

Support information

Three-dimensional Porous H_xTiS_2 Nanosheet-polyaniline Nanocomposite Electrodes for Directly Detecting Trace Cu (II) Ions

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ABSTRACT: In present work, three-dimensional porous H_xTiS_2 nanosheet-polyaniline (PANI) nanocomposites were first synthesized by a two-step method. Firstly H_xTiS_2 ultrathin nanosheets were prepared by the lithium-intercalation-and-exfoliation method, followed by the surface polymerization reactions of aniline. The influences of the amount of H_xTiS_2 nanosheets on the nanocomposite morphology and electrochemical performances of the nanocomposites modified glass carbon electrode (H_xTiS_2 nanosheet-PANI/GCE) were investigated. The results demonstrated that the incorporation of H_xTiS_2 nanosheets as a suitable substrate can regulate the growth of PANI, enhance the electrode stability and improve interfacial electron transfer rates. In addition, based on the nanocomposites, we developed a novel electrochemical sensor to directly detect trace Cu^{2+} , and discovered that the coordination interaction between Cu^{2+} and the nitrogen atoms of the imine moieties in PANI endowed the electrochemical sensor with high selectivity. Owing to the synergetic effects of H_xTiS_2 nanosheets and PANI, the as-prepared electrochemical sensor exhibited highly sensitive and selective assaying of Cu^{2+} with a detection limit of 0.7 nM (S/N=3) and a linear range from 25 nM to 5 μ M under optimal conditions.

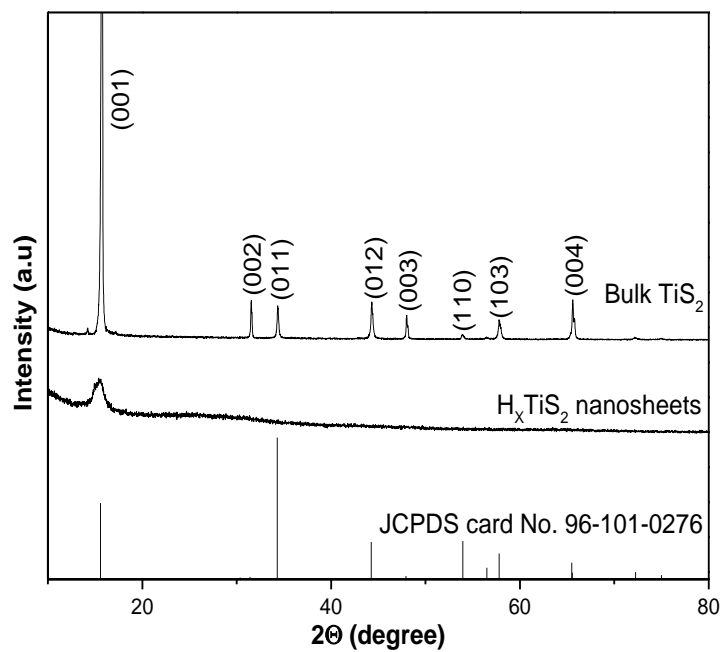


Figure S1. XRD pattern of bulk TiS_2 and H_xTiS_2 nanosheets.

