Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Ultratrace detection of toxic heavy metal ions found in water bodies using hydroxyapatite supported nanocrystalline ZSM-5 modified electrodes

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Supporting Information

Synthesis of Materials

In a typical synthesis of Nano-ZSM-5, 0.48 g sodium aluminate (53 wt.% Al_2O_3, 43 wt.% Na_2O) was dissolved in 25 mL distilled water (Solution A). 2.13 g PrTES was mixed with 25 mL TPAOH (Solution B). Solution A and solution B were mixed, and the resultant solution was stirred for 15 minutes at room temperature, until it became a clear solution. 19.13 g TEOS was added into the resultant solution and stirring was continued for 6 h. The molar composition of the gel mixture was 90 TEOS/10 PrTES/2.5 Al_2O_3/3.3 Na_2O/25 TPAOH/2500 H_2O. This mixture was transferred to a Teflon-lined autoclave, and hydrothermally treated at 443 K for 3 days under static conditions. The final product was filtered, washed with distilled water, and dried at 373 K. Material was calcined at 823 K for 6 h under flowing air. For comparison, conventional ZSM-5 was synthesized at 443 K using the same synthesis composition as mentioned above for Nano-ZSM-5, but without PrTES additive.

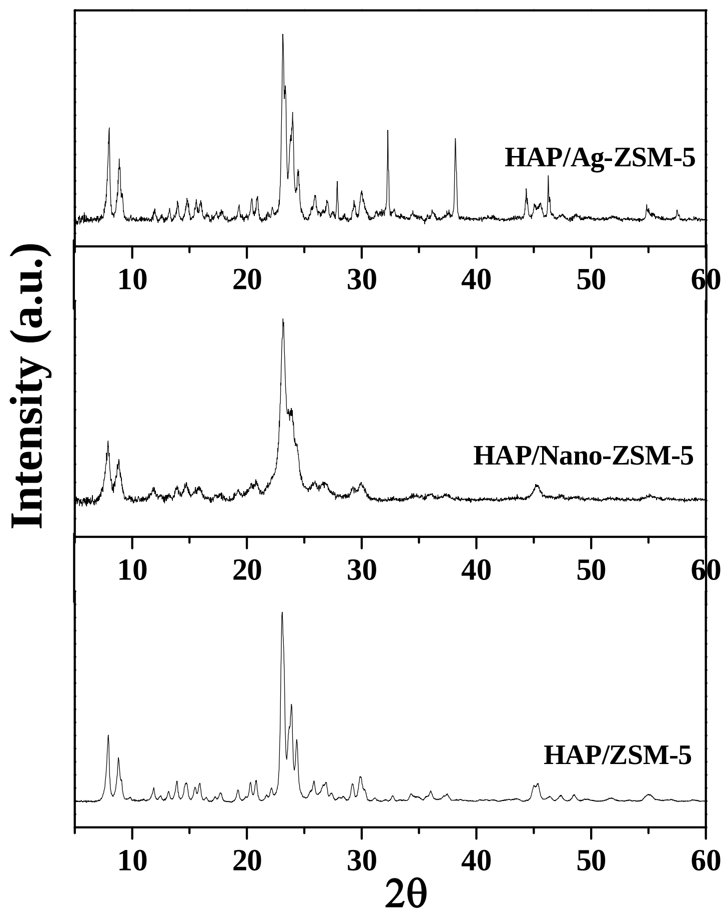

Fig. S1. XRD patterns of ZSM-5, Nano-ZSM-5, and Ag-ZSM-5 materials after immersion in SBF solution for 20 days.

