Electronic Supporting Material

Synthesis and Sensing Efficiency of CN Wrapped $ZnFe_2O_4$ Microspheres-Ionic Liquid Composite Towards Ultra-High Sensitivity Arsenic(III) Monitoring of Ground Drinking Water

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Section-1 Instrument details

1.1 X-ray diffraction (XRD)

The phase composition was analyzed by X-ray diffraction (XRD) measurements by using a Rigaku D/max-2550 instrument equipped with a Cu-Kα radiation source (λ=1.5418 Å). The crystallite size (D) was determined from the (1 1 1) peak using the Scherrer formula given below in equation.

$$D = k\lambda/\beta\cos\theta$$

Where, "D" is the average crystallite size in nm, 'k' (0.94) is the shape factor, λ (1.54056A) is the X-ray wavelength, β is FWHM in radian, and θ is the Bragg's diffraction angle.

1.2 Transmission electron microscope (TEM)

TEM, high-resolution TEM (HRTEM) images, and the angle annular dark field (HAADF-EDS) data were taken on a FEI Cs-corrected Titan 80–300 kV microscope with an accelerating voltage of 200 kV.

1.3 X-ray photoelectron spectroscopy (XPS)

The chemical compositions and bond characters were characterized by X-ray photoelectron spectroscopy (XPS) spectra recorded on AXIS Ultra DLD spectrometer (Kratos Analytical) under ultrahigh vacuum ($<10^{-8}$ Torr) and by using a monochromatic Al Kα radiations.

1.4 Raman spectroscopy

Raman spectra were recorded on Renishaw in Via-reflex spectrometer.

1.5 Fourier transform infrared (FTIR)

FTIR spectra of as obtained benzimidazolium-1-acatate ionic liquid (IL) were recorded using a Nicolet 6700 (Thermo-Fisher) spectrometer with a resolution of 4.0 cm^{-1} and in the range of 400−4000 cm^{-1} using KBr (ratio 5/95 wt. %) pellets.

1.6 1H NMR and ^{13}C NMR

1H NMR and ^{13}C NMR spectra of IL were recorded at 600 MHz with Bruker Avance 600 (USA) spectrometer in in CD3OD as solvent and TMS as internal standard.

1.7 Electrochemical experiments

All electrochemical experiments were performed with Metrohm Autolab (Sr. # AUT50296) instrument, controlled by Nova 1.11 software at room temperature measurements. The electrochemical cell was conventional three-electrode system, which consisted of a platinum wire as counter electrode, an Ag|AgCl as reference electrode and graphitic pencil (GP) electrode (GP: 0.5 mm diameter and 40 mm length) modified with our synthesized material as working electrode.

Section-2 Characterization analysis details

2.1 NMR analyses of benzimidazolium-1-acetate ionic liquid (IL)

The purities of IL were verified by NMR.

^{1}H NMR: δ = 1.97 (s, 3H), 7.23 –7.25 (m, 2H), 7.58 –7.6 (m, 2H), 8.23 (s, 1H) (Figure S1).

^{13}C NMR: 21.5 (methyl peak), 115.7, 122.1, 138.4, 142.3, 172.5 (carbonyl carbon of acetate ion) (Figure S2).

