

Electronic Supplementary Information for

**Bottom up fabrication of two-dimensional carbon nitride  
and highly sensitive electrochemical sensor for mercuric ions**

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## Experimental

### Synthesis of $C_3N_4$

Carbon nitrides ( $C_3N_4$ ) were produced by microwave assisted bottom up fabrication from formamide ( $HCONH_2$ ). Formamide (HPLC grade) was purchased from Merck (Darmstadt, Germany) and used as received without any further purification. In a typical synthesis procedure of carbon nitride dots (CNDs), 10 ml of formamide was heated by a MAS-II microwave synthesizer from Sineo Microwave Chemistry Technology Company (Shanghai, China) at  $180^\circ C$  for ~ 30 minutes. The resulting brown color solution was vacuum-evaporated in a rotary evaporator at  $180^\circ C$  to produce solid carbon nitride quantum dots (CNDs). Finally, these solids were washed with de-ionized water and dried under vacuum at room temperature. These CNDs are used as precursors for two dimensional sheets of carbon nitrides. The aqueous solutions of CNDs were prepared by dissolving 0.5 mg of CNDs in water with ultra sonic aid to form 1mg/L solution. The different concentration of CNDs solutions were made by diluting this 1mg/L solution with water. The two dimensional carbon nitrides are produced by drying these aqueous solution of CNDs in air at  $45^\circ C$  on solid substrate.

### Characterizations

The characterizations of  $C_3N_4$  sheets were done using tapping mode of AFM (Asylum MFP-3D Atomic Force Microscope) and transmission electron microscopy (TEM, JEOL JEM2010, operated at 200 kV). Powder X-ray Diffraction (p-XRD) patterns were performed on a Bruker DAVINCI D8 ADVANCE diffractometer equipped with Cu  $K\alpha$  radiation ( $\lambda = 0.15406$  nm). XPS measurements on the sample were done using a monochromatic Mg  $K\alpha$  X-ray source (XPS VG Microtech). XPS sample were prepared by drop casting few drops of aqueous solution

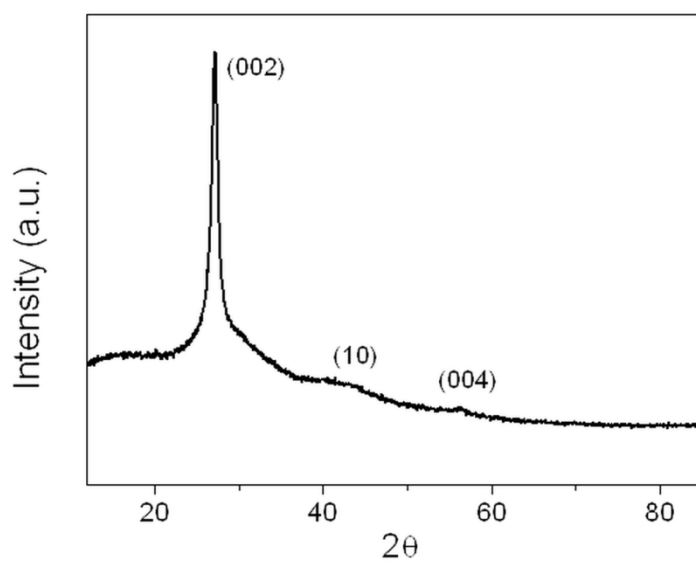
of CNDs on silicon substrate and drying in air at 45<sup>0</sup>C. FT-IR measurements of C<sub>3</sub>N<sub>4</sub> were performed using a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer. FT-Raman spectrum of C<sub>3</sub>N<sub>4</sub> was measured on Micro Raman (Model: STR 500; Seki Technotron, Japan) spectrometer using 488 nm laser. The thermo gravimetric analysis (TGA) of carbon nitride dots was done using Mettler Toledo 851e TGA/DTA (Mettler Toledo, Switzerland). SEM images of C<sub>3</sub>N<sub>4</sub> were obtained using field-emission scanning electron microscope (FESEM) system (Zeiss, Germany make, Model: Supra 55). Electrochemical measurements were performed with a conventional three electrode cell using an electrochemical workstation (CH Instrument, Model: 1100A).

