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Supporting Information

Evolution of tubular copper sulfide nanostructures from copper(I)-metal organic precursor: A superior platform for the removal of Hg (II) and Pb (II) ions

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S1. EXPERIMENTAL SECTION

Materials

All the reagents were analytical grade purity and used in the synthetic protocol without further purification. Copper(II) chloride dehydrate (CuCl₂.2H₂O) was purchased from Merck, India. Thioacetamide (TAA) was purchased from Spectrochem, India. Lead nitrate and mercuric nitrate, xylenol orange, 1, 5 diphenyl carbazide were used in the experiment as received from Loba Chemie. India. Throughout the whole study, double distilled water and ethanol were used to prepare the solutions. Ethanol was purchased from Merck, India. All the used glass apparatus were cleaned with double distilled water and dried well before the use.

Instrumentations

Phase purity of the synthesized samples were characterized by recording XRD on a BRUKER-AXS-D8-ADVANCE defractometer with Cu K α radiation ($\lambda = 1.5418$ Å) in the 2 θ range of 10°-80° at a scanning rate of 0.5° min⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was done with a VG Scientific ESCALAB MK II spectrometer (UK) equipped with an Mg K α excitation source (1253.6 eV) and a five-channeltron detection system. The detailed morphology of the product were analyzed by Field Emission Scanning Electron Microscopy (FESEM) using a (Supra 40, Carl Zeiss Pvt. Ltd.) microscope at an accelerating voltage of 20 kV. Compositional analysis of the sample was completed with an energy dispersive X-ray micro analyzer (OXFORD ISI 300 EDAX) attached to the scanning electron microscope. Transmission electron microscopic (TEM) analyses of the samples were performed on a Hitachi H-9000 NAR transmission electron microscope, operating at 100 kV. The nitrogen gas adsorption and desorption study was performed using a Quantacrome autosorb iQ automated gas sorption analyzer. For adsorption study the sample was dried in vacuum for overnight and 20-25 mg amount was loaded in a 6 mm sample holder. In desorption study the sample was used for degassing at 70°C for 2 h and Brunauer–Emmett–Teller (BET) calculations were performed for the analysis of surface area of the sample. Fourier transform infrared spectroscopy (FTIR) spectral analysis was carried out with Nexus 870 Thermo-Nicolet instrument coupled with a Thermo-Nicolet Continuum FTIR Microscope. Conductance measurements were performed using Systronics conductometer. All the UV-vis absorption spectra were recorded on SPECTRASCAN UV 2600 digital spectrophotometer (Chemito, India).

UV-vis study for the calculation of $C_{\mbox{final}}$

To evaluate the value of C_{final} of metal ion solution in the equation of adsorption capacity, absorbance of some known concentration of metal ion solutions were taken using UV-visible spectrophotometer. In case of Hg(II) ion, 4 mL Hg(II) solution (six different solutions of known concentration) was mixed with 0.1 mL 10⁻³ M diphenyl carbazide and recorded absorbance was plotted against concentration (Figure S1a). For Pb(II) ion, similar procedure was followed by adding 0.5 mL 10⁻³ M Xylenol orange in 3 mL known concentration Pb(II) solution of five different known concentration and the absorbance value has been plotted against concentration of metal ions (Figure S1b). Now, C_{final} can easily be obtained from the below two plots as we know the absorbance value of the metal ion solution after adding respective complexing agents from UV-vis spectrophotometer.



Fig. S1 Plot of absorbance vs. concentration for (a) Hg(II) and (b) Pb(II) ion solution.



Fig. S2 Rietveld refinement of as-synthesized copper sulfide.

In this work	Cu ₂ S(JCPDS No. 01-072-1071)	CuS (JCPDS No. 79-2321)
2θ (°)	20 (°)	20 (°)
21.6869	-	21.71
23.5915	23.5979	-
27.3181	27.3229	-
27.752(07.71
27.7526	-	27.71
21 (20)	21 (274	
31.6296	31.03/4	-
21.7096		21.92
31./980	-	31.82
32 6323	32 6407	
52.0525	32.0407	-
35 4899	35 4990	
55.4077	33.4770	
38 9659	_	38.91
50.9059		50.71
39.0662	39.0446	_
39.8683	39.8654	_
44.3961	-	44.39
45.3830	45.3842	-
46.0682	46.0957	-
47.7727	-	47.79
47.0064		47.01
47.9064	-	47.91
10 27/1	10 2705	
40.2/41	40.2703	-
51 7667	51 7614	
51.7007	51./017	-
52 7026	_	52 76
52.7020		52.70
53.8055	53.7574	_
57.0642	57.0006	_

Table S1. Comparison of peak position of copper sulfide with Cu_2S and CuS



Fig. S3 XRD pattern of copper sulfide after 30 days storage.

To study the nature of bonding between Cu(I) and TAA in the metal organic complex and its conversion to copper sulfide were investigated by FTIR. The FTIR spectrum (Fig. S4a) of the product after 3 day of ageing shows stretching vibrations e.g. N-H, C=S and C-N are decreasing and increasing respectively with respect to pure TAA (Fig. S4b). Thus results of this analysis confirmed that the Cu(I) bonded with TAA through Cu-S bond by electron donation of lone pair electrons of sulfur to vacant d-orbital of Cu(I) and form the a metal organic complex. But the FTIR spectrum of product obtained after 14 days does not exhibit any signature of the stretching vibration of N-H and C-N bonds.



Fig. S4 (a) Comparative FTIR spectra of copper sulfide after 3 days, 14 days and

(b) FTIR spectrum of pure thioacetamide (TAA).