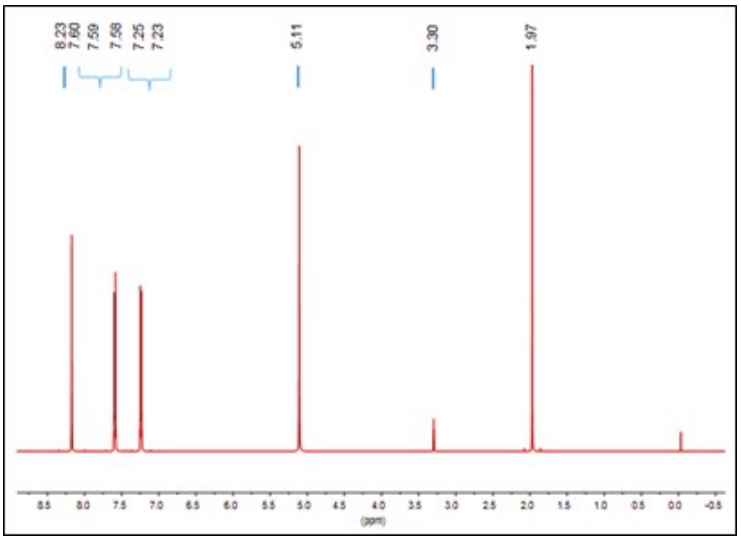

Figure S1 ^{1}H NMR of IL

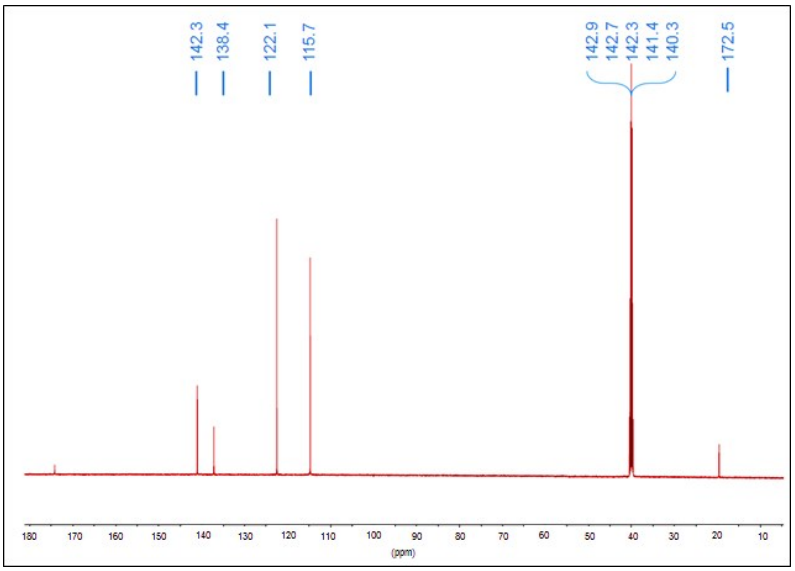

Figure S2 ^{13}C NMR of IL

2.2 Fourier transforms infrared (FTIR) spectroscopy analyses of IL

FTIR spectroscopy has been employed to analyse the chemical structure of as-synthesized IL. The band at 2981 cm^{-1} is assigned to the alkyl group. The peak around 3112 cm^{-1} corresponds to alkenyl C—H stretching. The band at 1701 and 1619 cm^{-1} are due to the occurrence of C=O bonds and C=N, respectively. Also, the absence of stretching vibrations around 3000 cm^{-1} (O—H) verify the presence of acetate ion.

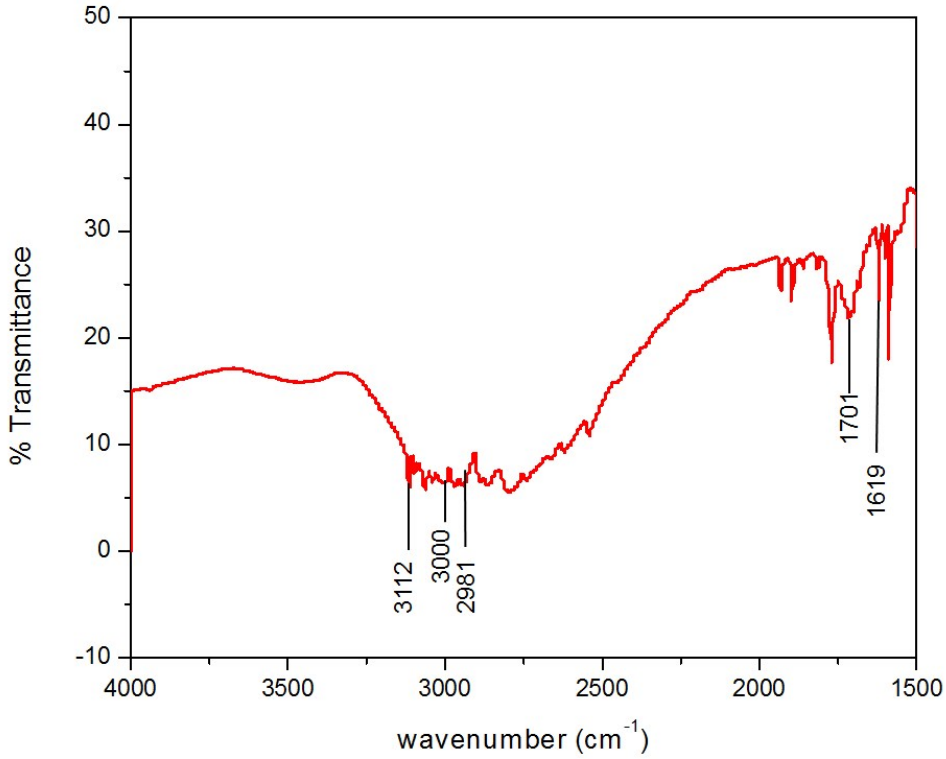

Figure S3 FTIR analysis of IL.

2.3 Working electrode fabrication

Before modification, the graphitic pencil (GP: 0.5 mm diameter and 40 mm length) electrodes were pre-treated according to the reported literature.[22] Briefly, the GP electrodes were dipped and sonicated in concentrated nitric acid (65 %) solution for 90 minutes to oxidize the electrode surface. Next, these electrodes were washed with Milli-Q water several times and dried at room temperature. For the modification, GP electrodes were dipped in 5 mL solution of synthesized material (2 mg) and Milli-Q water for 4 hours under room temperature. The modified electrode was further dried overnight and before using it edge of the GP electrode was cut down via sharp blade to get the clean and smooth surface. The electrical contact of the electrode was made by using Cu wire.