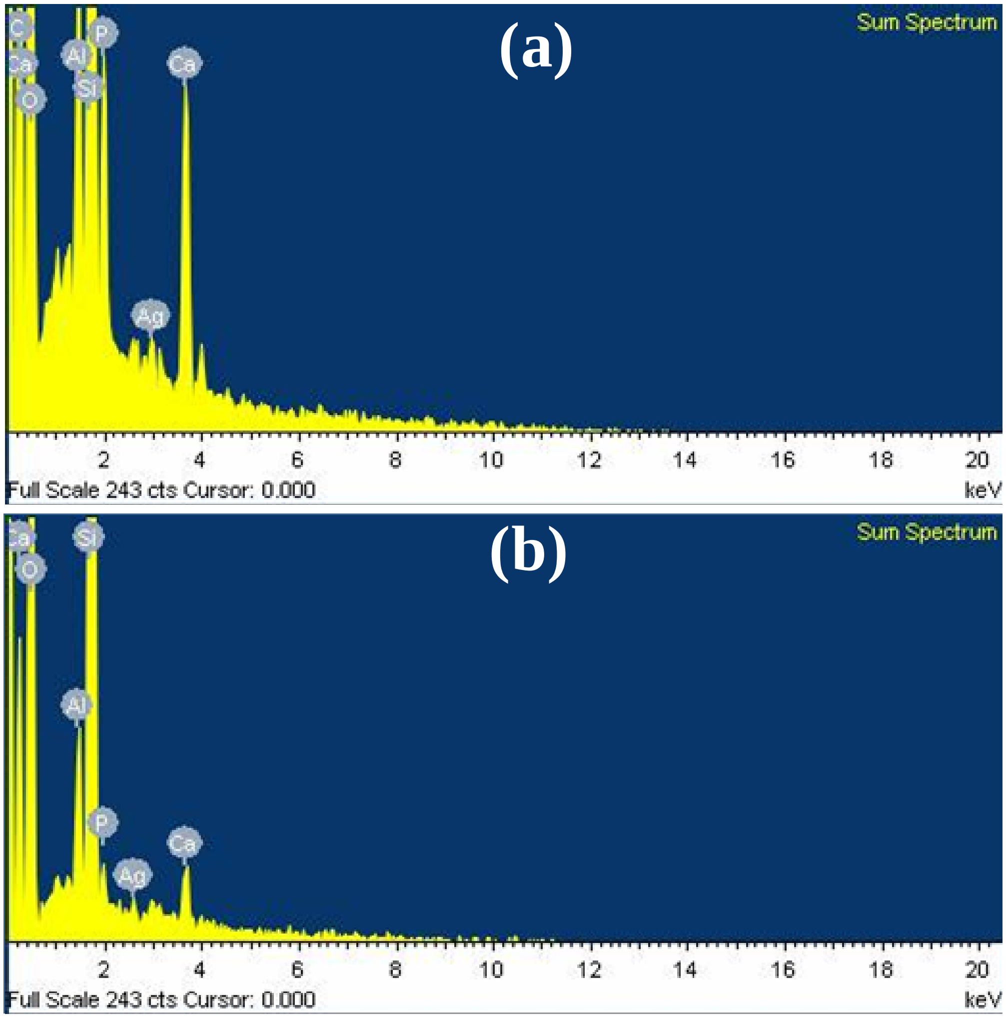

Fig. S2. EDX elemental maps of representative elements in (a) Ag-Nano-ZSM-5 and (b) Ag-ZSM-5 materials after immersion period of 20 days.

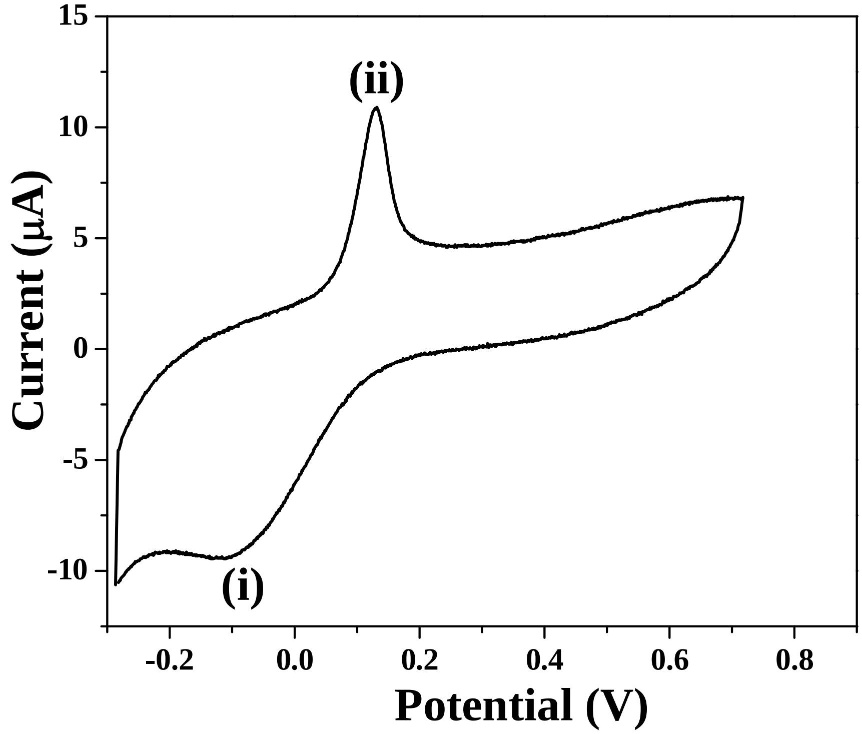

Fig. S3. CV at HAP/Ag-Nano-ZSM-5/GCE in the presence of As^{3+} (50 ppb) in 0.1 M PBS (pH 7) at a scan rate of 20 mV/s. The CV shows a reduction peak (i) at 0.08 V which corresponds to the reduction of As^{3+} to As^{0} and an oxidation peak (ii) at 0.150 which corresponds to the oxidation of As^{3+} to As^{0}.

