

Pure Inorganic Gel: A New Host with Tremendous Sorption Capability

Chanchal Mondal,^a Mainak Ganguly,^a Jaya Pal,^a Ramkrishna Sahoo,^a Arun Kumar Sinha,^a Tarasankar Pal^{*a}

^aDepartment of Chemistry, Indian Institute of Technology, Kharagpur-721302, India

E-mail: tpal@chem.iitkgp.ernet.in

Electronic Supplementary Information

ESI 1

Experimental section

Material:

AgNO₃, Ag(OAc), Ag₂SO₄, NH₄VO₃, Na₃VO₄, methylene blue, methyl green, eosin, malachite green and other chemicals were purchased from E-Merck. All the glass wares were cleaned with aqua regia and double distilled water prior to use.

Analytical Instrument:

Powder X-ray diffraction (XRD) was done in a PW1710 diffractometer, a Philips, Holland, instrument. The XRD data were analyzed by using (JCPDS) software.

Reflectance spectra were measured using DRS (Diffuse Reflectance Spectra) mode with a Cary model 5000 UV-vis-NIR spectrophotometer.

Raman spectra were obtained with a Renishaw Raman Microscope, equipped with a He-Ne laser excitation source of emitting wave length 633 nm and a peltier cooled (-70°C) charge coupled device camera (CCD).

Fourier Transform Infrared Spectroscopy i.e., FTIR measurements of the samples were done in KBr pellets in reflectance mode with a Nexus 870 Thermo-Nicolet instrument coupled with a Thermo-Nicolet Continuum FTIR microscope.

Field emission scanning electron microscopy (FESEM) was performed with a supra 40, Carl Zeiss Pvt. Ltd. instrument.

Transmission electron microscopy (TEM) was performed with an H-9000 NAR instrument, Hitachi, using an accelerating voltage of 300 kV.

For the gel sample, rheological measurement was carried out on a Bohlin Gemini (Malvern, UK) controlled-stress rheometer using 20 mm diameter parallel plate geometry with a constant tool gap of 100 µm. The gel sample was located on the lower plate, and a stress

amplitude sweep experiment was done at a constant frequency at 25 °C to get storage or elastic modulus, G', and loss or viscous modulus, G''. The frequency sweep measurements were performed at a constant stress in the linear viscoelastic range.

The gas sorption experiment was carried out using a Quantacrome autosorb iQ automated gas sorption analyzer.

The absorption of the dye solution was recorded using a Shimadzu UV-1601 UV-vis spectrophotometer.

Method:

Preparation of gel:

In a typical preparation of the inorganogel, 0.1 mL 0.1 M aqueous solution of NH_4VO_3 was added all at a time to a 1 mL 0.01M AgNO_3 aqueous solution. The minimum gelator concentration was 5×10^{-3} M. After keeping the mixture at room temperature for 1 hr gel formation occurs which was confirmed by an inverted vial method. After completion of the gel formation the gel was dried and reserved for characterization. Other silver salts e.g., Ag(OAc) , Ag_2SO_4 and vanadate salts e.g., Na_3VO_4 are also used to verify the effect of counter ions on the gel formation.

Dye sorption study:

At first the gel was prepared using 10 mL .01 M aqueous solution of AgNO_3 and 1 mL 0.1 M ammonium vanadate in a beaker. Then the gel was kept in contact with the 50 mL 1×10^{-4} M aq. solution of methylene blue. Within a period of time the dye solution starts fading while the gel takes the colour of the dye. This indicates the sorption of the dye molecules within the gel matrix. The concentration of the dye was monitored using UV-visible spectrophotometer at various time intervals.

To verify the capability of dye sorption of the gel we have chosen other dye molecules like methyl green, eosin, malachite green and found that they can also be adsorbed on the surface of the gel.

Likewise, aqueous solution of sodium arsenate and mercuric chloride was also kept in contact with the gel prepared in a vial for one day. Then the gel was collected and subjected to elemental mapping and EDX analysis.