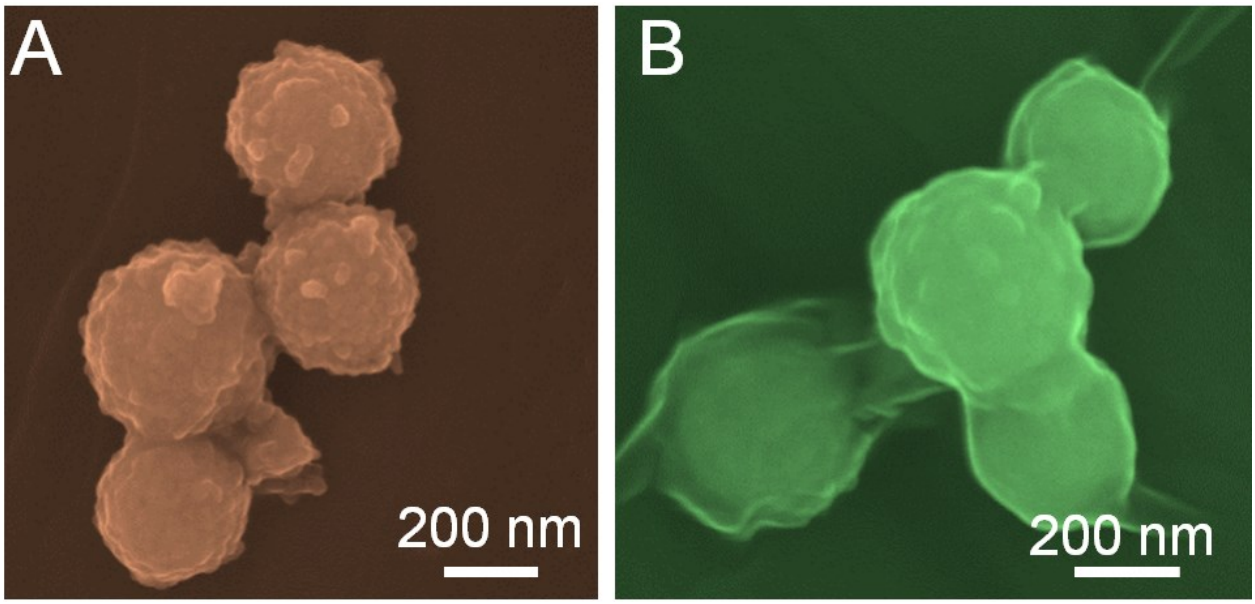

Figure S4 FE-SEM images clearly showing the formation of CN@ZF-Ms (A) and CN@ZF-Ms-IL (B).

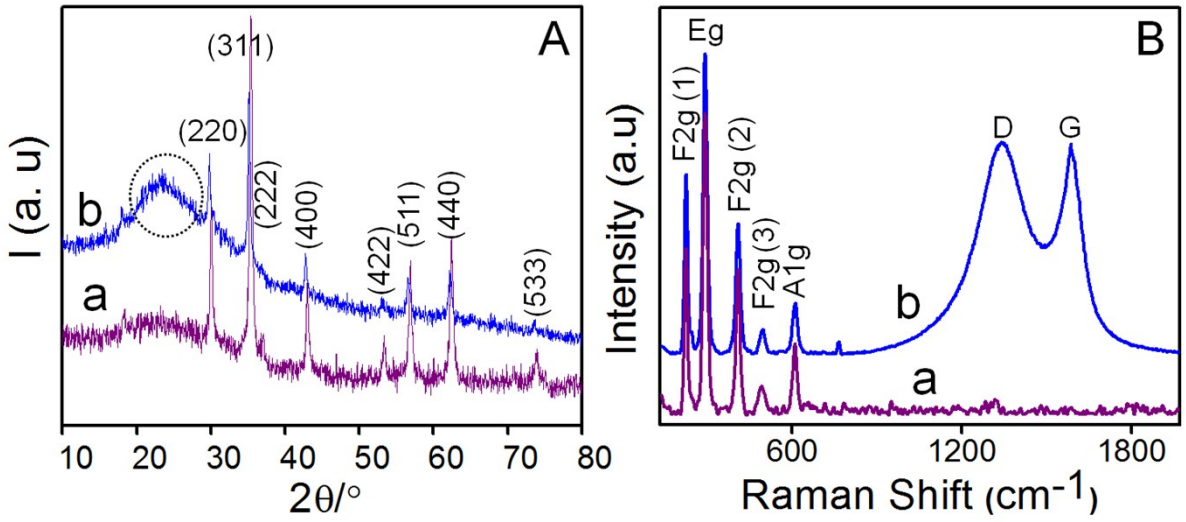

Figure S5 XRD (A) and Raman measurements (B) of ZF-Ms (a) and CN@ZF-Ms (b), respectively.

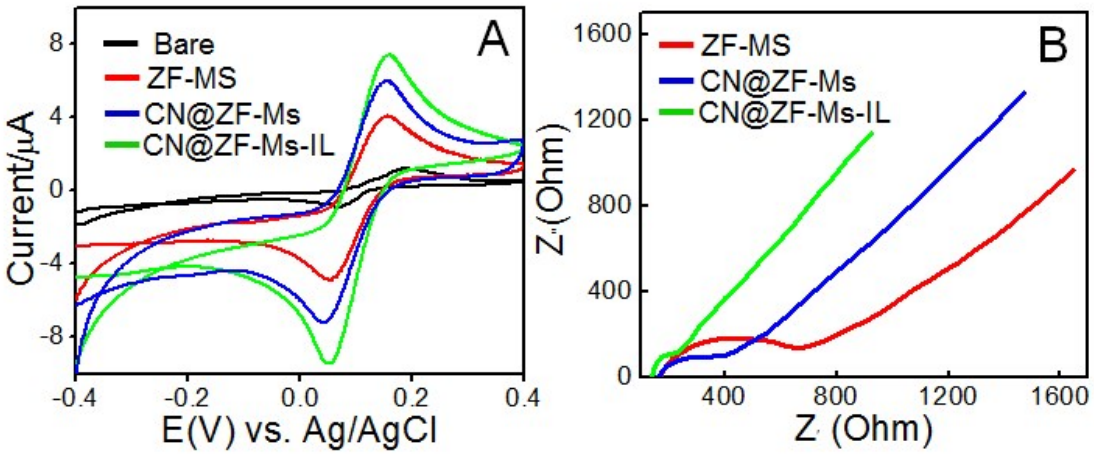

Figure S6 (A) CV curve of 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 KCl solution at scan rate 50mVs-1 with Bare (black line), ZF-Ms (red line), CN@ZF-Ms (blue line) and CN@ZF-Ms-IL (green line) respectively.(B) Impedance measurement (nyqist plot) at ZF-Ms (red line), CN@ZF-Ms (blue line) and CN@ZF-Ms-IL (green line) respectively in 0.1 KCl solution containing 5 mM $[Fe(CN)_6]^{3-/4-}$.