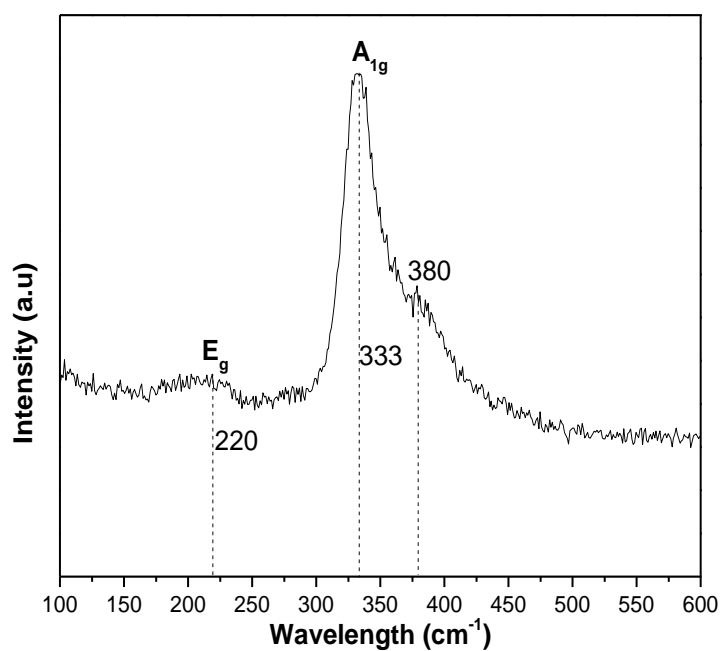


Figure S2. The Raman spectra of H_xTiS_2 nanosheets.

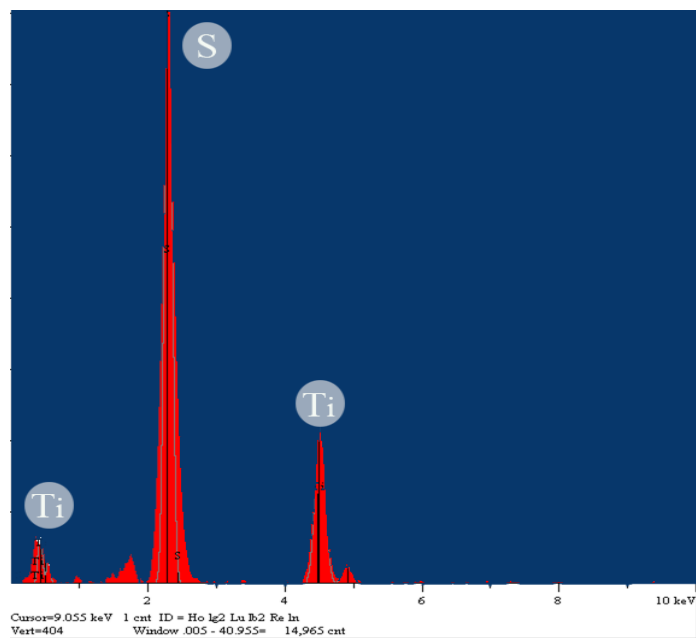


Figure S3. EDX spectrum of the H_xTiS_2 nanosheets.

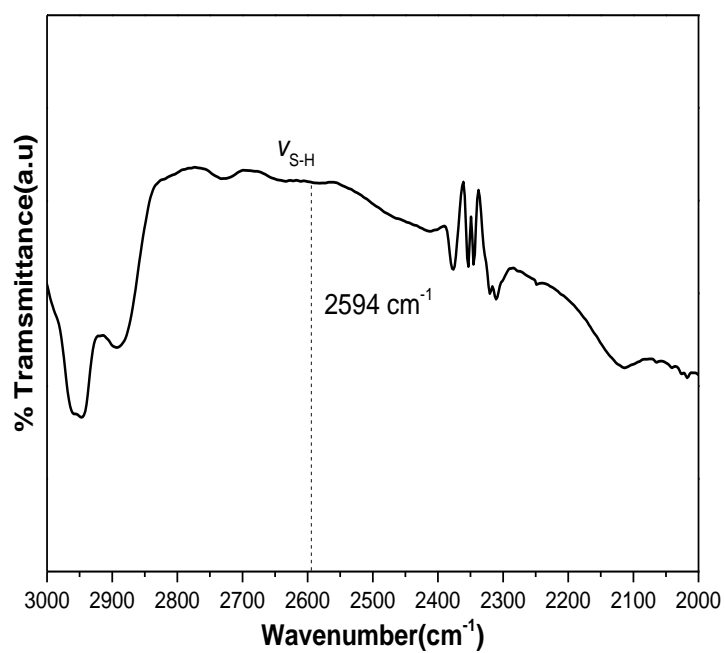


Figure S4. S-H bond in FT-IR spectra of the H_xTiS_2 nanosheets.