ESI 2

FTIR study:

Figure S4 describes the FTIR spectrum of the xerogel. The observed bands at 967, 918, 847, 849 and 742 cm⁻¹ assigned to the stretching vibration of V=O species. The weak signature at 546 cm⁻¹ attributed to V–O stretching vibration. The band present at 849 cm⁻¹ assigned to both of the V–O stretching vibration and the Ag–O–V vibration. The silver ions are placed next to the VO₅ groups forming a lamellar double chain, thus generates a favorable conditions for Ag–O–V bonding. The bands at 3470 and 1630 cm⁻¹ are due to the stretching of O–H and flexural vibrations of the O–H in free water, respectively. The circle drawn in the figure from 750-950 cm⁻¹ suggests the presence of polymeric vanadate groups in the hydrogel.

Raman study:

Figure S5 displays the Raman spectrum of the xerogel of the as prepared material. The highly intense peak at 888 cm⁻¹ arises due to V–O–Ag and /or V–O–V vibrations. Relatively weak signature at 847 cm⁻¹ corresponds to the stretching vibrations of VO₃ groups in the (V₂O₇)⁴⁻ ion. The presence of the band 807 cm⁻¹ authenticates stretching vibrations of the Ag–O–Ag bridges. Relatively weaker bands at 728 cm⁻¹ and 516 cm⁻¹ assigned to asymmetric and symmetric stretches bridging V–O–V bond in the polymeric metavandate chains respectively. Presence of the peaks at 393, 336, 248, and 172 cm⁻¹ corroborate the formation of channel-structured silver vanadate hydrogel.



Fig. S1: Digital image of the gel obtained exploiting 70 ml 0.01 M AgNO_3 and 7 ml 0.1 M NH_4VO_3

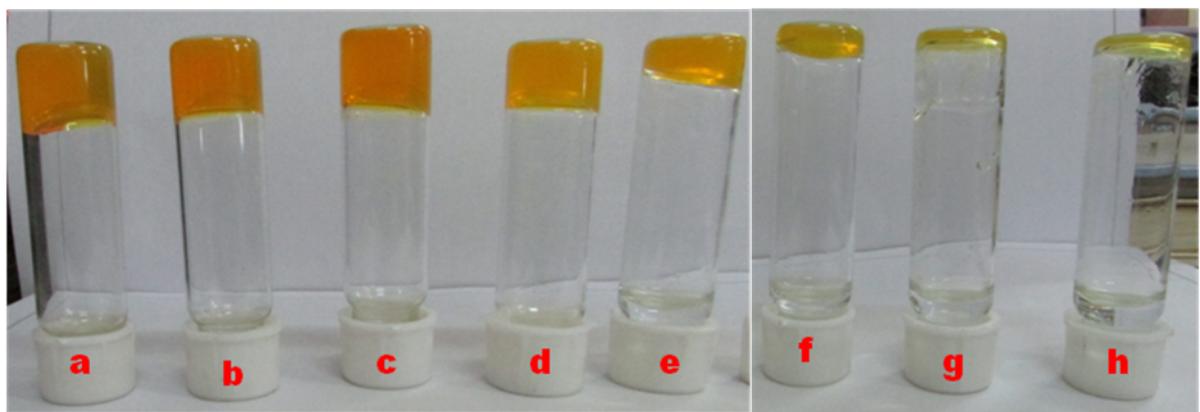


Fig. S2: Gels formed by 1 ml 0.01M AgNO₃ and various volumes of 0.1 M NH₄VO₃ (a) 0.1 ml, (b) 0.08 ml, (c) 0.06 ml, (d) 0.05 ml, (e) 0.04 ml, (f) 0.03 ml, (g) 0.02 ml, (h) 0.01 ml.