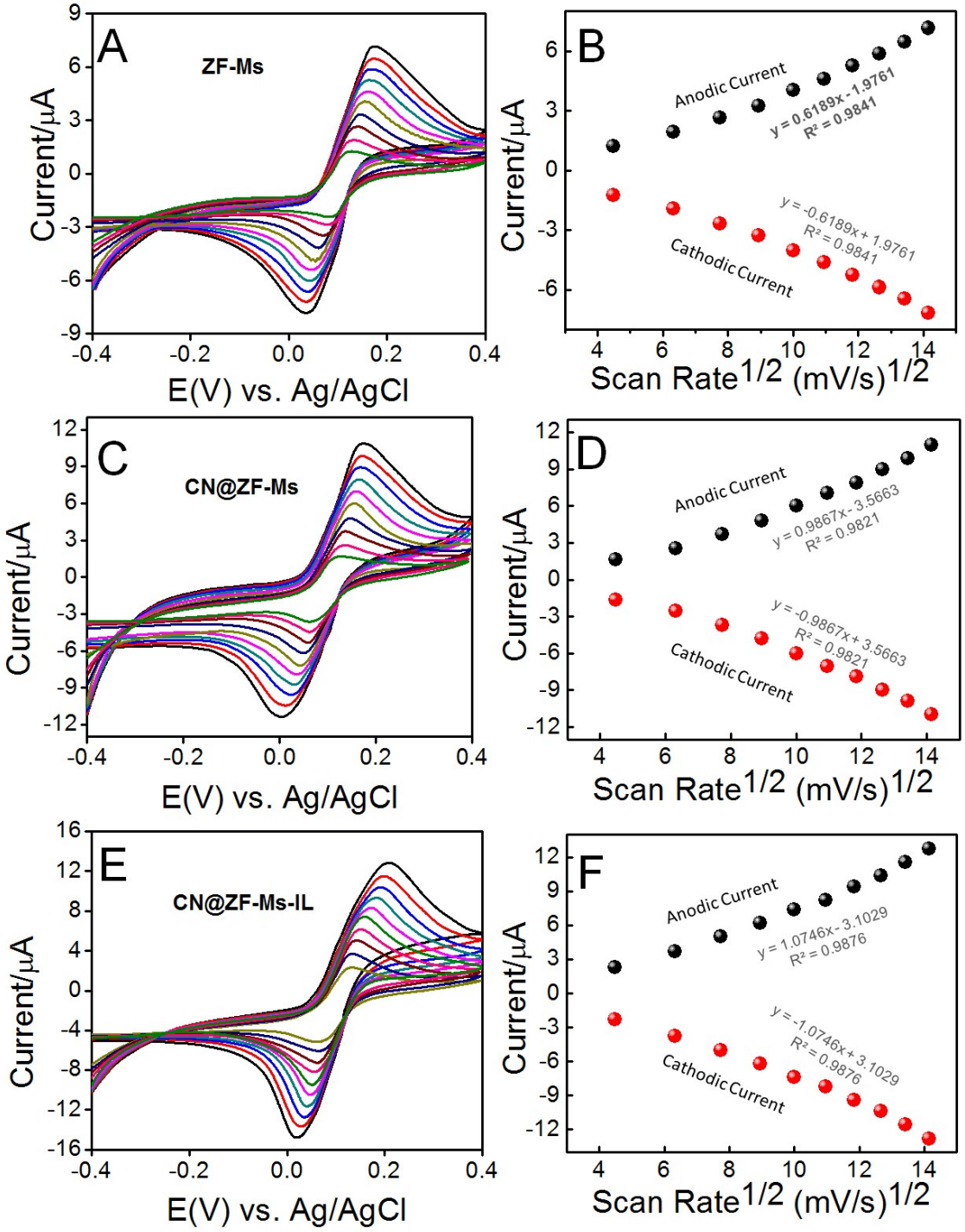

Figure S7 Scan rate (0.02 to 0.2 Vs-1) study of (A) ZF-Ms, (B) CN@ZF-Ms and (E) CN@ZF-Ms-IL towards 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl respectively. Corresponding (B), (D) and (F) plot of anodic/cathodic current versus the square root of the scan rate.

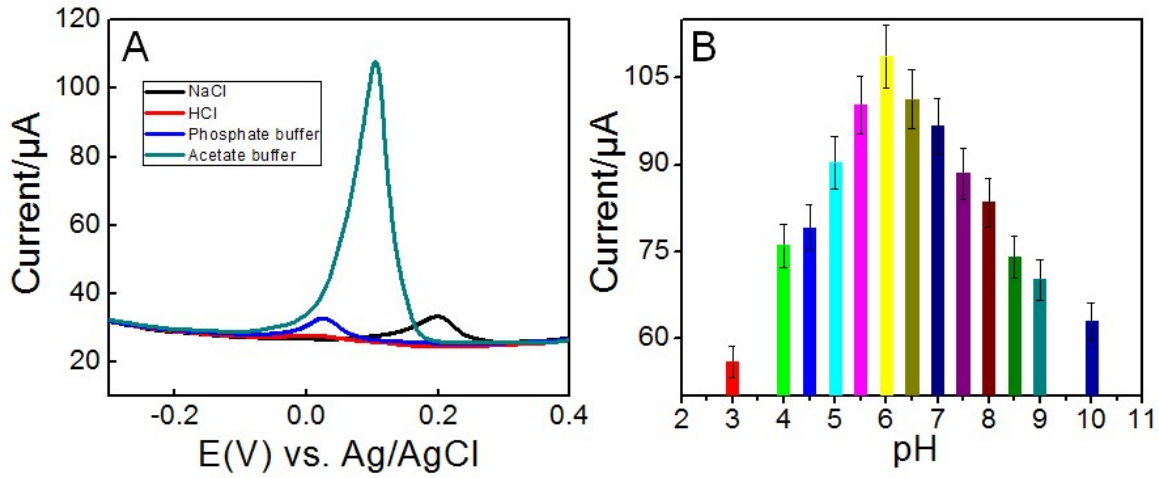

Figure S8 Impact of (A) supporting electrolytes (0.1M) and pH (B) on the electrochemical response of ZF-Ms towards 10 ppb As(III) by using SWASV.

