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Electrochemical Synthesis of Gold Atomic Cluster-Chitosan Nanocomposite Film Modified Gold Electrode for Ultra-Trace Determination of Mercury

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Supporting Information

i) MALDI-TOF-MS

Matrix assisted laser desorption ionization time of flight mass spectrometry was used to find out exact masses of the electrochemically formed AuAC and AuAC-Chit modified film. Both are deposited on the polycrystalline gold electrode from aqueous CTAB solutions (with and without 0.2% chitosan) above critical micelle concentration (CMC) (0.92 mM) and then washed with distilled water. The particles were then displaced from the electrode by sonicating in 50 mM of CTAB solution and then collected. The matrix α-cyano-4-hydroxycinnamic acid (α-cyano, CHCA) (5 mg) was weighed accurately and dissolved in 1 mL of 0.1% Trifluoroacetic acid: ACN (50:50% v/v). 10 μL of the sample (clusters dissolved in CTAB/H_2O-solution form) was mixed with10 μL of the matrix in a micro centrifuge tube (capacity: 500 μL). It was vortexed for 5 minutes at 2000 rpm to ensure the complete mixing of the content. The solution was found clear after vortexed. Then approximately 1μL of premix sample was spotted on to clean MALDI plate and allowed to dry in air for about 15 minutes and loaded in the MALDI-TOF- MS set up.

ii) High Resolution Transmission Electron Microscopy (HRTEM)

In order to show the size and morphology of AuAC and AuAC-Chit particles, high resolution transmission electron microscopy (TEM) pictures were taken. After electrochemical formation of AuAC and AuAC-Chit modified film on polycrystalline gold electrode, it was sonicated in 2mL of 1mM CTAB solution and drop casted (10 μL) on carbon coated copper grids (400 meshes). Grids were dried in room temperature for overnight for slow evaporation and kept in vacuum desiccator for 2 days.

iii) Dynamic Light Scattering (DLS)

Dynamic light scattering studies were conducted to monitor the size distribution of AuAC and AuAC-Chit modified film prepared by the electrochemical cycling in presence of 50 mM CTAB (with and without chitosan) in the range -1.30 - 1.20 V. The deposited particles were sonicated into 4 mL of 50 mM aqueous CTAB solution and the DLS measurements were taken in polyethylene disposable cuvettes.

iv) X-ray Photoelectron Spectroscopy (XPS)

To get evidence for oxidation state of AuAC, X-ray photoelectron spectroscopy (XPS) were carried out. Particles were collected by sonicating AuAC modified electrode in 2 mL of acetone and drop casted on glass plate for analysis.

v) Fluorescence spectrometry

Fluorescence is one of the characteristic properties of small noble metal clusters such as Au, Cu, Ag, and Pt, shows size dependent emission spectrum. For these studies electrochemically formed AuAC-Chit film modified electrodes were sonicated and collected into 4 mL of 50 mM CTAB solution.

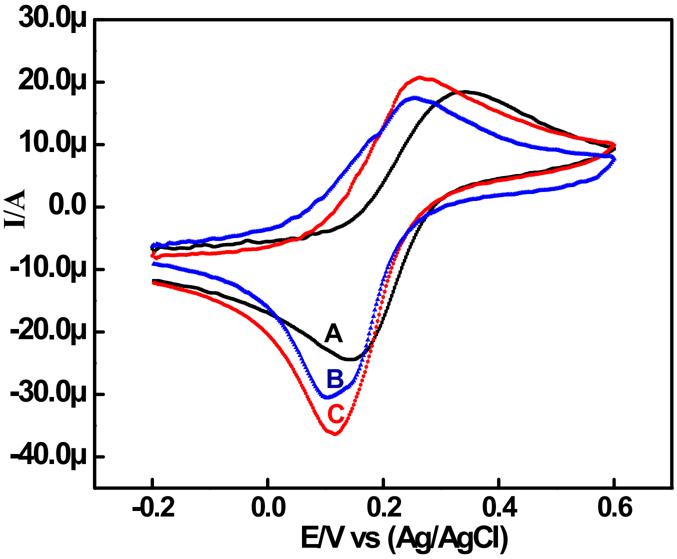

Figure S1. Cyclic voltammogramms of 5mM $K_3[Fe(CN)_6]$ at (A) Bare gold (B) AuAC modified (C) AuAC-Chit nanocomposite modified electrode in 0.1M KCl. Scan rate 100 mVs^{-1}.