#### **Preparation of C<sub>3</sub>N<sub>4</sub> modified GC electrode**

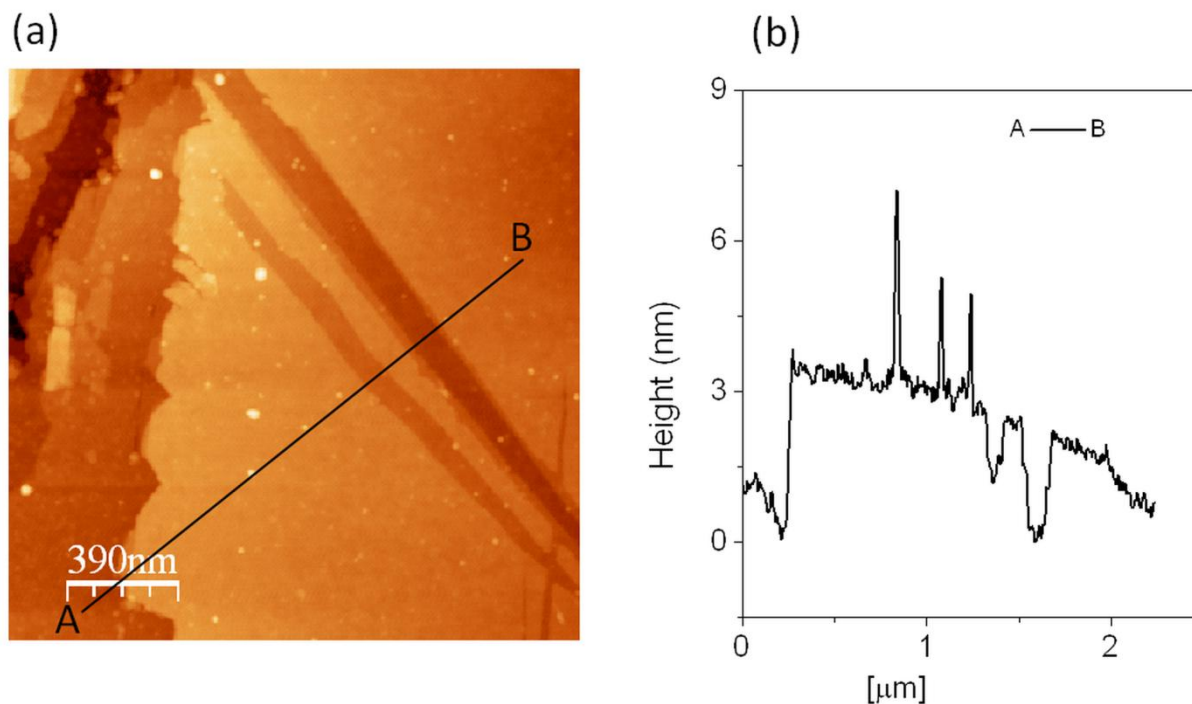
Glassy carbon (GC) electrode was polished first with 1.0 and 0.05-μm alumina slurry on Buehler microcloth polishing cloth. After rinsing with distilled water, the electrode was sonicated in distilled water for about 5 minutes. 0.25 mg of CNDs was dispersed in water with ultra sonic aid to form 0.01mg/L solution. This solution is then centrifuged at 15000 rpm for ~ 1 hour. Finally, 30 μL of this solution was drop cast on the active surface of cleaned GC electrode and allowed to evaporate the solvent under flowing N<sub>2</sub>. Hence, GC electrode is coated with the film of C<sub>3</sub>N<sub>4</sub>.

**Table S1:** Average size of carbon nitride quantum dots in aqueous solution, measured by dynamic light scattering measurements, at different concentrations.