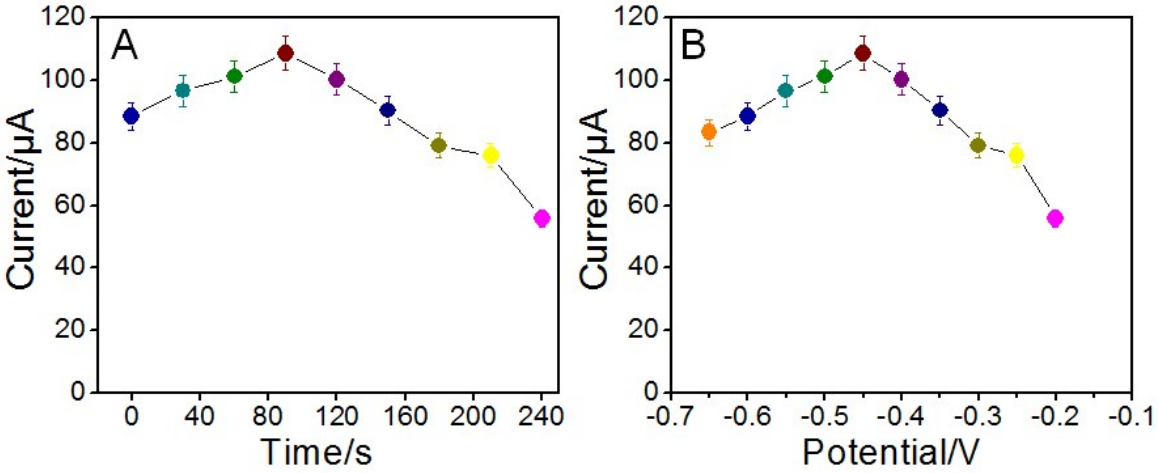

Figure S9. Impact of deposition time (A) and potential (B) on the electrochemical response of ZF-Ms towards 10 ppb As(III) by using SWASV.

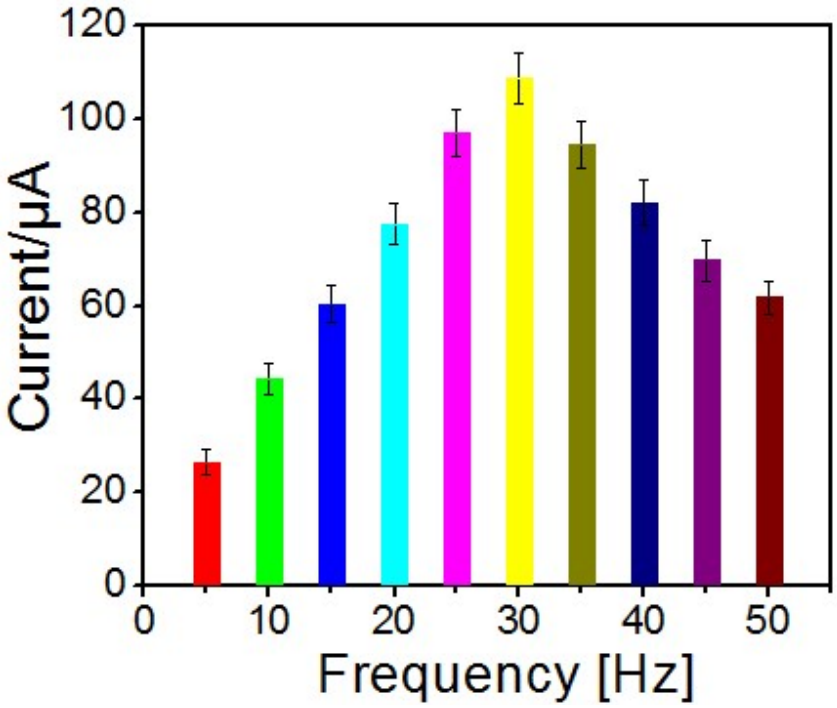

Figure S10. Impact of deposition frequency on the electrochemical response of ZF-Ms towards 10 ppb As(III) by using SWASV.

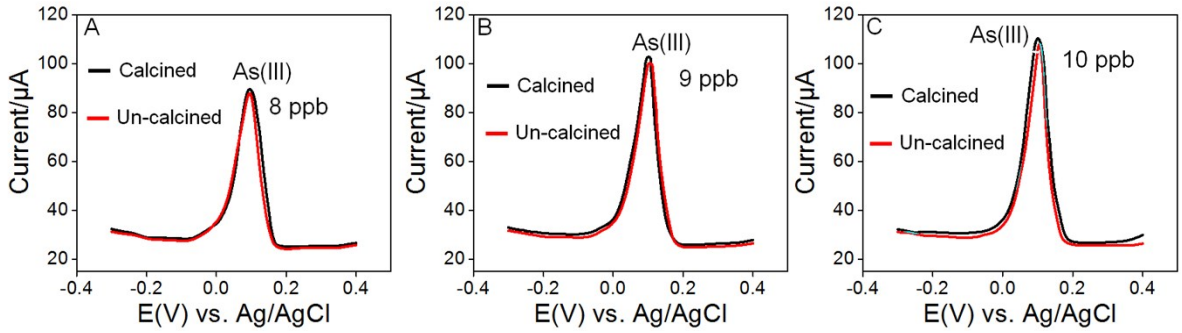

Figure S11 Square wave anodic stripping voltammograms of calcined ZF-Ms (black line) and un-calcined ZF-Ms (red line) towards As(III) into 0.1 M acetate buffer with concentrations 8 ppb (A), 9 ppb (B) and 10 ppb (C).