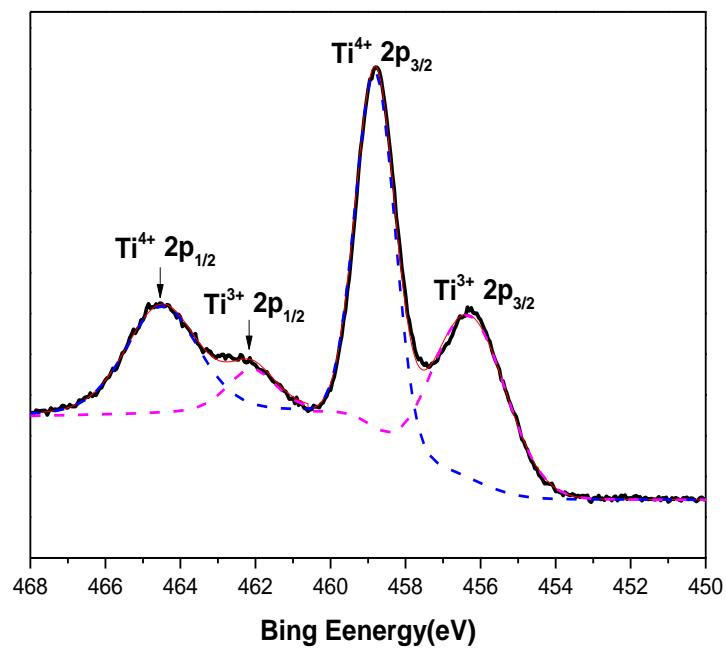


Figure S5. XPS of Ti 2p core level peak regions of H_xTiS_2 nanosheets.

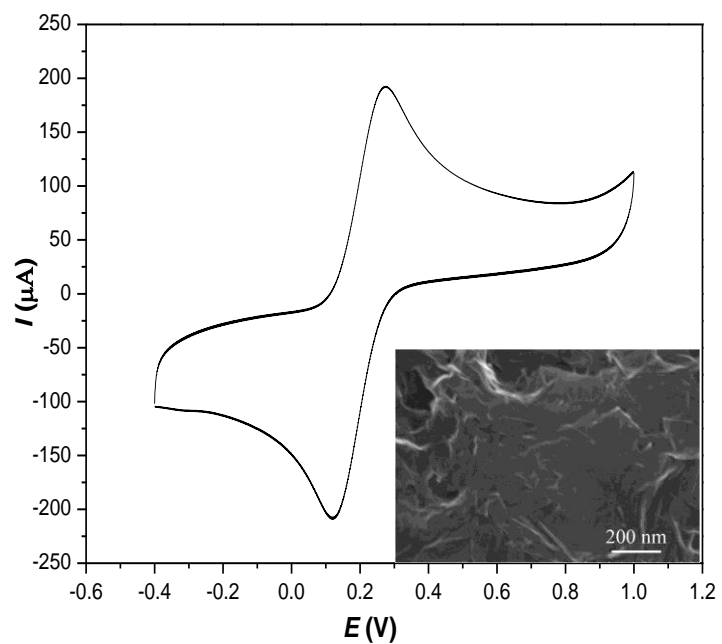


Figure S6. Cyclic voltammogram of RGO/GCE in potassium ferricyanide solution containing 0.1 M KCl, 10 mM $K_3[Fe(CN)_6]$ and 10 mM $K_4[Fe(CN)_6]$ at a scan rate 100 mV/s. The inset is the SEM of RGO.