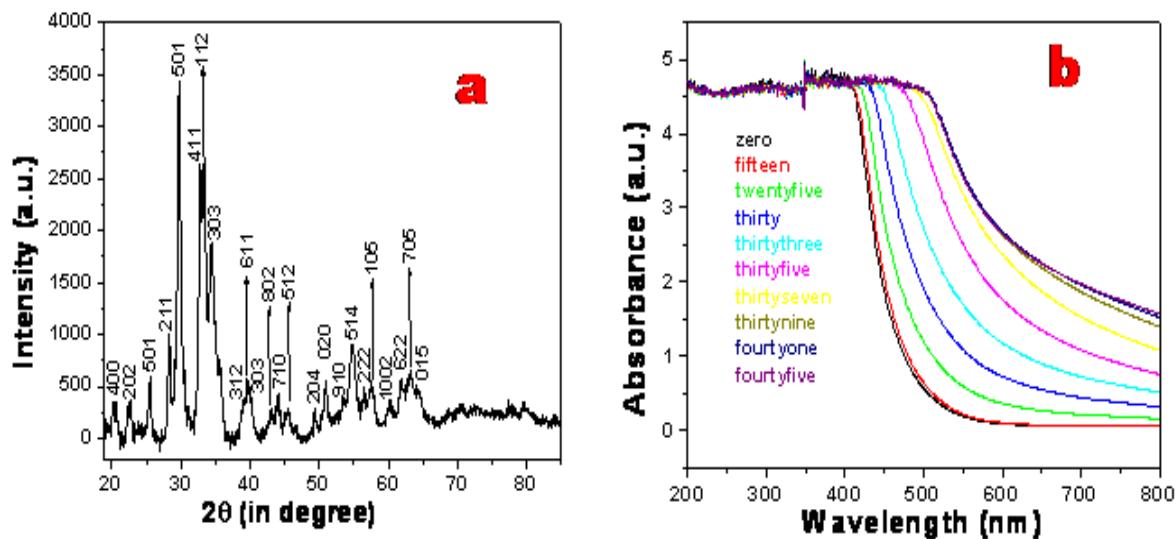


Fig. S3: (a) Powder XRD pattern of the xerogel (b) DRS spectra of the gel at various interval of its formation.

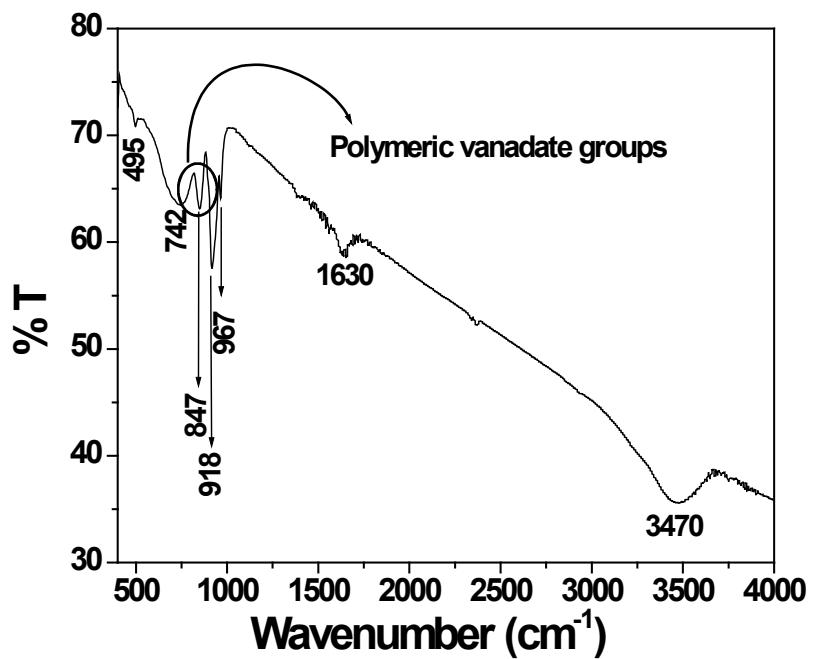


Fig. S4: FTIR spectrum of the xerogel.

