{Pb}^{2+}$  showing good



**Fig. 5** (a) SWASV response of the  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE for  $\text{Pb}^{2+}$  ( $0.1 \mu\text{M}$ ) in presence of  $\text{Cd}^{2+}$  ( $0.5 \mu\text{M}$ ) and  $\text{Cu}^{2+}$  ( $0.5 \mu\text{M}$ ). (b) Selectivity plot-SWASV response of the  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE at  $-0.6$  V for different heavy metals. (c) The stability of  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE – SWASV responses for 5 repetitive cyclic measurements with  $0.2 \mu\text{M}$   $\text{Pb}^{2+}$ . (d) The repeatability of  $\text{Nb}_4\text{C}_3\text{T}_x$ /GCE – SWASV responses for 5 different electrodes with  $0.2 \mu\text{M}$   $\text{Pb}^{2+}$ .



**Table 2** Recovery of Pb<sup>2+</sup> in drinking water and tap water using the Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE sensor

Sample	Pb <sup>2+</sup> added (μM)	Pb <sup>2+</sup> detected (%)	RSD (%)
Drinking water (bottled)	0.05	95.8	2.35
	0.1	99.5	1.81
	0.2	96.5	2.57
Tap water	0.05	102.3	2.95
	0.1	97.5	3.02
	0.2	95.5	2.13

repeatability between different electrodes with RSD value of 3.67 (Fig. 5(d)).

### Practical applications

To evaluate the practical applications of the developed Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub>/GCE sensor, the response of the sensor has been measured after spiking the Pb<sup>2+</sup> in bottled and tap water samples. The SWASV response of the sensor has been measured and the results are given in Table 2. The sensor exhibited a promising recovery between 95% and 102% with a relative standard deviation of 1.8–3.0%. From these results, it was confirmed that the developed sensor can be used for the detection of Pb<sup>2+</sup> from samples.

### Conclusions

The electrochemical behaviour of Nb<sub>2</sub>CT<sub>x</sub> and Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> was investigated to explore its potential in electrochemical applications. The Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> has demonstrated promising electrochemical performance and its electrochemical response is higher than Nb<sub>2</sub>CT<sub>x</sub>. The electrochemical detection capability of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> towards Pb<sup>2+</sup> ions has been investigated by stripping analysis at optimized conditions. Evident by the high sensitivity and good reproducibility, the large interlayer spacing of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> can accommodate Pb<sup>2+</sup> ions without destroying the layered structure of the electrode. The results showed that Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> can be used as an immobilization platform for sensitive detection of Pb<sup>2+</sup> with wide linear range and detection limit of 12 nM. This work validates the potential application of Nb<sub>4</sub>C<sub>3</sub>T<sub>x</sub> for the first time towards electrochemical sensing applications.

### Conflicts of interest

There are no conflicts to declare.

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