Growth mechanism of porous tubular copper sulfide from white metal organic complex was studied by various spectroscopic techniques. A large number of well faceted microrods with a strong XRD peak at 20~17.99 corroborates the formation of metal organic complex (See Fig. S5a-c, ESI⁺) which is also authenticated by elemental area mapping (See Fig. S6, ESI⁺). After 7 days small flower like particles consists of flakes are observed on the surface of the microrods (See Figure S5d-f). In a few days the microrods are found to be covered with micro porous flowers and become hollow whereas 14 days of ageing results in the complete conversion of microrods into microtubes with an envelope of porous microflowers (See Fig. S5g-I, ESI⁺). This happens due to the release of Cl⁻ ions from the interior of the metal organic complex which is also supported by conductance measurement results (See Table S2, ESI⁺). It is neither a kirkendall effect nor a galvanic replacement reaction but a self sacrificed template reaction may be called as auto degenerative hollowing (ADH). This decomposition is supported by SHAB theory. The soft-soft interaction between Cu(I) and S^{2-} predominates unlike the corresponding unusually stable bromide complex. It is worth mentioning that the as-synthesized chlorocomplex is not oxidized under ambient condition²⁸ instead decomposed to evolve porous copper sulfide as mentioned above. On the other hand competitive binding i.e., balanced share of electron density of copper by Br and S²⁻ offer exceptional stability to the bromide complex. It is interesting to note that the XRD peak corresponds to metal organic complex goes gradual decrease with subsequent conversion to mixed valence copper sulfide as indicated in Fig. S5c, f, i (ESI[†]). Area mapping analysis confirmed that the synthesized flowers are consisting of only Cu and S without any other element (See Fig. S7, ESI[†]).



Fig. S5 FESEM images and XRD patterns of the synthesized products after (a-c) 1 day, (d-f) 7

days, (g-i) 14 days.



Fig. S6 Elemental area mapping of as-synthesized product after 1 day (metal organic complex).

Substrates	Conductance (mS)
Aqueous CuCl ₂ solution	6.9
Aqueous TAA solution	0
After instant mixing	5.8
	(The conductance value of $CuCl_2$ decreased
	due to metal organic complex formation)
Completion of metal organic complex	5.9
After 14 days	7.7
(Mixed valence copper sulfide)	(The increase in conductance value is due to
	the decomposition process of Cu-Cl-Cu
	bridging bond during the evolution of tubular
	structure.)

Table S2. Conductance Measurement.



Element	Weight%	Atomic%
S K	37.73	54.56
Cu K	62.27	45.44
Totals	100.00	

Fig. S7 Elemental area mapping of as-synthesized product after 14 days.

The importance of Cl⁻ in the synthesis of tubular, porous copper sulfide was studied by varying anion part of precursor Cu(II) salt. In case of CuSO₄ and Cu(ClO₄)₂, initial formation of metal organic complex was not recognized, rather it resulted in CuS even at room temperature. But in case of CuBr₂, an exceptionally stable metal organic complex was formed where the subsequent copper sulfide transformation at room temperature is not observed. To elaborate the importance of Cl⁻ ion, we introduced NaCl as an external Cl⁻ ion source to the reaction mixture containing Cu(ClO₄)₂ and TAA. In that case we observed the formation of morphologically similar copper sulfide after two weeks again via metal organic complex formation. This observation helped us to conclude that both Cl⁻ and Br ion are very important for the formation of rod like metal organic complex because of their bridging capability. However, the stability of the metal organic

complex containing Br⁻ ion deters the evolution of copper sulfide due to similar interaction between Cu(I)-Br as Cu(I)-S according to SHAB theory whereas the porous hierarchical morphology was evolved in case of Cl⁻ due to the stronger Cu(I)-sulfur interaction compared to Cu(I)-Cl. Under such affinity driven condition C=S bonds of the metal organic complex ruptured as a results of which the interior of the metal organic complex rods became hollow.



Fig. S8 FESEM images of copper sulfide using different precursor salts (after 14 days).

To investigate the effect of the concentration variation of metal salt on morphology, we found the formation of initial metal organic framework and followed by their conversion to hierarchical tubular morphology (after 14 day) is feasible up to ligand-metal ratio 1:0.6 whereas brownishyellow product with irregular shape is identified with lower ligand-metal ratio. This observation clearly signifies about the optimized ligand to metal ratio of 1:0.6 for the desired morphology of copper sulfide.



Fig. S9 FESEM images after 1 day with TAA:Cu(II) at (a) 1:1, (c) 1:0.6, (e) 1:0.4 mol ratio and

(b, d, f) corresponding FESEM images after 14 days.

The for the investigation of adsorption mechanism of Hg(II) and Pb(II) on copper sulide the pseudo first order (Fig. S9a, c) and Freundlich isotherm (Fig. S10b, d) were also studied.



Fig. S10 Pseudo first order (a, c) and Freundlich isotherm (b, d) for Hg(II) and Pb(II) ion adsorption by copper sulfide respectively.

The other parameters were represented in Table S3. Here, R² values of pseudo first order and Freundlich isotherm shows a disagreement of experimental values with the above two model.

Material	K ₁	q _{e,cal}	R ²	K _F	n	R ²
	(min ⁻¹)	(mg/g)		[(mg ¹⁻ⁿ L ⁿ		
)/g]		
Pb(II)	0.0429	887	0.9001	6.79009	3.91	0.7891
Hg(II)	0.0475	7943	0.9421	6.73061	3.87	0.6997

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Pseudo-first-order

Freundlich Isotherm



Fig. S11 XRD pattern and elemental area mapping of Pb(II) adsorbed copper sulfide.



Fig. S12 Adsorption rate of Hg(II) and Pb(II) by copper(II) sufide.