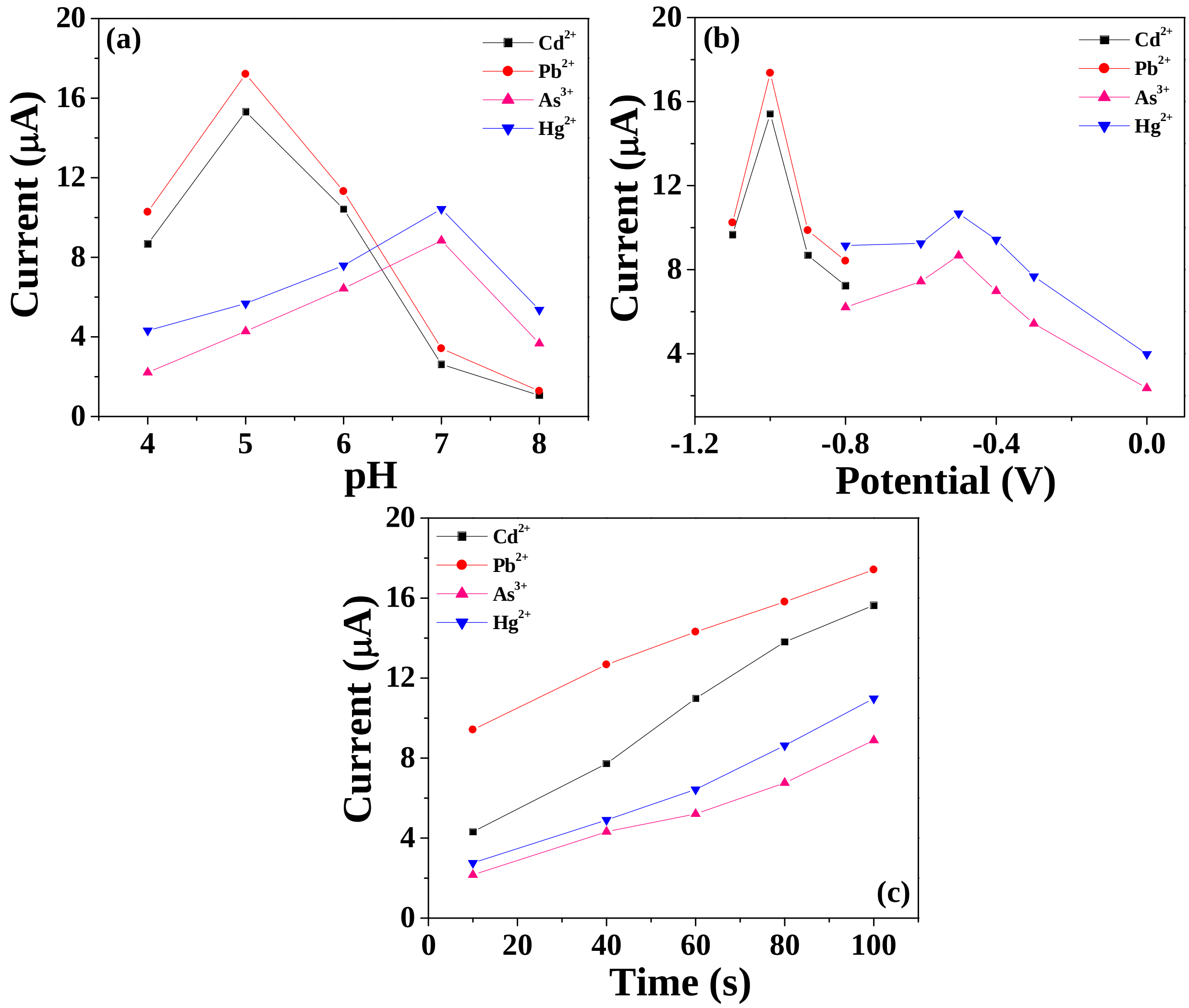

Fig. S4. Optimization of experimental conditions: Influence of (a) pH of supporting electrolyte, (b) deposition potential, and (c) deposition time on the stripping peak current response of HAP/Ag-Nano-ZSM-5/GCE in the presence of 50 ppb of each heavy metal ions (Cd^{2+}, Pb^{2+}, As^{3+}, and Hg^{2+}) individually. SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; and square wave frequency 15 Hz.