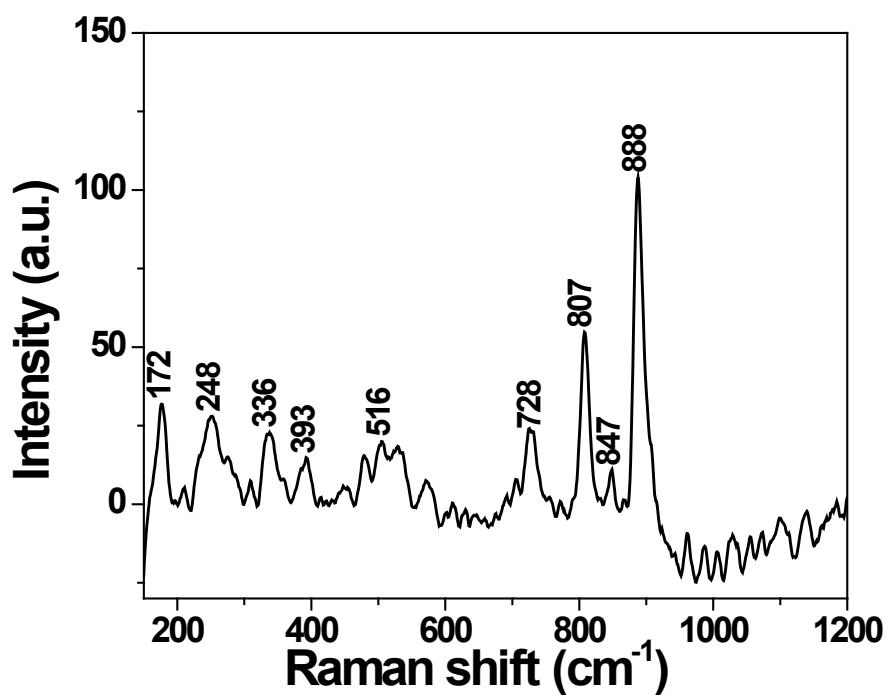


Fig. S5: Raman spectrum of the xerogel.

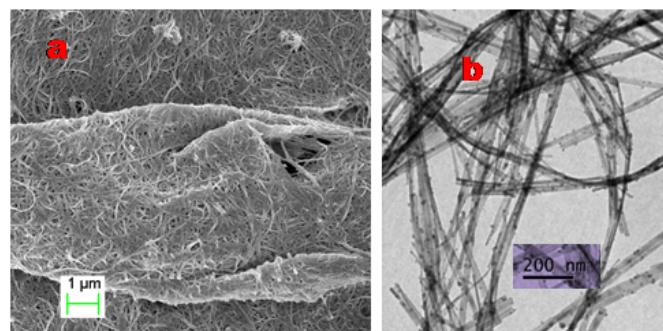


Fig. S6: (a) Low magnification FESEM image of the xerogel, (b) TEM image of the xerogel.

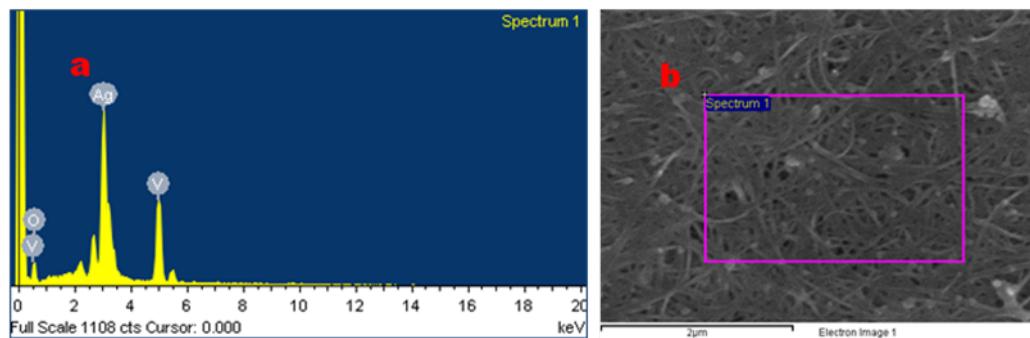


Fig. S7: (a) EDS spectrum of the xerogel and (b) its corresponding scan area.