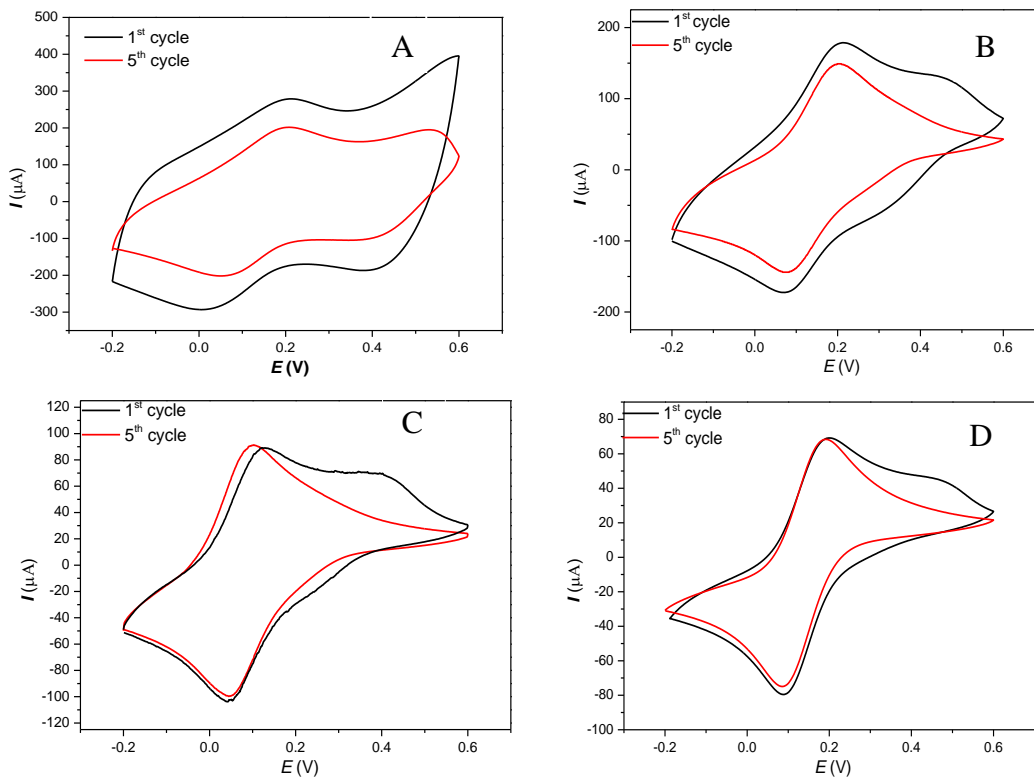


Figure S7. Cyclic voltammograms of PANI (A), $S_{1:3.5}$ (B), $S_{1:1.5}$ (C), $S_{1:0.5}$ (D) before and after five cycles in potassium ferricyanide solution containing 0.1 M KCl, 2.5 mM $K_3[Fe(CN)_6]$ and 2.5 mM $K_4[Fe(CN)_6]$ at a scan rate 50 mV/s.

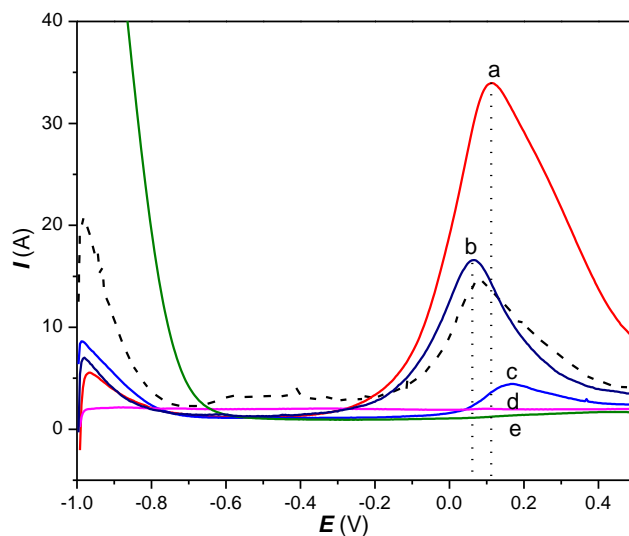


Figure S8. SWASV detection plots of 0.5 μM Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} and Hg^{2+} on PANI/GCE (a), $S_{1:1.5}$ /GCE (b), H_xTiS_2 nanosheet/GCE (c), bare GCE (d) and oxidized H_xTiS_2 nanosheet/GCE (e). The black dash line represents SWASV detection plot of 0.5 μM Cu^{2+} on $S_{1:1.5}$ /GCE without other metal ions.