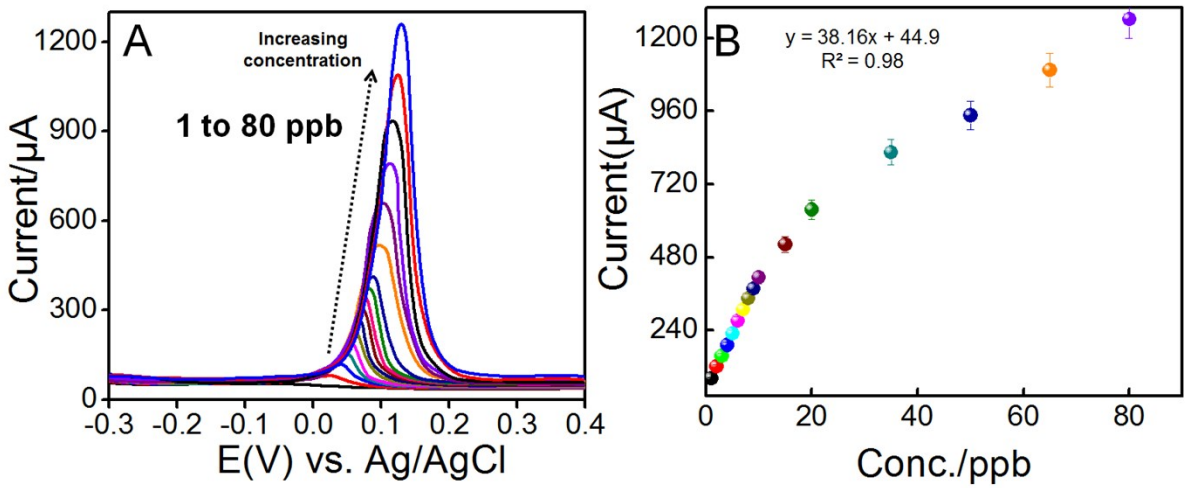

Figure S12 Square wave anodic stripping voltammograms of (A) CN@ZF-Ms-IL towards increasing concentration (1-80 ppb) of As(III) into 0.1 M acetate buffer electrolyte under optimized conditions, whereas Panel (B), shows its calibration plot.

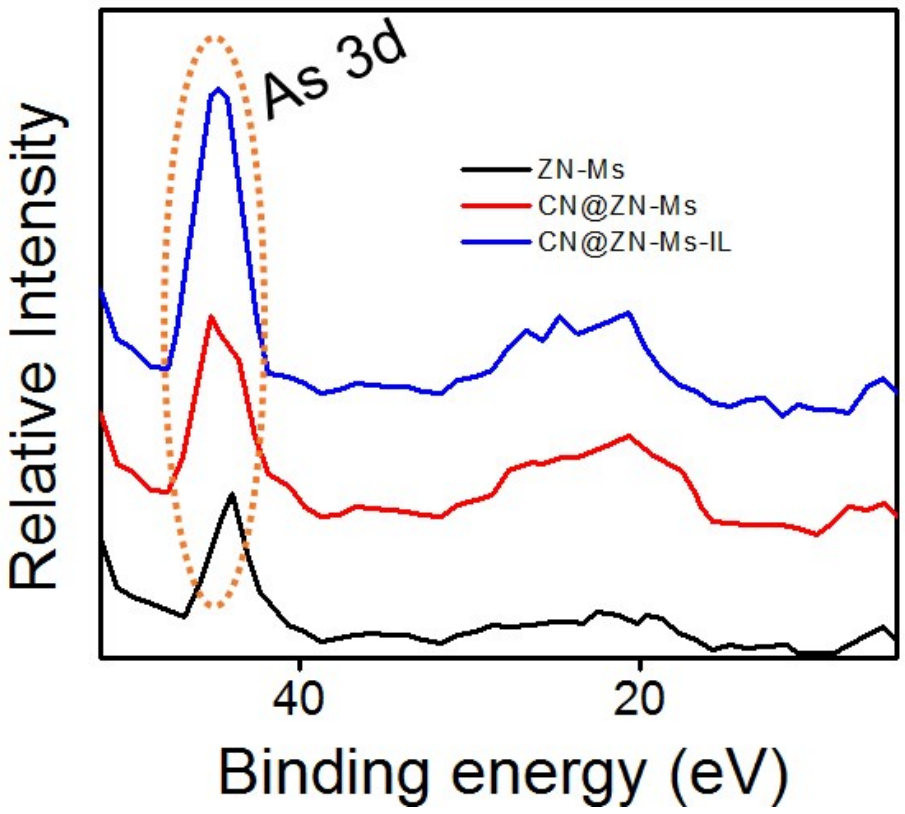

Figure S13 Typical XPS spectra of As(III) adsorbed on ZF-Ms (black line), CN@ZF-Ms (red line) and CN@ZF-Ms-IL (blue line).