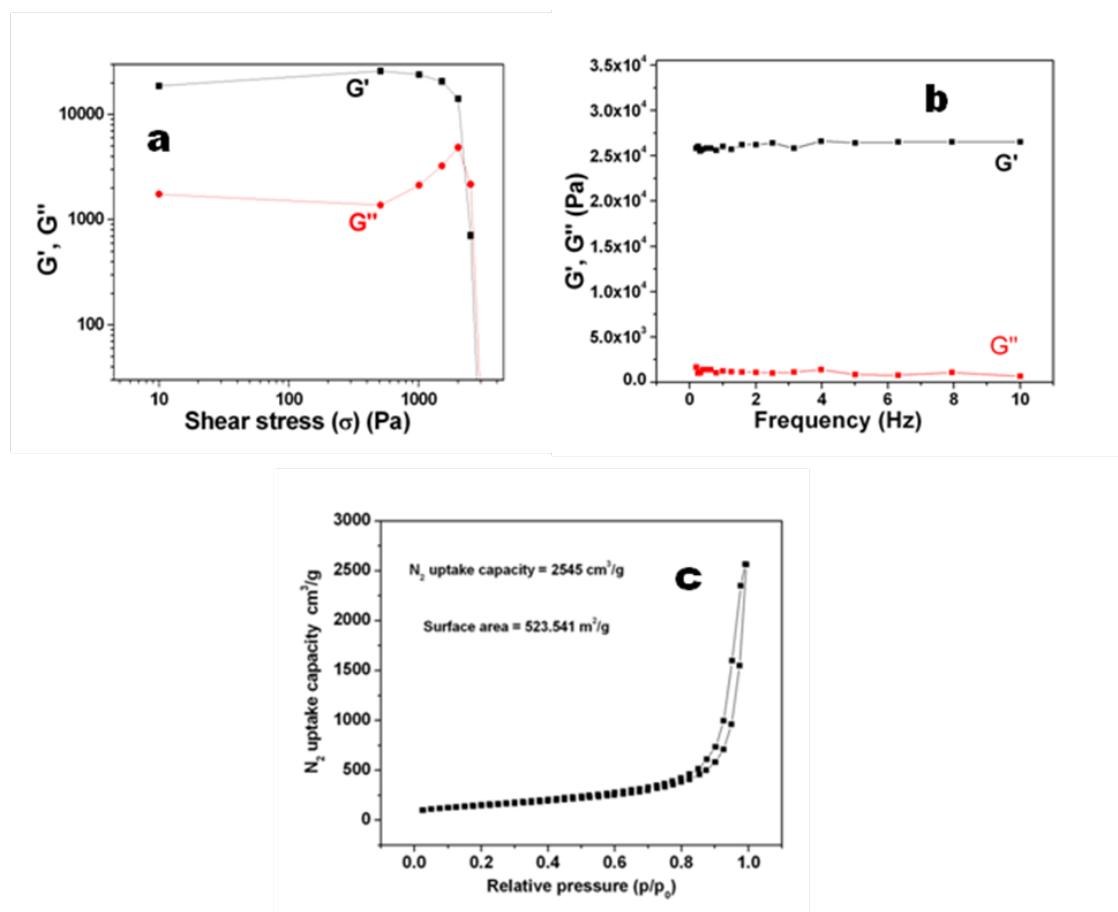


Fig. S8: Variation of storage modulus (G') and loss modulus (G'') with (a) shear stress (b) frequency; (c) N_2 gas adsorption–desorption isotherm of the xerogel.