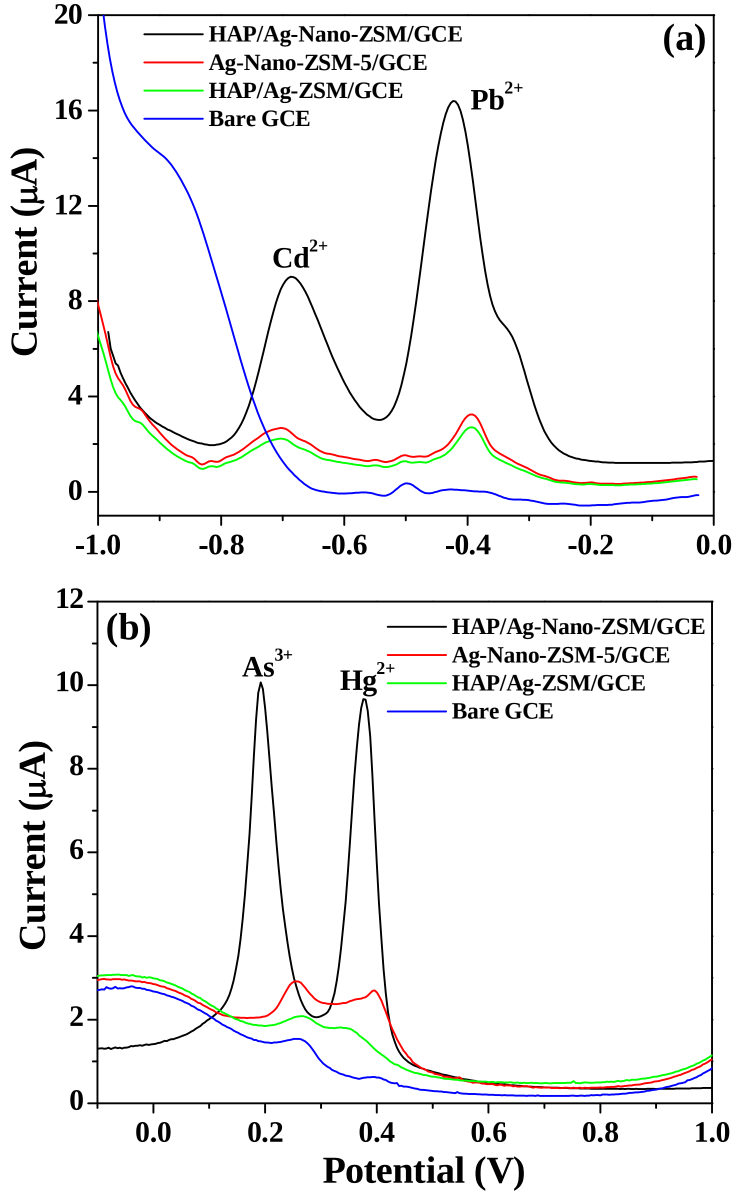

Fig. S5. Comparison of SWSV of 50 ppb each of (a) Cd^{2+}, Pb^{2+} in 0.1 M PBS (pH 5) at a deposition potential of -1 V and (b) As^{3+}, Hg^{2+} in 0.1 M PBS (pH 7) at a deposition potential of -0.5 V at different modified electrodes (HAP/Ag-Nano-ZSM-5/GCE, Ag-Nano-ZSM-5/GCE, HAP/Ag-ZSM-5/GCE) and bare GCE. SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

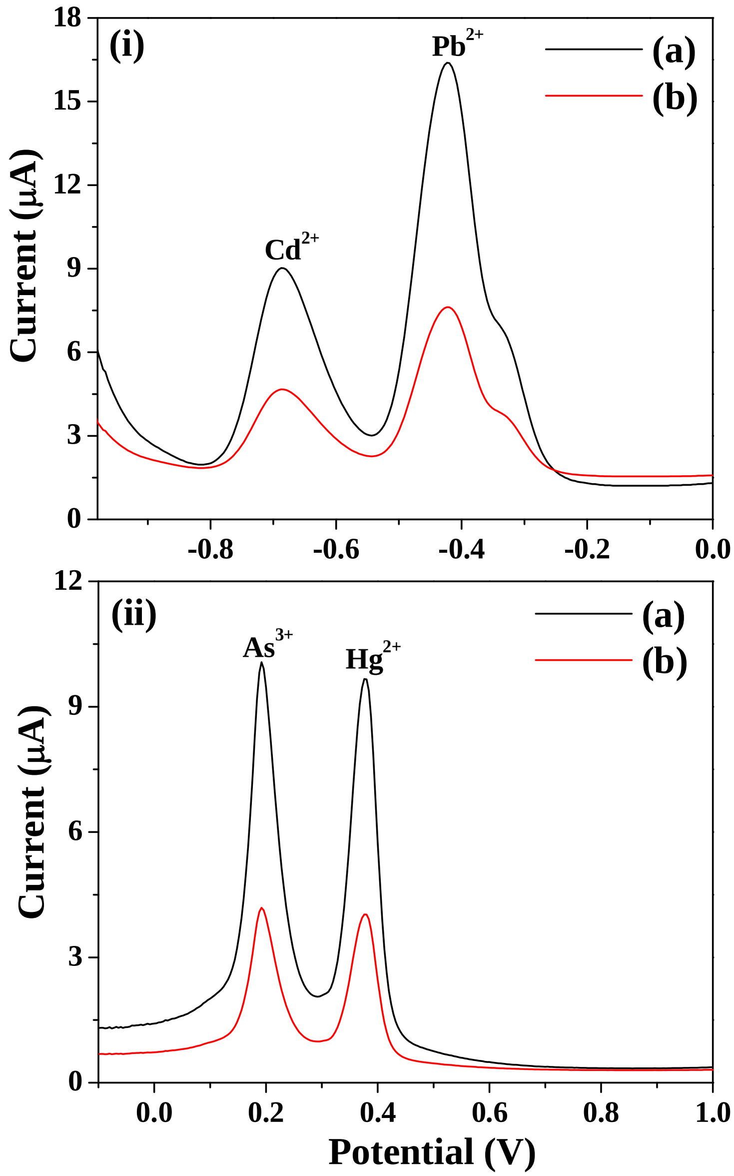

Fig. S6. Comparison of SWSV of 50 ppb each of (i) Cd^{2+}, Pb^{2+} in 0.1 M PBS (pH 5) at a deposition potential of -1 V and (ii) As^{3+}, Hg^{2+} in 0.1 M PBS (pH 7) at a deposition potential of -0.5 V at (a) HAP/Ag-Nano-ZSM-5/GCE and (b) physically mixed conventional HAP and Ag-Nano-ZSM-5 modified GCE. SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