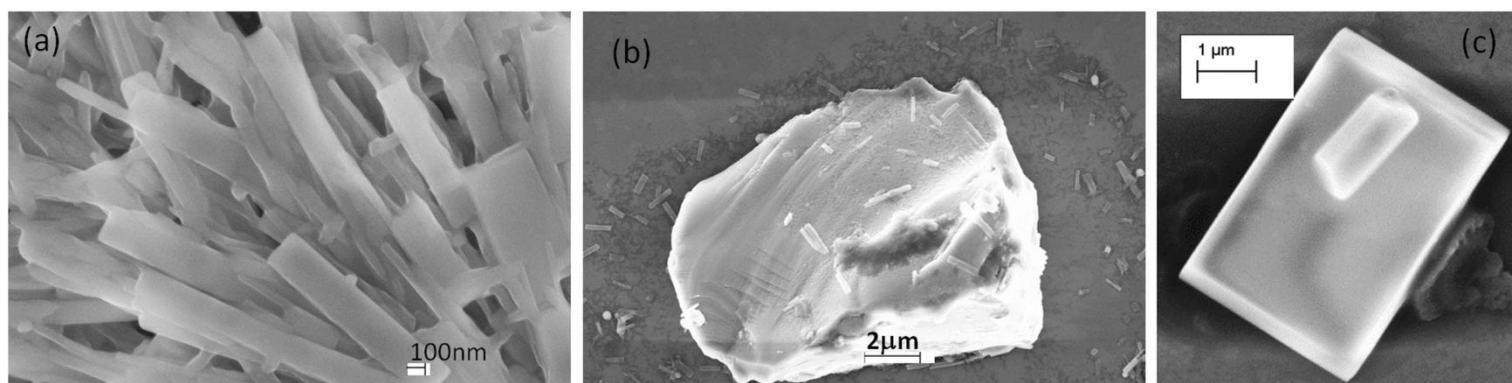
|   | Concentration of CNDs | Average Diameter |
|---|-----------------------|------------------|
| 1 | 1 mg/L                | 432 nm           |
| 2 | 0.001 mg/L            | 188.9 nm         |
| 3 | $10^{-5}$ mg/L        | 104.5 nm         |
|   | $10^{-7}$ mg/L        | 28.5 nm          |



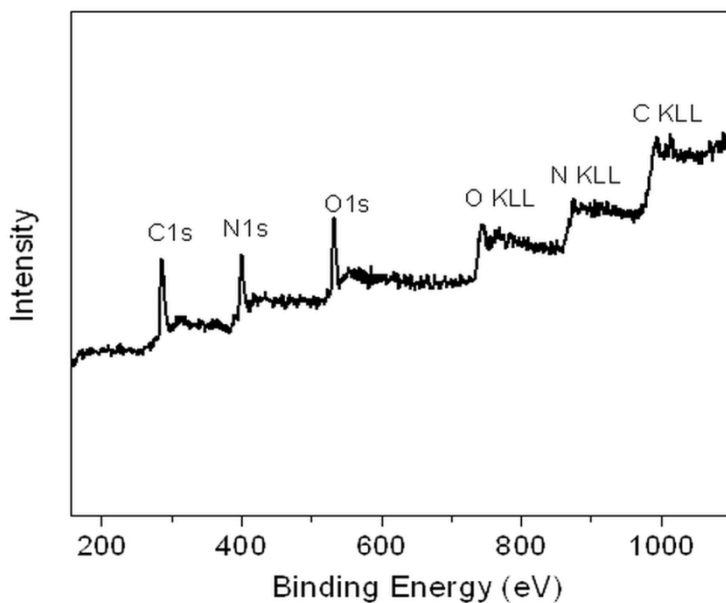
**Fig. S1:** Powder X-ray diffraction pattern of the carbon nitride.



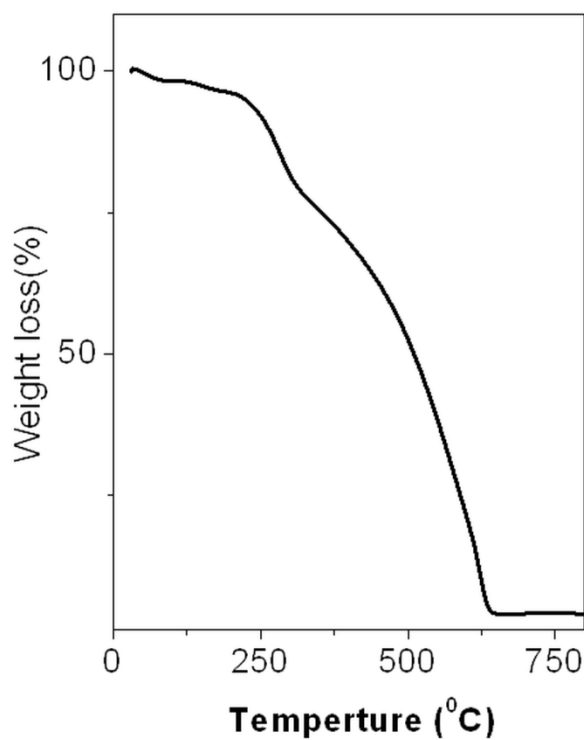
**Fig. S2:** (a) AFM image of C<sub>3</sub>N<sub>4</sub> sheets produced by drying a higher concentration (1mg/L) of CNDs solution (10 μL). (b) The line profile along the line AB in image (a) indicating the presence of C<sub>3</sub>N<sub>4</sub> quantum dots on the surface on C<sub>3</sub>N<sub>4</sub> sheet.