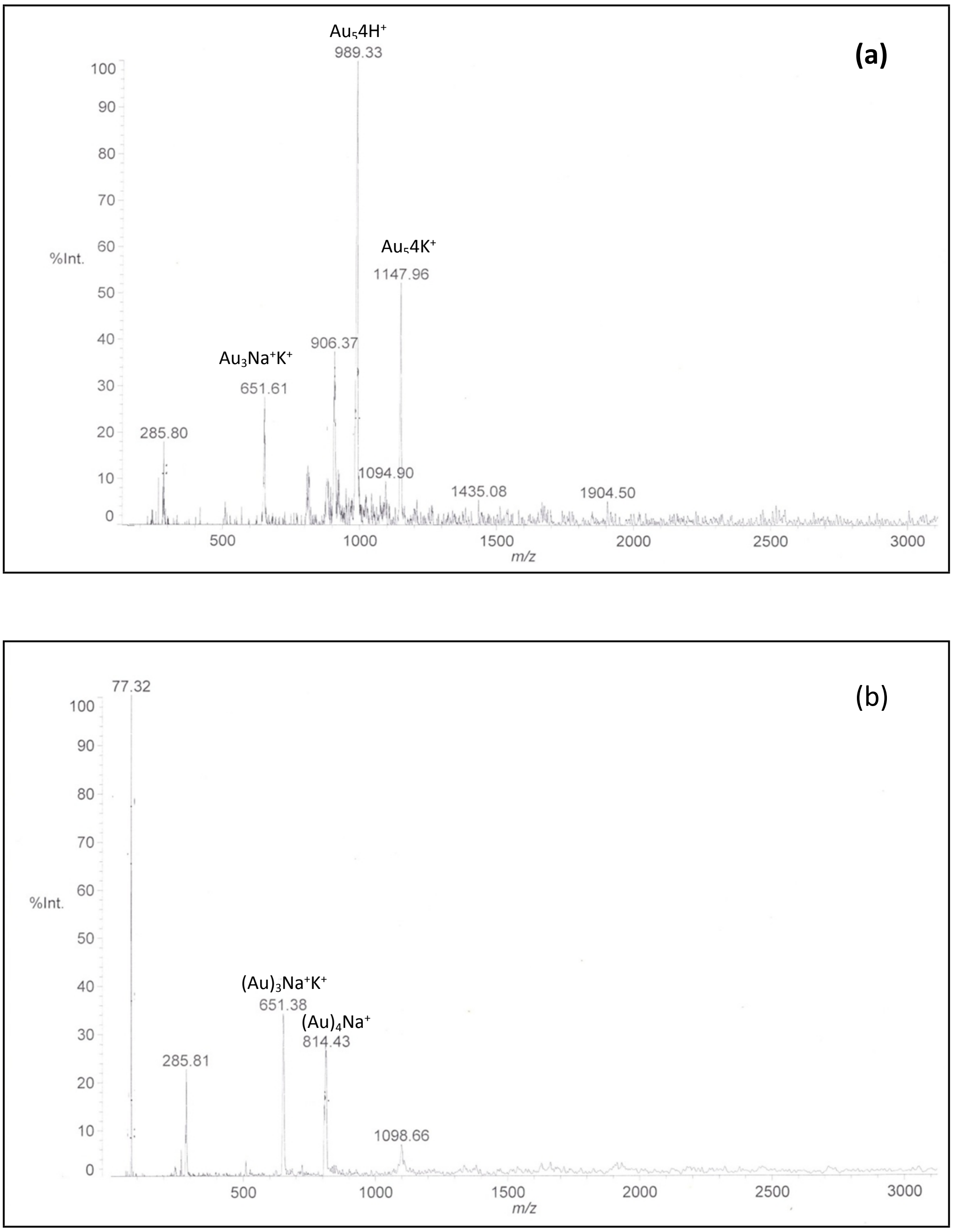

Figure S2: MALDI-TOF-MS spectra of gold atomic clusters formed from 50 mM CTAB in the presence of 0.2% chitosan (a) and in its absence (b).

Single step chronoamperommetric studies

Single step potential chronoamperometry was employed to investigate the electrochemical process at the chemically modified electrode. Fig.S3 shows the current-time curve of AuAC-Chit modified electrode towards 10^{-3} M of Hg (II) in 0.1M of HNO_3 by setting the working electrode potential at +0.80 V of first potential step and +0.45V of second potential step (black line) and redline represents the potential step to +0.55V. In both potential step the current is almost zero.

The rate constant for Hg (II) catalysed Au oxidation can be evaluated by chronoamperometry according to the equation

$$I_C/I_L=\pi^{1/2}(kCt)^{1/2}$$

From the plot of I_C/I_Lvs $t^{1/2}$ for AuAC-Chit modified electrode in Fig S3 (see inset), the rate constant was found to be $=4.094\times10^{4}$ $cm^3mol^{-1}s^{-1}$.