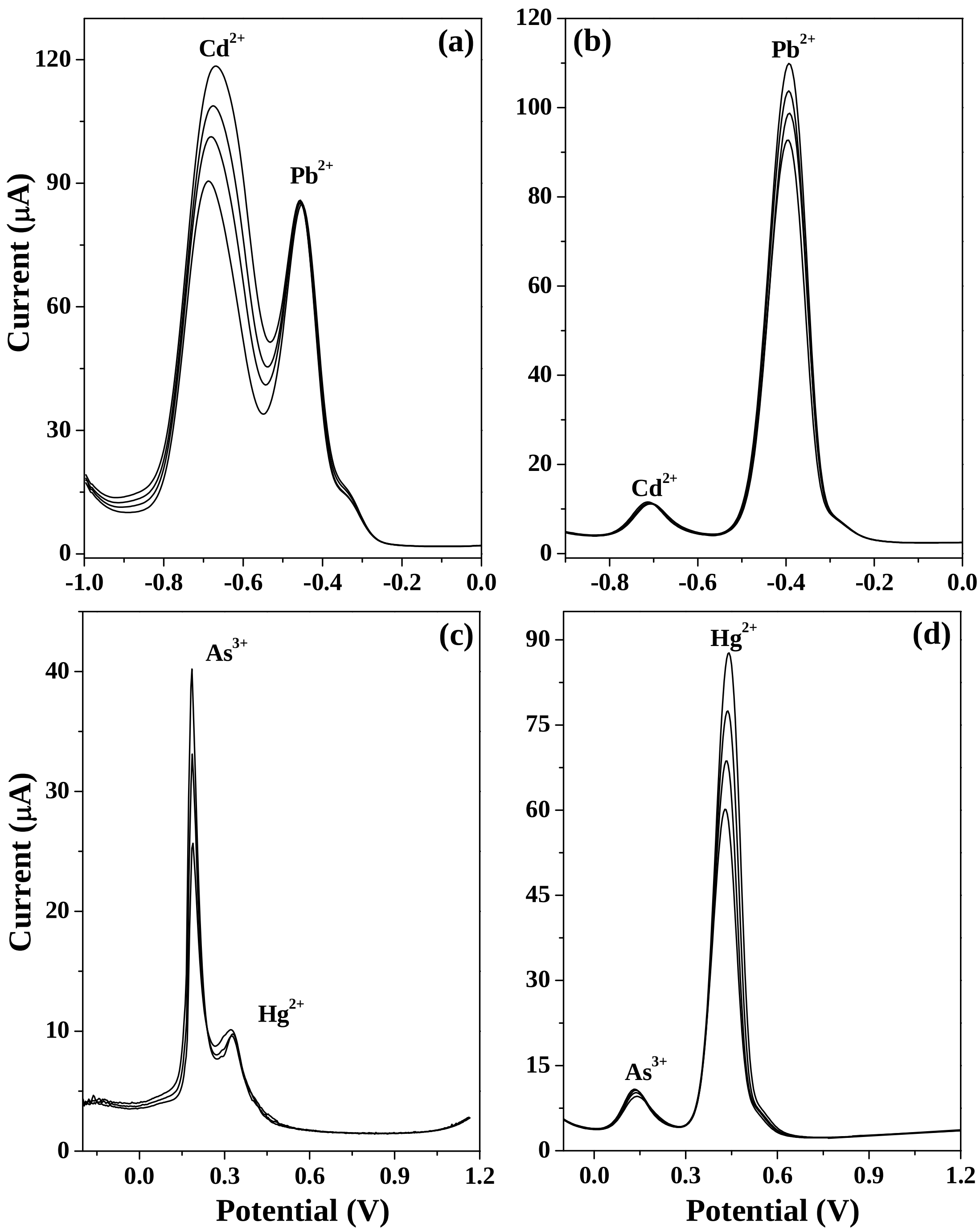

Fig. S7. Interference study: SWSV at HAP/Ag-Nano-ZSM-5/GCE by varying the concentration of one metal ion whereas that of second was kept constant under the optimized conditions. SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

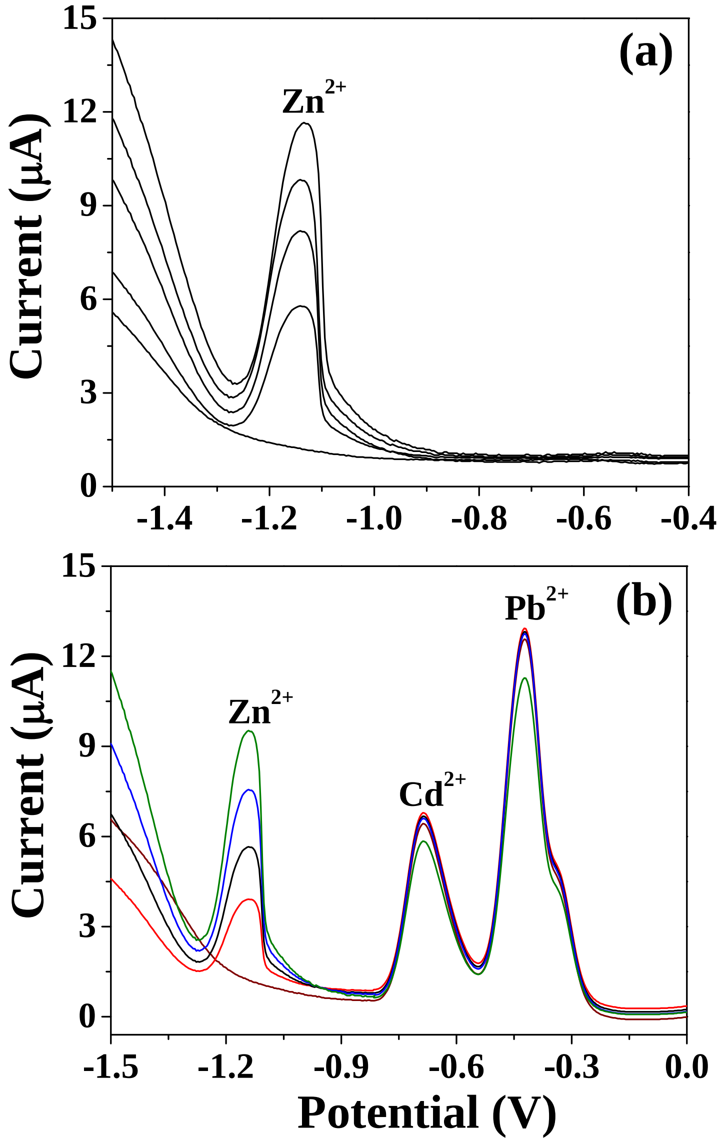

Fig. S8. SWSV response at HAP/Ag-Nano-ZSM-5/GCE for (a) individual analysis of Zn^{2+} with different concentrations (from inner to outer of curves 50, 200, 500, 800, 1000 ppb); and (b) interference study with varying concentrations of Zn^{2+} (from inner to outer of curves 50, 150, 200, 500, 800 ppb) in the presence of a fixed concentration (10 ppb) of Cd^{2+}, Pb^{2+} in 0.1 M PBS (pH 5). SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