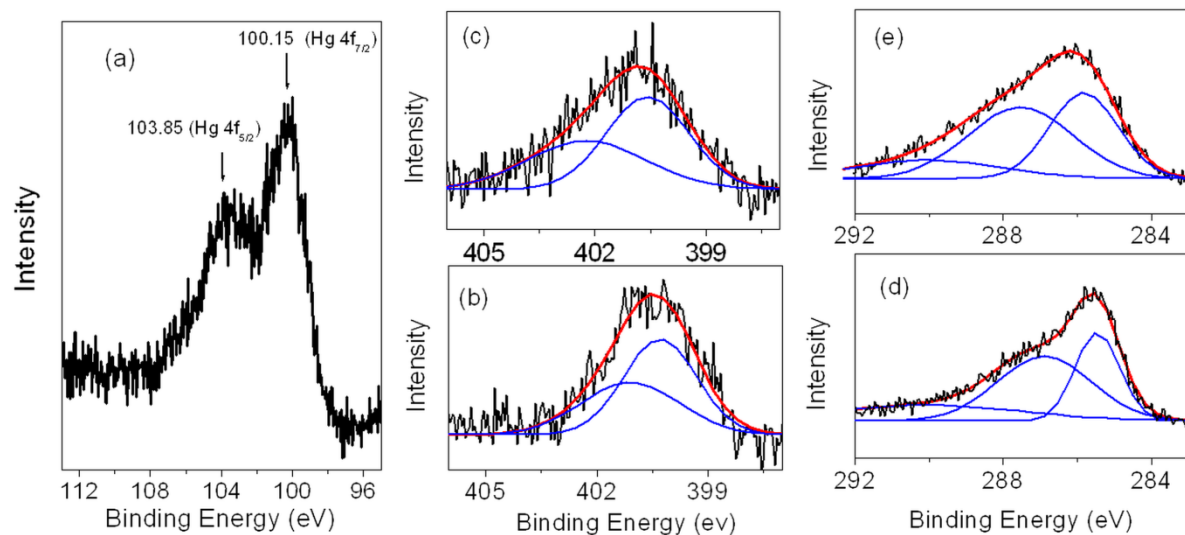
**Fig. S3:** SEM image of C<sub>3</sub>N<sub>4</sub>, prepared by evaporation of 30μL solution (1mg/L) CNDs in air at 45°C.