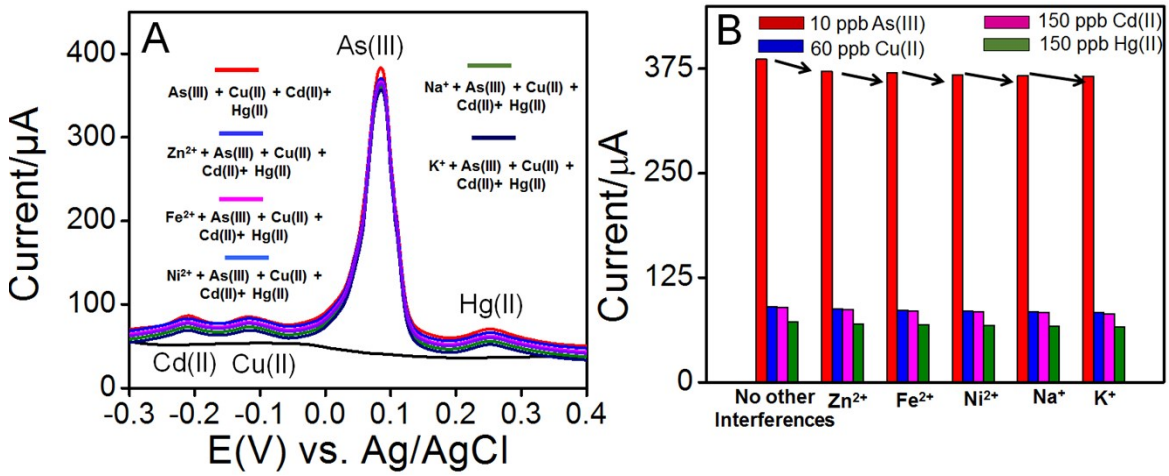

Figure S14 (A) Square wave anodic stripping voltammograms of CN@ZF-Ms-IL towards constant concentration As(III) (10 ppb), Cu(II) (60 ppb), Cd(II) (150 ppb), Hg(II) (150 ppb) with 50 ppb of electroactive (e.g. Zn^{2+}, Fe^{2+} and Ni^{2+}) and non-electroactive (Na^{+} and K^{+}) cations in 0.1 M acetate buffer (pH :6). (B) The peak current of As(III), Cu(II), Cd(II), Hg(II) derived from plot A, in relation to electroactive and non-electroactive cations

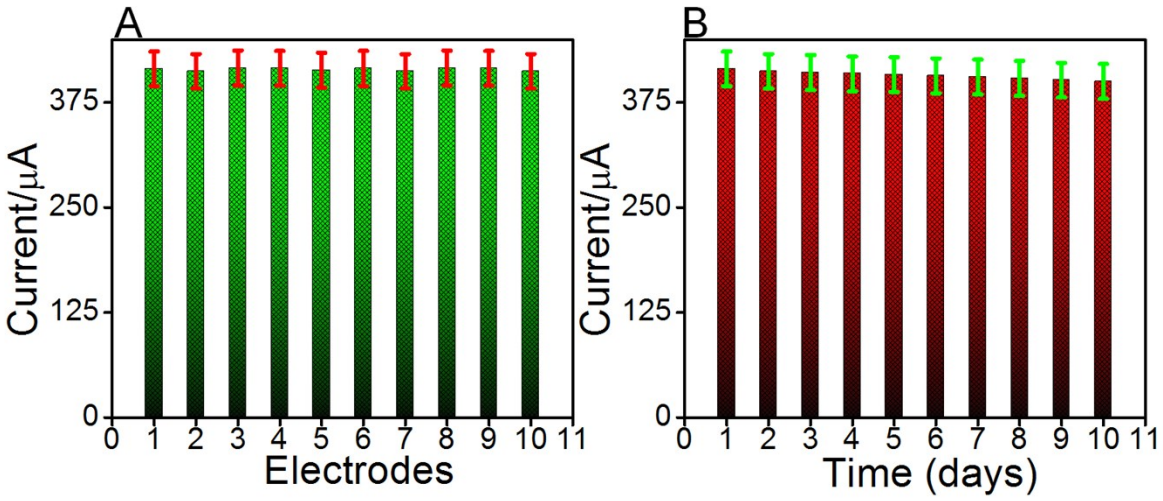

Figure S15 (A) Square wave anodic stripping voltammograms peak current of 10 CN@ZF-Ms-IL electrodes towards 10 ppb of As(III) in 0.1 M acetate buffer (pH :6). (B) Square wave anodic stripping voltammograms peak current response of CN@ZF-Ms-IL electrode towards 10 ppb of As(III) in 0.1 M acetate buffer (pH :6) for 10 days.

Table S1 comparative evaluation and performance of different electrodes with our designed sensor towards As(III).

Sr. #	Electrodes	Electrolyte	linear range (ppb)	sensitivity (μA ppb^{-1})	LOD (ppb)	references
1	Au-NPs/GCE	1 M HCl	0-7.5	0.24	0.0096	ES1
2	Au-UMEA	2 M HCl	0-500	0.044	0.013	ES2
3	Au-NPs/GCE	3M HCl	0-87	4.27	1.8	ES3
4	Sonically assisted gold micro disk electrode	0.1 M HNO_3	7.5-75	0.363	0.28	ES4
5	Au-NPs/GCE	0.1 M HNO3	0.5-15	0.024	0.25	ES5
6	Au coated diamond thin film electrode	1 M HCl	0.01-40	0.0097	0.005	ES6
7	Gold Nano- electrode ensembles	1 M HCl	0.1-3	3.14	0.02	ES7
8	Au (iii) poly crystalline gold electrode	PBS (pH=1)	0-1125	0.3636	0.28	ES8
9	Au@C electrode	0.1 M HNO_3	1.5-16.5	0.133	0.375	ES9
10	Au@MWCNTs electrode	Acetic Buffer (pH=4)		0.236		ES10
11	IrOx/BDD electrode	PBS (pH=4.3)	1.5-3750	0.056	0.15	ES11
12	PBSPE	KCl/HCl (pH=4)	3.75-22500	3.87 X 10-4	0.875	ES12
13	MWCNT/Aro/GCE	PBS (pH=7)	0-500	0.00143	1	ES13
14	CoOx/GCE	PBS	15-300	0.00148	0.825	ES14