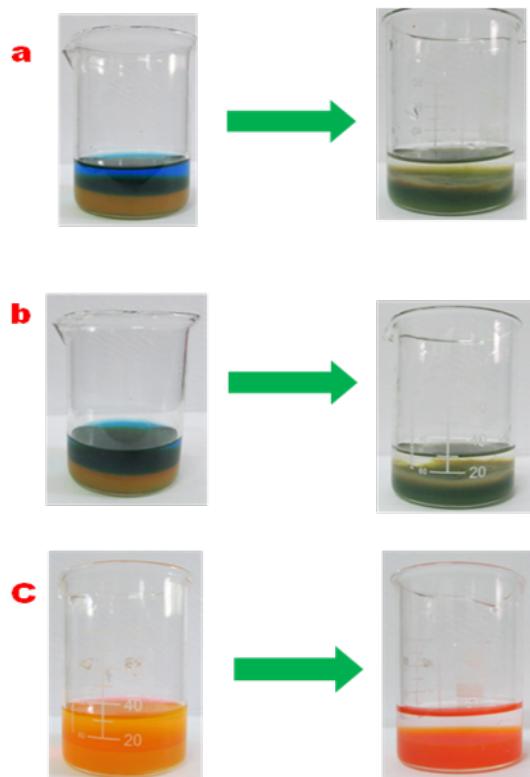


Fig. S9: Digital images of the dyes before (left) and after (right) adsorption (a) methyl green, (b) malachite green, (c) Eosin.