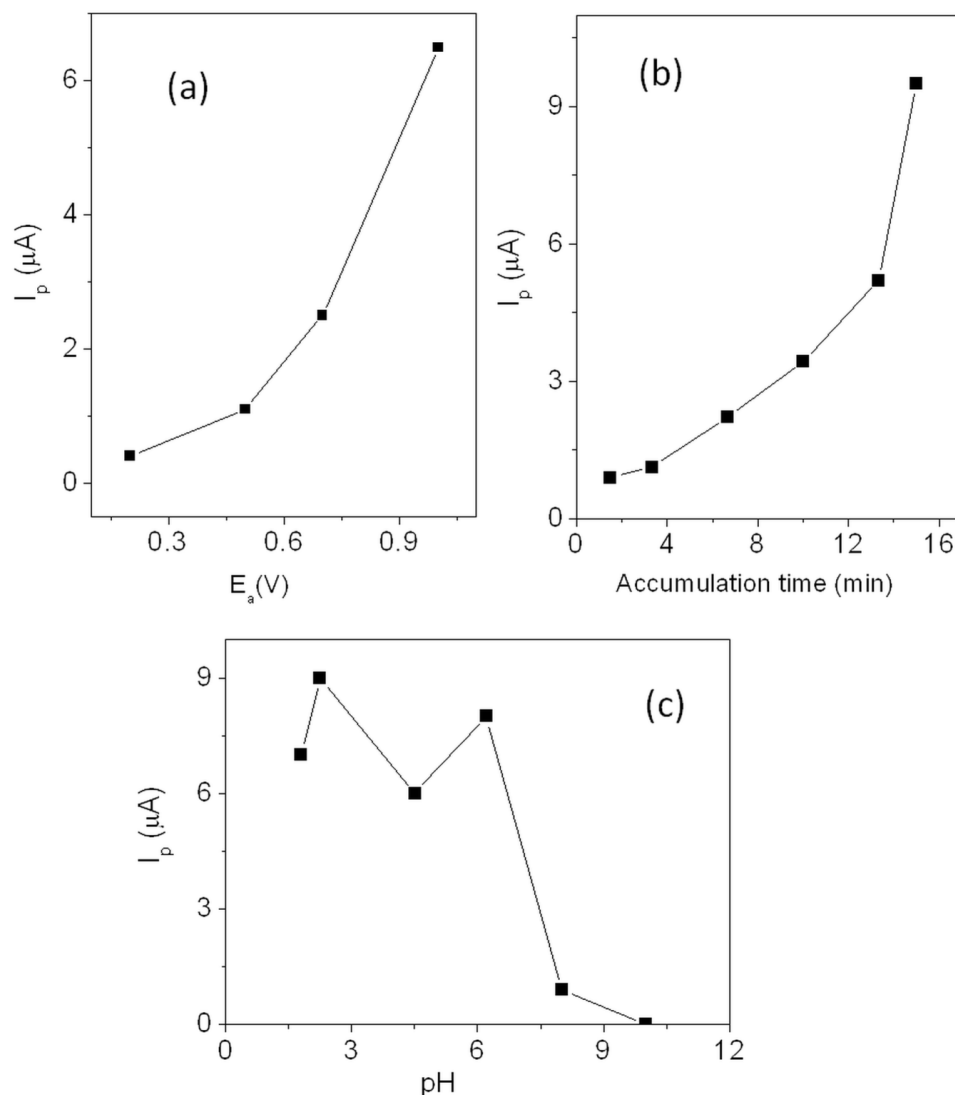
**Fig. S4:** XPS survey scan of carbon nitride.



**Fig. S5:** TGA of  $C_3N_4$  quantum dots. It shows the little quantity of weight loss at 250 °C and then gradual decrease of weight till 640 °C. The decomposition of edge groups can be attributed for 1<sup>st</sup> weight loss and then slowly decomposition of s-triazine in the sample. This indicates CNDs are fairly stable over a wide temperature range, similar to reported bulk carbon nitride.