		(pH=7)				
15	Fe_3O_4@RTIL/SPCE	Acetic Buffer (pH=5)	1-10	4.91	0.0008	ES15
16	Au-CRE@rGO film	PBS (pH=7)	2-48	2.38	0.36	ES16
17	BTC@GCE				71.9 pM	ES17
18	HMDE				1.3 nM	ES18
19	Au-disk	1M HNO3		13.1	0.86	ES19
20	Au NPs/BPPG	1 M HCl		3.52	17.5	ES20
21	Au/GNE	0.1M HNO^3		39.54	0.08	ES21
22	$Co_{0.6}Fe_{2.4}O_4$	0.1M Na-Acetate Buffer	1-20	2.12	0.093	ES22
23	Au NPs/SPE	1 M HCl	0.5-12	0.057	0.22	ES23
24	rGO/MnO_2/NH/GCE	0.1 M Acetic Buffer (pH=5)	0.1-50	0.176	0.05	ES24
25	AuNPs-PCWEs	3M HCl	2-50	0.083	2.2	ES25
26	FePt NPs/Si	10mM PBS (pH=7)	1-15	0.42	0.8	ES26
27	AgNPs-CT/GCE	0.1M HNO^3	10-100	0.309	1.2	ES27
28	Au-Pd/GCE	0.1 M Acetic Buffer (pH=4.5)	1-25	0.172	0.5	ES28
29	AuNPs/αMnO_2/GCE	0.1 M Na_2CO_3/ $NaHCO_3$ (pH=9)	1-10	0.828	0.019	ES29

30	Co SAC /SPCE	0.1M PBS (pH= 5.3)	0.1-10	11.44	0.023	ES30
31	**CN@ZF-Ms-IL**	**0.1 M Acetate Buffer (pH:6)**	**1-60**	**41.08**	**0.0006**	**Current System**

[1] Au- ultra microelectrode array

[2] Boron doped diamond electrode modified with iridium oxide

[3]Prussian blue modified screen-printed electrode

[4] Fe_3O_4 functionalize with ionic liquid screen-printed carbon electrode

[5]Au-Crystal violet electrode

[6]Bis- Triazole appended Calix (4) arene

[7]Au NPs/ basal plane pyrolytic graphite

[8]Gold Nano textured electrode

[9]Cobalt single atom anchored on Carbon /screen-printed carbon electrode

Table S2: Arsenic related complete data report of the selected area. Arsenic is measured by using MERCK 117917 Arsenic Test kit.

Sr.#	Bait Name	Basti Name	Arsenic (ppm)
		W.H.O Guideline	**0.01**
1	Mulana	Surani	0.05
2	Mulana	Pathan Wala	0.01

3	Mulana	Pathan Wala	0.025
4	Mulana	Kurae	0
5	Mulana	Chah Photi Wala	0.01
6	Mulana	Shery Wali	0.01
7	Mulana	Khabar	0.01
8	Mulana	Khosa	0
28	Musa Mulana	Janu Wala	0.1
29	Musa Mulana	Pitafi + Janu Wala	0.05
30	Musa Mulana	Zor	0.05
31	Chan Wala	Awan Gerbi	0.05
32	Chan Wala	Awan Sharki	0.05
33	Chan Wala	Kaleem Abad	0.05
34	Chan Wala	Sipal	0.1
35	Chan Wala	Noon	0.05
36	Chan Wala	Angra	0.025
37	Chan Wala	Shorti	0.01
38	Chan Wala	Chandia	0.025
39	Chan Wala	Chan	0.05
40	Chan Wala	Lashkari Chandia	0.025
41	Chan Wala	Lashkari Chandia	0.025
42	Chan Wala	Angra	0.025
43	Chan Wala	Almani+ Machi Wala	0
44	Utra	Utra	0.01
45	Utra	Utra + Qurai	0.01

46	Utra	Hulli	0
47	Utra	Bhati	0.05
48	Utra	Bhati	0
49	Utra	Feroz Abad	0.05
50	Utra	Khosa	0.01
51	Utra	Pachar	0
52	Utra	Javeed Colony	0
53	Utra	Javeed Colony	0.025
54	Utra	Javeed Colony	0.01
55	Utra	Gormani	0
56	Utra	Gormani	0.05
57	Utra	Qurai	0
58	Utra	Rind	0
59	Utra	Sial	0.025
60	Utra	Sial	0.05
61	Utra	Sial	0.05
62	Utra	Daownaan	0.1
63	Utra	Daownaan	0.025
64	Utra	Daownaan	0
65	Utra	Daownaan	0
66	Utra	Daownaan	0.01
67	Utra	Arain	0.01
68	Utra	Arain	0
69	Utra	Wahocha	0

70	Utra	Wahocha	0.01
71	Utra	Gareeb Abad	0
72	Utra	Rind	0.025
73	Utra	Ghazi Ghat	0
74	Haji Shah	Kishani Wala	0
75	Haji Shah	Mehmeed Wala	0
76	Haji Shah	Mehmeed Wala	0
77	Haji Shah	Ranjhay Wala	0.01
78	Haji Shah	Qureshi Wala	0
79	Haji Shah	Qureshi Wala	0
80	Haji Shah	Lal Wala	0
81	Haji Shah	Lal Wala	0
82	Sohni	Gut Wala Gerbi	0
83	Sohni	Gut Wala Gerbi	0
84	Sohni	Gut Wala Sharki	0.05
85	Sohni	Sial	0.1

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