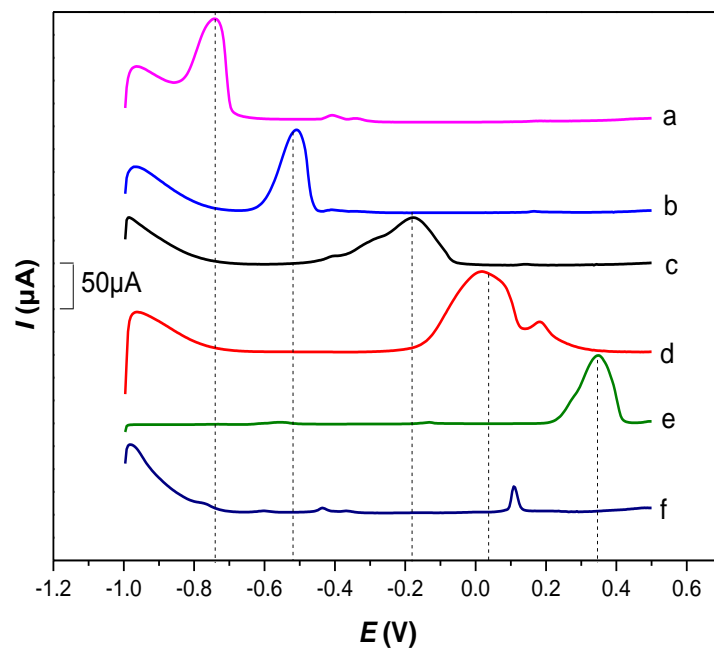


Figure S9. SWASV plots of exclusive detecting 1 mM Cd^{2+} (a), Pb^{2+} (b), Ni^{2+} (c), Cu^{2+} (d), Hg^{2+} (e), and simultaneous detecting 0.02 mM Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} (f) on H_xTiS_2 nanosheet/GCE.

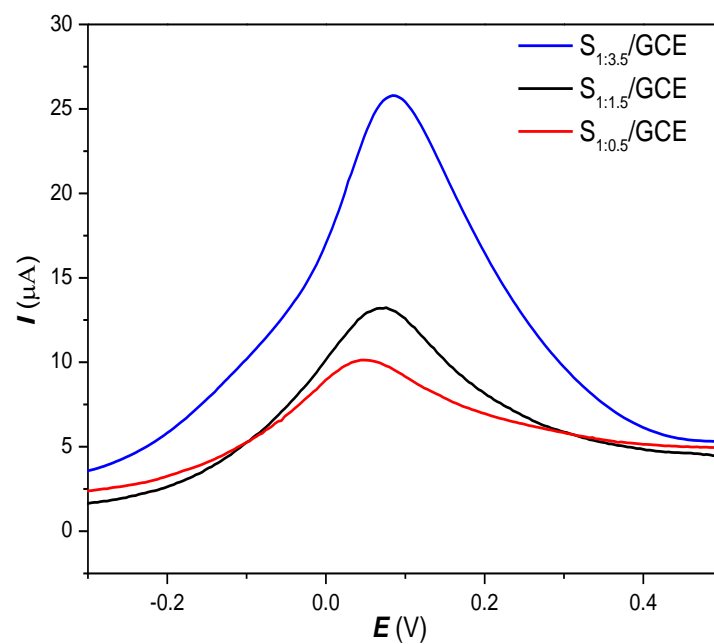


Figure S10. SWASV detection plots of 0.2 μM Cu^{2+} on $\text{S}_{1:3.5}/\text{GCE}$, $\text{S}_{1:1.5}/\text{GCE}$ and $\text{S}_{1:0.5}/\text{GCE}$.