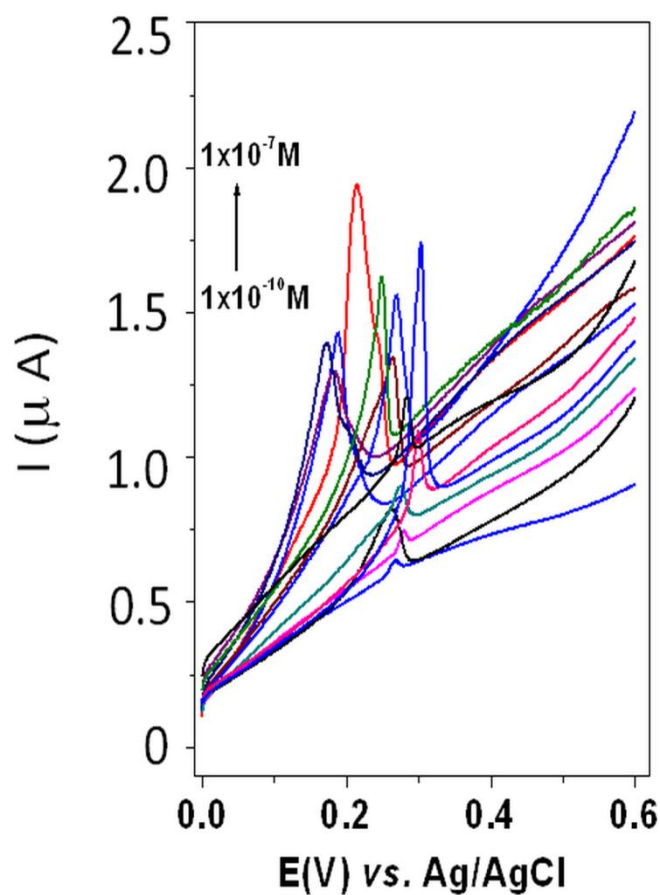


**Fig. S6:** (a) Hg 4f XPS spectra of C<sub>3</sub>N<sub>4</sub>, obtained after electrochemical accumulation of Hg<sup>2+</sup> ions at C<sub>3</sub>N<sub>4</sub>-GC electrode. XPS spectra in the N 1s region of (b) free C<sub>3</sub>N<sub>4</sub> and (c) after electrochemical accumulation of Hg<sup>2+</sup> ions. XPS spectra in the C 1s region of (d) free C<sub>3</sub>N<sub>4</sub> and (e) after accumulation of Hg<sup>2+</sup> ions. The electrochemical accumulation was done at C<sub>3</sub>N<sub>4</sub>-GC electrode on 1.0× 10<sup>-6</sup> M Hg<sup>2+</sup> solution at -1V for 15 min. After accumulation, C<sub>3</sub>N<sub>4</sub>-GC electrode was sonicated in distilled water for ~ 20 minutes to dissolve C<sub>3</sub>N<sub>4</sub>. Then, XPS samples was prepared by drop casting of this solution on Si substrate and then allowed to dry in air.

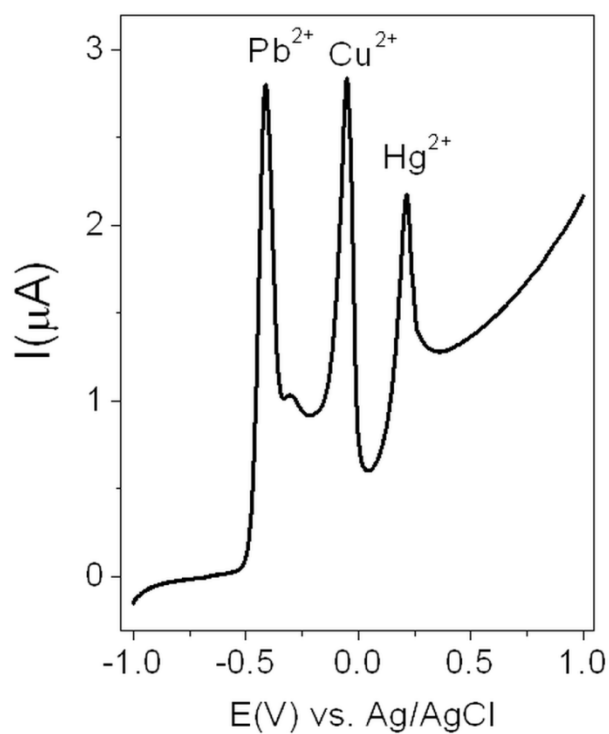


**Fig. S7:** (a) Effect of accumulation potential  $E_a$  (V) on anodic stripping cyclic voltammetric response for  $1 \times 10^{-6}$  M of  $Hg^{2+}$  at  $C_3N_4$  modified GC electrode. Electrolyte: 0.02 M HCl, accumulation time: 15 minutes (b) Effects of accumulation time on anodic stripping cyclic voltammetric response for  $1 \times 10^{-6}$  M of  $Hg^{2+}$  at  $C_3N_4$  modified GC electrode.  $E_a = -1$  V. (c) Effect of pH of the solutions on anodic stripping cyclic voltammetric response for  $1 \times 10^{-6}$  M of  $Hg^{2+}$  at  $C_3N_4$  modified GC electrode.  $E_a = -1$  V and accumulation time = 15 minutes. The higher anodic peak current at more negative potential and longer accumulation time is due to the efficient reduction of  $Hg^{2+}$  to  $Hg^0$  at  $C_3N_4$  modified electrode surface. The enhancement of anodic stripping current with lowering the pH of the solution is probably due to formation of stable complex between  $Hg^{2+}$  ions and  $C_3N_4$  surface at lower pH.

