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Title: Alanine based coordinating ligands mediated hydrothermal synthesis of CuS nano/microstructures and morphology dependent photocatalysis

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Dear Editor,

Along with this covering note we are submitting the revised manuscript. We are thankful to the referee for giving critical comments. In this regard, we have repeated the experiments as suggested by the referee. Below we provide the specific comments of the referee (in italics) and our response.

Further to the suggested revisions, we have made some additional changes in the manuscript to improve the presentation quality. We hope that the revised manuscript will get positive consideration for publishing in *CrystEngComm*.

Sincerely yours

S. Philip Anthony

Referee

Most of the questions given in my earlier report is not answered properly. It seems authors not focusing the particular questions rather they want to answer something to make reviewer happy! For examples, we asked to provide better FE-SEM images but not supplied. Author should put better quality low magnified FE-SEM image to understand the overall morphology of the sample.

We strongly apologize to the reviewer. As suggested by the reviewer, we have performed FE-SEM for all samples. The images are given below. Unfortunately, we could not get better quality images than the previously given in the manuscript and hence we did not include in the revised manuscript. The images were recorded after sonicating the samples. We sonicated the samples in an effort to de-aggregate nanoparticles for better visualization of morphology.



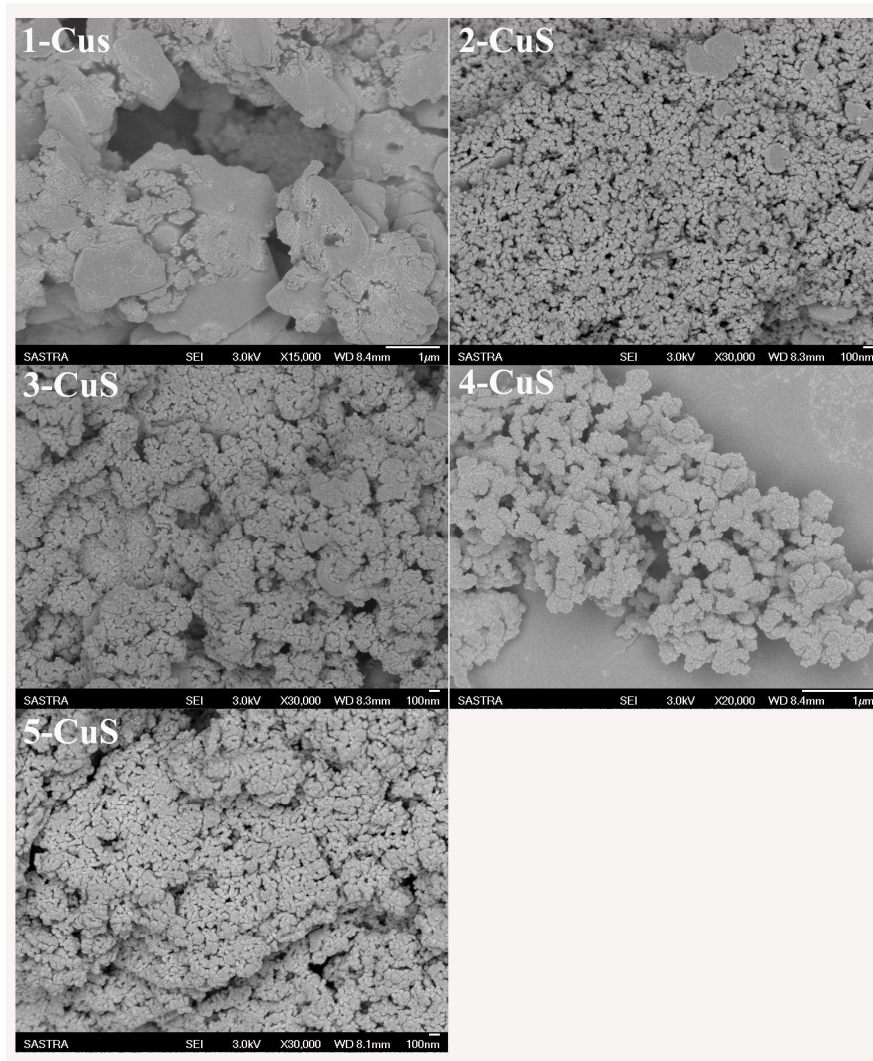
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The FT-IR analysis not at all satisfactory. It is not clearly explained why they have done this analysis? Need to compare with only alanine and alanine coordinated CuS. Moreover, the proper mode of vibration should be included.