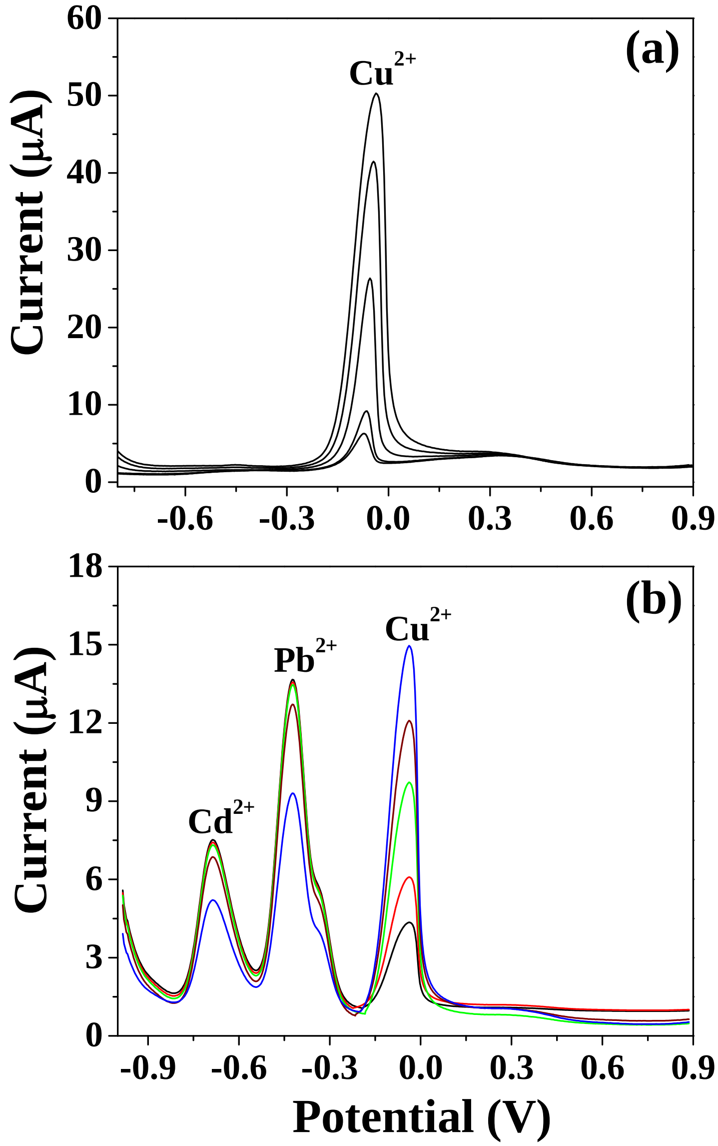

Fig. S9. SWSV response at HAP/Ag-Nano-ZSM-5/GCE for (a) individual analysis of Cu^{2+} with different concentrations (from inner to outer of curves 30, 50, 500, 1000, 1500 ppb); and (b) interference study with varying concentrations of Cu^{2+} (from inner to outer of curves 10, 30, 50, 100, 200 ppb) in the presence of a fixed concentration (10 ppb) of Cd^{2+}, Pb^{2+} in 0.1 M PBS (pH 5). SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

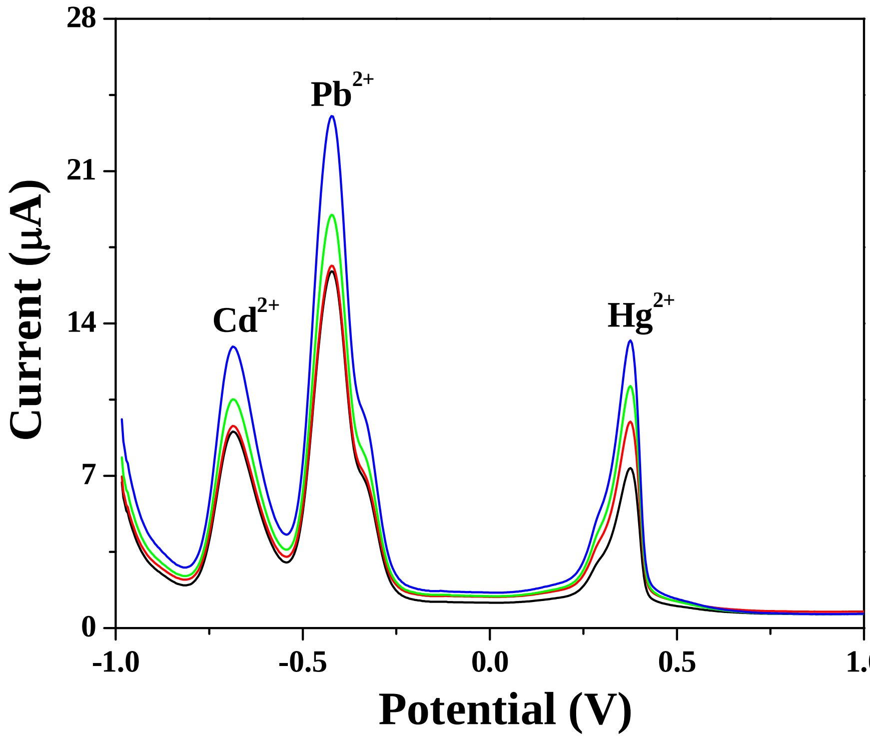

Fig. S10. SWSV response at HAP/Ag-Nano-ZSM-5/GCE for the interference study with varying concentrations of Hg^{2+} (from inner to outer of curves 2, 10, 50, 100 ppb) in the presence of a fixed concentration (10 ppb) of Cd^{2+}, Pb^{2+} in 0.1 M PBS (pH 5). SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