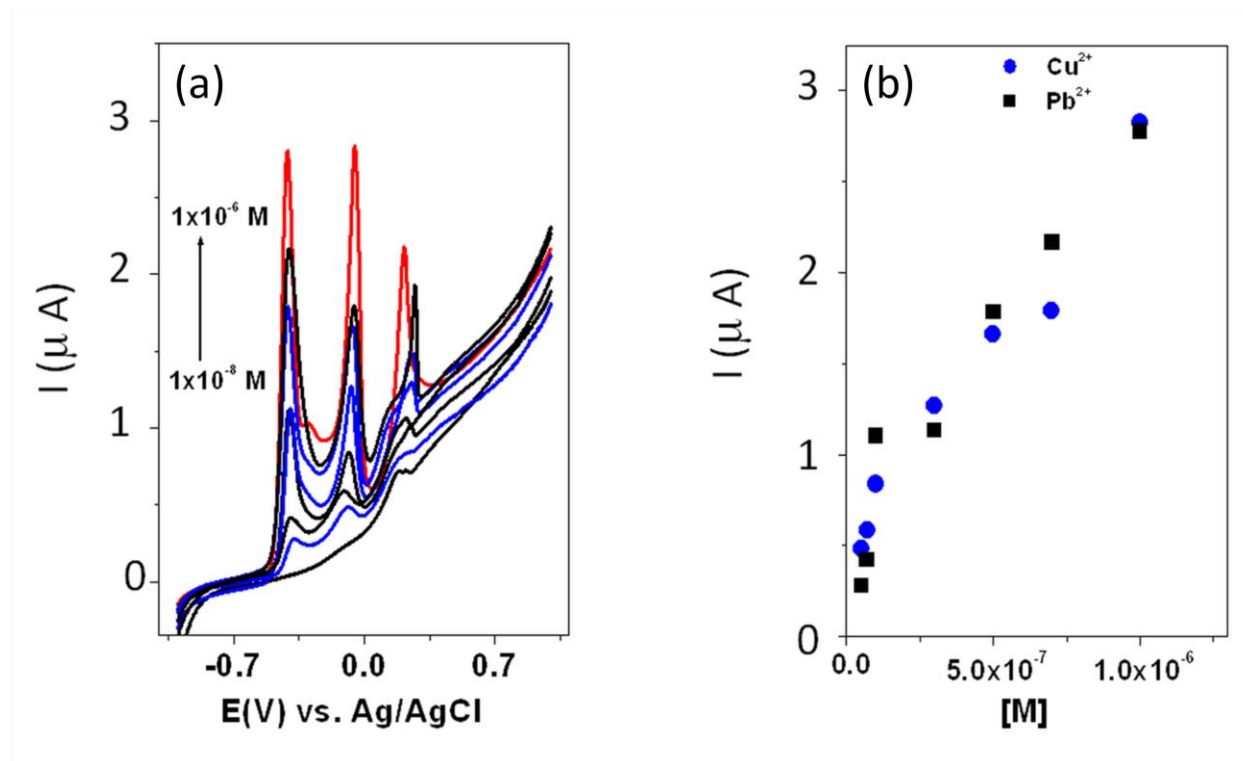




**Fig. S8:** The anodic stripping cyclic voltammograms of different concentration of  $Hg^{2+}$  at  $C_3N_4$  modified GC electrode under optimum conditions. For each stripping voltammetric measurement fresh new electrode was used. However, similar results were obtained when  $C_3N_4$  modified GC electrode was reused by holding at +1V for 15 minutes.



**Fig. S9:** The anodic stripping voltammograms of  $1 \times 10^{-6} \text{ M Hg}^{2+}$  in presence of  $1 \times 10^{-6} \text{ M}$  each of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  ions at  $\text{C}_3\text{N}_4$  modified GC electrode under optimum conditions.



**Fig. S10:** (a) Anodic stripping voltammograms for the different concentrations of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> at C<sub>3</sub>N<sub>4</sub> modified GC electrode under optimum conditions. (b) The calibration curve of Pb<sup>2+</sup> and Cu<sup>2+</sup>.