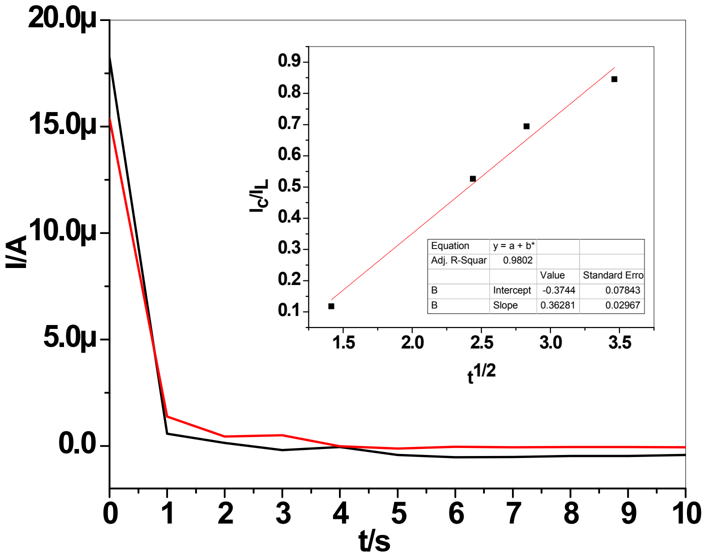

Fig. S3. Potential step chronoamperometric curves obtained for AuAC-Chit modified gold electrode. Potential step from +0.80V to +0.45V (black line) and to +0.55V (redline) respectively. Inset: Corresponding dependence of $I_{catalytic}(I_C)/I_{Limiting}(I_L)$ on time ($t^{1/2}$) .

Table: S1. Comparison with selected electrochemical sensor for Mercury

Electrode Modification	Techniques in detail	Linear range(nM)	LOD(nM)	Reference
Gold atomic cluster chitosan nanocomposite film modified gold electrode	DPASV	10^{-5} to 100	0.8×10^{-5}	Present work
GO-IL composites-AuNPs modified GCE	ASV	0.1-100	0.03	40
Polypyrrole/reduced graphene oxide nanocomposite	SWASV	0-100	15	41
Surface ion imprinting films on gold nanoparticles/single-wall carbon nanotube modified GC	DPASV	0.4–96.0	0.08	42
Supersandwich DNA structure modified electrode	DPV	0.1- 10^3	1×10^{-5}	43
Sensor chip containing Au and Ag electrodes	CC	6-1.1×10^3	1	44
Mesoporous NiOnanosheet modified GCE	DPV	800- 5×10^5	40	45
Gold nanoparticles electrodeposited on glassy carbon	SWASV	0.80 to 9.9	0.40	46
Surface ion imprinting strategy in electropolymerizedmicroporous poly(2-mercaptobenzothiazole) films.	SWASV	1-160	0.1	47
His-Phe-His-Ala-His-Phe-Ala-Phe modified electrode	CV	250-810	9.5	48
Novel poly (1,8diaminonaphthalene)/carbon nanotubes composite on silicon chip	SWV	50-100	50	49
Controlled assembly of SWCNTs on the MHA/SAM-modified gold electrode.	DPASV	1×10^{-4} - 1×10^{-3}	1.6×10^{-5}	50
Screen-printed gold electrodes	SWASV	25-1.5×10^2	5.5	51
Mercury ion imprinted polymer based electrode.	DPASV	2.5-5.0×10^2	0.52	52
Bimetallic Au-Pt inorganic-organic hybrid nanocomposite modified glassy carbon electrode	SWASV	0.04-0.5	0.04	13
Thymine-Hg^{2+}-thymine structure based biosensor	DPV	1-500	0.32	53
Target-induced structure-switching DNA based gold electrode	DPV	0.1-5×10^3	0.06	54
Monodispersed Au nanoparticles decorated graphene	SWASV	0-300	0.03	55
Microfabricated on-chip integrated Au–Ag–Au three-electrode system	DPV	10 - 5×10^3	15	56

Mercury-specific oligonucleotide probe dased gold nanoparticles	SWASV	0-100	0.5	57
Thymine-Hg^{2+}-thymine coordination chemistry based gold electrode.	ASV	1.0 to 2×10^3	0.5	58
Polyviologen modified glassy carbon electrode	DPASV	5 - $5x10^2$	1.5	59
Gold nanoparticles/carbon nanotubes composites	ASV	0.5-1.25×10^3	0.3	60
Gold nanoparticle-modified glassy carbon electrode	SWASV	50-2.5×10^5	0.075	61
Gold ultra-microelectrode arrays	LSV	0.1 to 103	16	62

(LSV: Linear sweep voltammetry, SWASV: Square wave anodic stripping voltammetry, SWV: Square wave voltammetry, ASV: Anodic stripping voltammetry, DPASV: Differential pulse anodic stripping voltammetry, DPV: Differential pulse voltammetry, CC: Chronocoulometry).