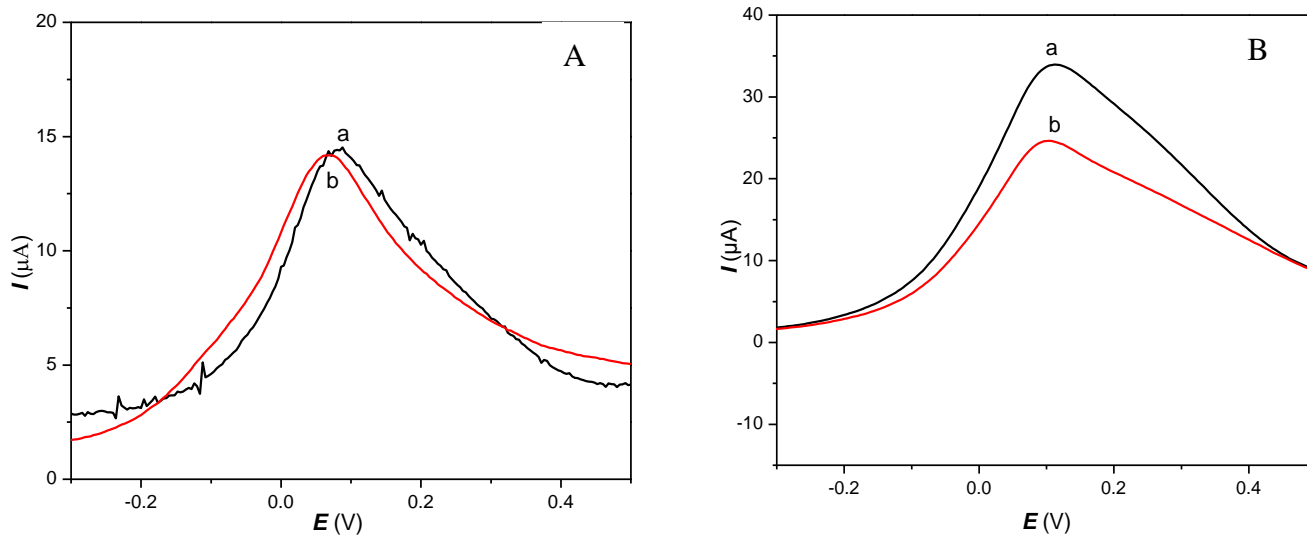


Figure S11. SWASV detection plots of $0.5 \mu\text{M Cu}^{2+}$ on $\text{S}_{1.1.5}/\text{GCE}$ (A) and PANI/GCE (B) before (a) and after (b) one month storage in darkness at room temperature.

Table S1

Performance comparison between this proposal strategy and other electrochemical detection assays for Cu^{2+} .

Method	Linear range	Detection limit	Analytical technique	Reference
DNAzyme/GCE	6.5–40 μM	6.5 μM	EIS	3
IP6-MWCNTs-ITO	0.01–0.8 μM	2.5 nM	DNPV	8
$\text{SnO}_2/\text{RGO}/\text{GCE}$	0.1–1.3 μM	0.2269 nM	SWASV	9
AuNPs-GR/GCE	5–100 nM	0.028 nM	ASV	10
CoO/EG	1.6–314.7 μM	1.47 μM	SWASV	11
C-Dot-TPEA/GCE	1–60 μM	~100 nM	DPASV	41
$\text{H}_x\text{TiS}_2\text{-PANI}/\text{GCE}$	25-5000 nM	0.7 nM	SWASV	Our work

RGO: reduced graphene oxide; IP6: phytate; MWCNTs: multi-walled carbon nanotubes; C-Dot: carbon dots; TPEA: (N-(2-aminoethyl)-N, N', N'-tris(pyridine-2-yl-methyl)ethane-1,2-diamine); CoO/EG: cobalt oxide modified exfoliated graphite electrode; GCE: glass carbon electrode; GR: electrochemical reduction of graphene oxide; SWASV: square wave anodic stripping voltammograms; ASV: anodic stripping voltammetric; DNPV: differential normal pulse anodic stripping voltammetry; DPASV: Differential pulse anodic stripping voltammetry; EIS: electrochemical impedance spectroscopy.