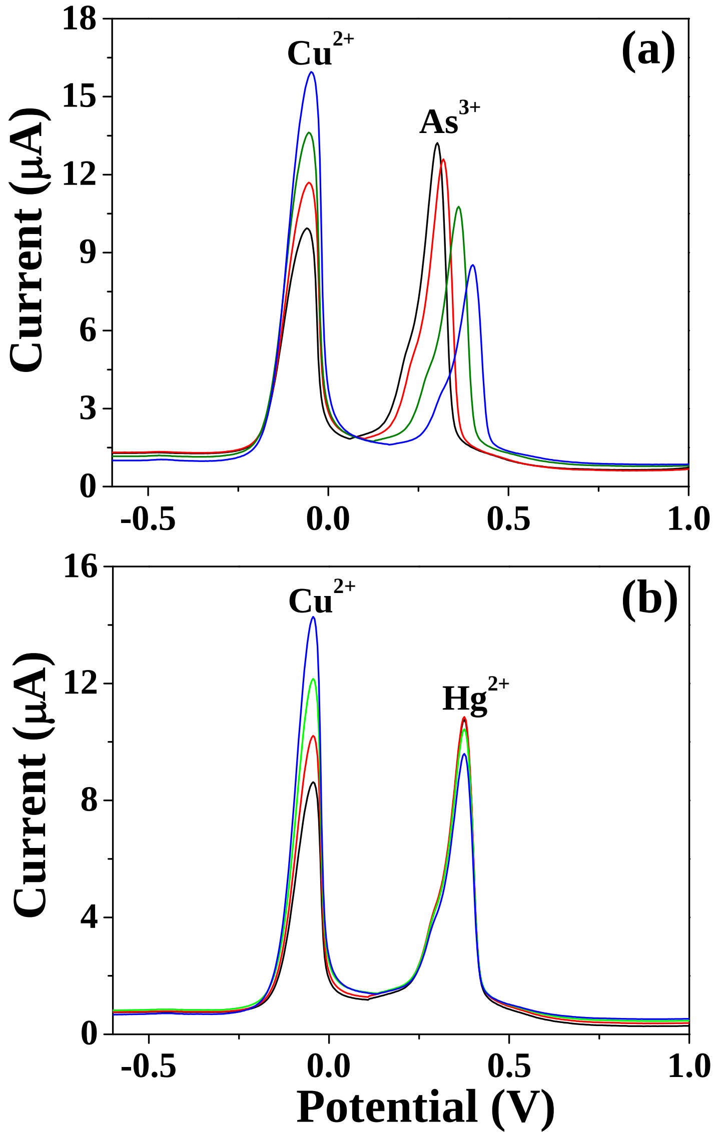

Fig. S11. SWSV response at HAP/Ag-Nano-ZSM-5/GCE in 0.1 M PBS (pH 7) for the interference study (a) with varying concentrations of Cu^{2+} (from inner to outer of curves 50, 100, 200, 500 ppb) in the presence of a fixed concentration (10 ppb) of As^{3+} and (b) with varying concentrations of Cu^{2+} (from inner to outer of curves 30, 50, 100, 150 ppb) in the presence of a fixed concentration (10 ppb) of Hg^{2+}. SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