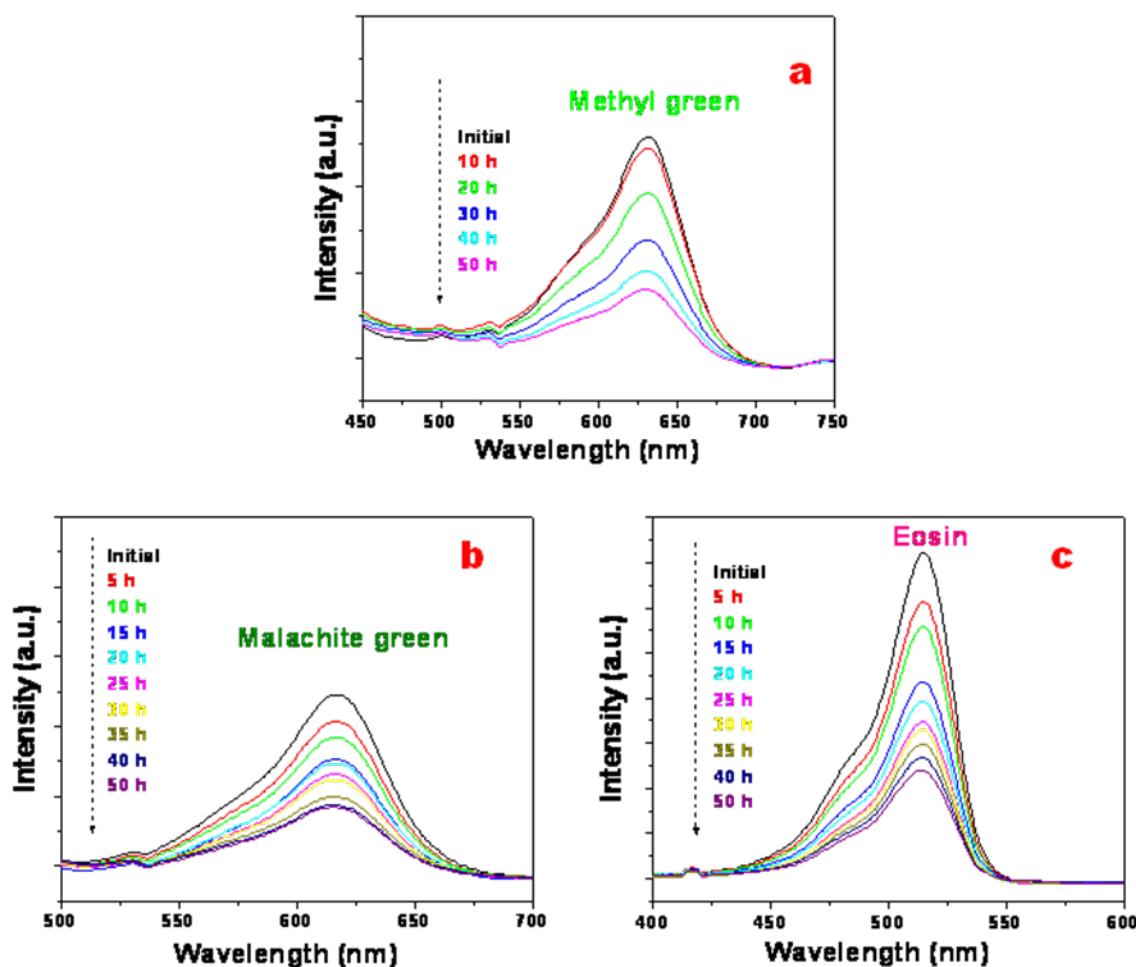


Fig. S10: UV-Vis spectra of aq. solution of dyes kept contact with hydrogel (a) Methyl green, (b) Malachite green, (c) Eosin

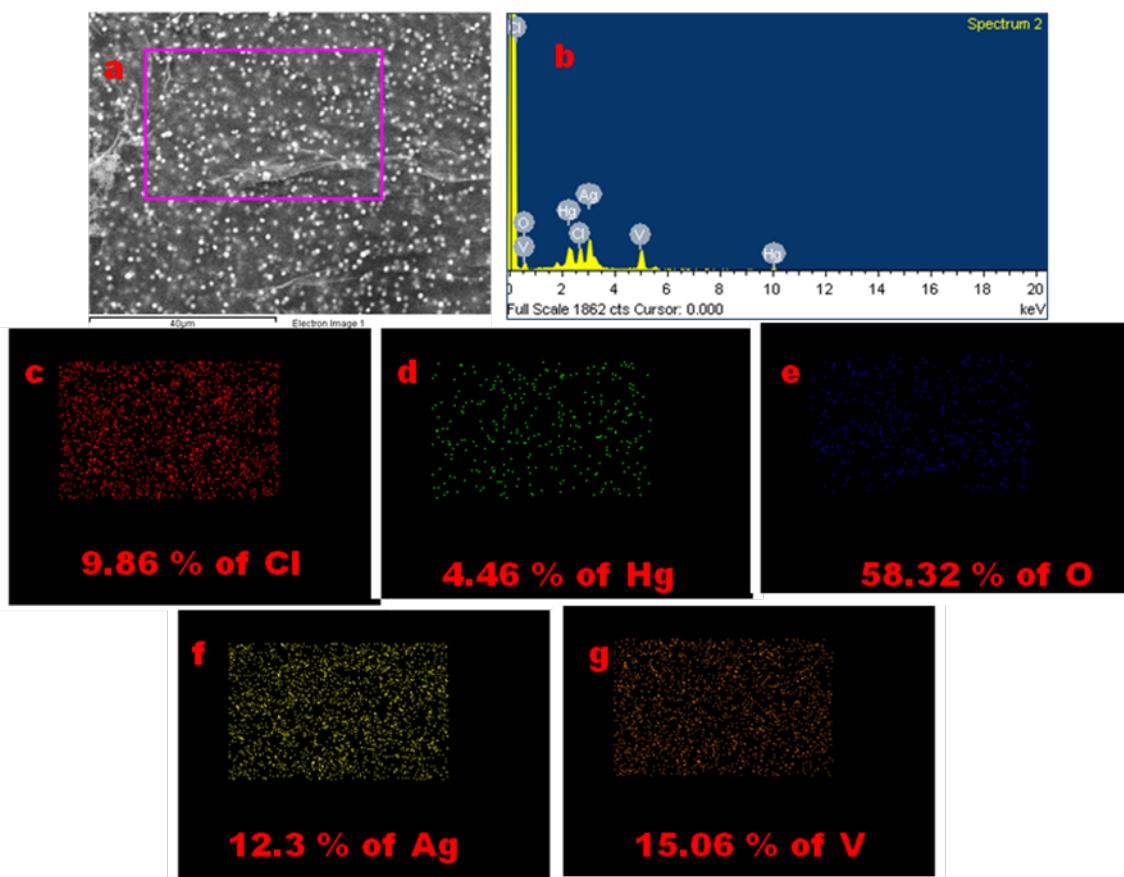


Fig. S11: Mapping of xerogel after keeping it in contact with HgCl_2 .

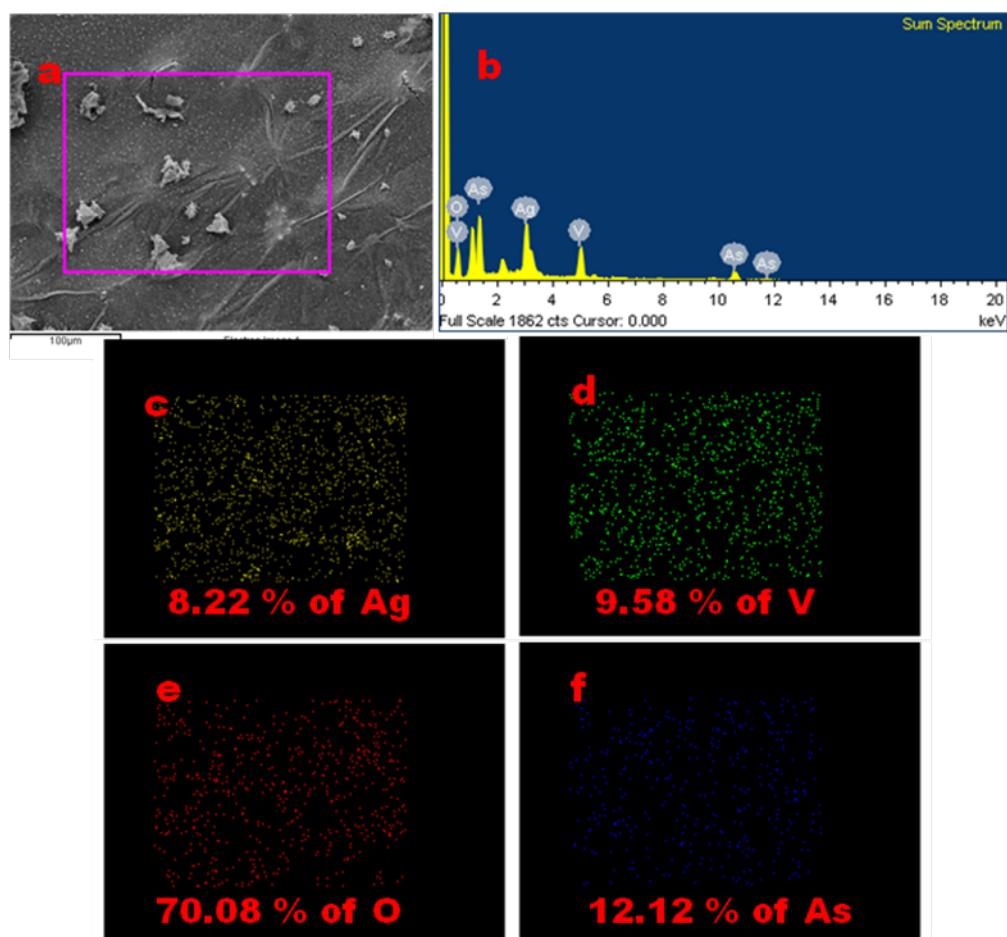


Fig. S12: Mapping of xerogel after keeping it in contact with Na_3AsO_4 .