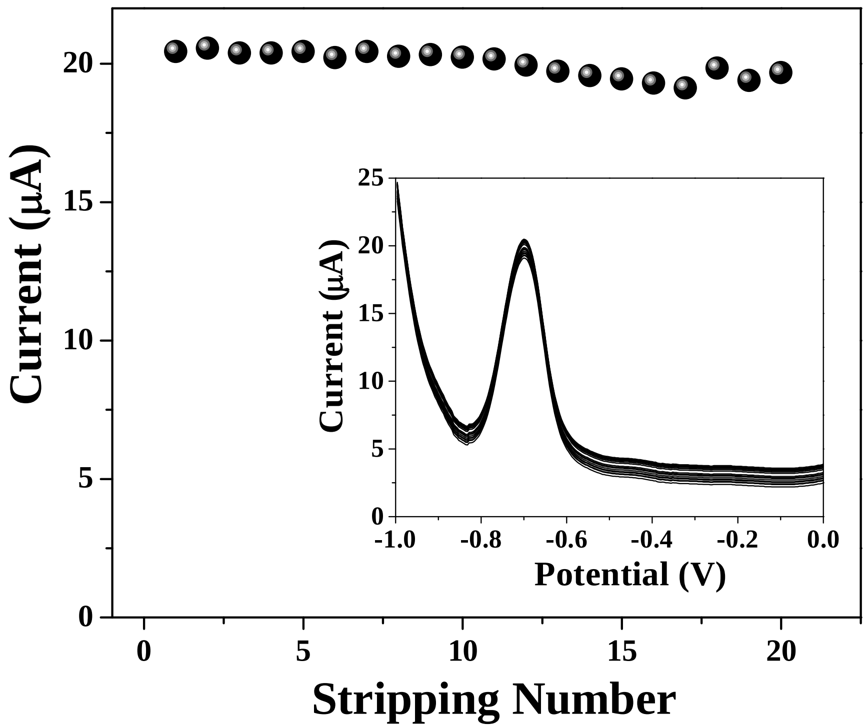

Fig. S12. The stability response for 20 times repetitive SWSV measurements in the presence of 50 ppb Cd^{2+}. Inset shows corresponding SWSV response at HAP/Ag-Nano-ZSM-5/GCE in the presence of 50 ppb Cd^{2+} in 0.1 M PBS (pH 5). SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

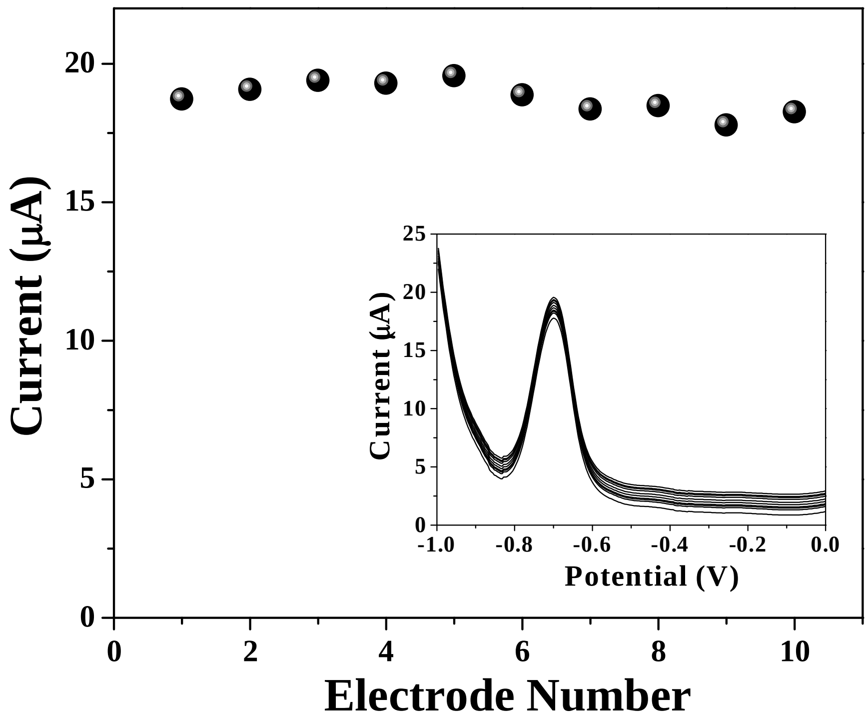

Fig. S13. The current response at different HAP/Ag-Nano-ZSM-5/GCEs (n=10) in the presence of 50 ppb Cd^{2+}. Inset shows corresponding SWSV response at 10 different HAP/Ag-Nano-ZSM-5/GCEs in the presence of 50 ppb Cd^{2+} in 0.1 M PBS (pH 5). SWSV parameters were selected as: Step potential 4 mV; square wave amplitude 25 mV; square wave frequency 15 Hz and deposition time 100 s.

Table S1. Ionic compositions (mM) of SBF.

Ion	**Na^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**Cl^-**	**HCO^{3-}**	**HPO_4^{2-}**	**SO_4^{2-}**
SBF	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5

Table S2. Comparison of HAP/Ag-Nano-ZSM-5/GCE with other electrodes reported in the literature for heavy metal ion detection.

S.No.	Modified electrode	Analyte	Linear range	Detection limit	Reference
1.	AuNP–SWCNT film electrode	Pb^{2+}	3.31 ppb - 22.29 ppb	0.546 ppb	[1]
2.	GC/NHAP/ionophore/Nafion electrode	Pb^{2+}	1.04 ppb - 166 ppb	0.2 ppb	[2]
3.	AuNPs/GC electrode	Cd^{2+} Pb^{2+} Hg^{2+}	- - -	3.4 ppm 6.2 ppm 6.0 ppm	[3]
4.	SNACs/GCE	Cd^{2+} Pb^{2+} Hg^{2+}	10 ppb – 539.6 ppb 18.6 ppb – 1.2 ppm 18.0 ppb -198.6 ppm	2.7 ppb 1.2 ppb 4.9 ppb	[4]
5.	carbon nanoparticle-based SPEs	Cd^{2+} Pb^{2+} Hg^{2+}	5 ppb - 100 ppb 5 ppb - 100 ppb 1 ppb - 10 ppb	- 3 ppb -	[5]
6.	γ-AlOOH@SiO_2/ Fe_3O_4 electrode	Cd^{2+} Pb^{2+} Hg^{2+}	1.1 ppb – 15.7 ppb 0.4 ppb – 99.5 ppb 4 ppb – 56.2 ppb	- - -	[6]
7.	HAP/Ag-Nano-ZSM-5/GCE	Cd^{2+} Pb^{2+} As^{3+} Hg^{2+}	0.5 ppb - 1600 ppb 0.6 ppb - 1600 ppb 0.9 ppb - 1800 ppb 0.8 ppb - 1800 ppb	0.1 ppb 0.1 ppb 0.2 ppb 0.2 ppb	This work

References

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