As suggested by the reviewer, we have performed FT-IR studies for the ligands as well as 1-5-CuS nanoparticles to confirm the organic ligand surface functionality on the nanoparticles surface. New figure for IR along (both pure ligands as well as with CuS) has been added in the revised manuscript (Fig. 5). The comparison of IR spectra of ligands and ligands with CuS clearly suggest the presence of organic functionality in the nanoparticles. The sentences for IR studies have also been modified in the revised manuscript at page no. 3, line 72-85.



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From PXRD it is not possible to confirm about the formation of CuS nano/microstructures. How author confirm that there is no formation of CuO? There is strong chance for the formation of mixed materials like CuS and CuO. It will be better if author take more initiation to do the XPS experiment from other institutions nearby. Without XPS, it is meaningless to confirm the formation of CuS.

Further as suggested by the reviewer, we have also performed XPS analysis for CuS prepared using ligand 2 and that clearly confirmed the formation of CuS nanoparticles. New XPS spectrum has been included in the supporting information (Fig. S6) and the corresponding discussion have been included in the revised manuscript at page no. 3, line 54-64.

Few new references related to photocatalytic degradation of dyes should be included. Crystal Engineering Communications, 2013, 15, 482. Nanoscale, 2014,6, 8117-8123; Journal of Nanoparticles Research, 2012, 14, 1040. Langmuir, 2012, 28 (35), pp 12893–12900; Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014, 446, 199. Dyes & Pigments, 2006, 69, 177.

The suggested references have been added in the revised manuscript. Reference number 1f, 2c-e and 12 (c,d).

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ARTICLE TYPE

Alanine based coordinating ligands mediated hydrothermal synthesis of CuS nano/microstructures and morphology dependent photocatalysis

V. Vinod Kumar, P. S. Hariharan, D. Eniyavan, Natarajan Hari and Savarimuthu Philip Anthony*

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CuS nano/microstructures with different morphologies, solid microspheres with blocks (1-CuS), nanospheres (2-CuS) and microspheres of nanoflakes (3-CuS), were synthesized using alanine based coordinating ligands (1-3) as structure controlling agents in hydrothermal synthesis. Interestingly, copper coordination polymers (4 and 5) that are prepared using same ligand (2) but differed subtly in the coordination and water molecule presence, produced distinctly different nano/microstructures. Hydrogen bonded network polymer, 4, gave CuS microspheres composed of nanocrystals (4-CuS) whereas coordination network polymer without water molecule, 5, yielded nanocrystalline powdered materials (5-CuS). Importantly the synthesised CuS nano/microcrystals exhibited dye degradation (methylene blue (MB), methyl orange (MO) and Rhodamine blue (RB)) at room temperature without using any specific light source. The CuS nano/microcrystals also showed morphology dependent dye degradation properties. Highest dye degradation was observed for nanosphered 2-CuS whereas 1-CuS and 4-CuS exhibited comparatively slow dye degradation. Thus the present work demonstrate the utility of simple coordinating ligands and subtle change in the coordination network for tuning CuS morphologies which showed morphology dependent dye degradation.

1. Introduction

The synthesis of inorganic nanomaterials with controlled size, morphology, crystallinity and anisotropic growth have attracted strong attention owing to their potential applications in various field.¹ The organic molecules such as surfactants/ligands that have been used for preventing aggregation of nanoparticles were extensively investigated for controlling the size, morphology and anisotropic growth of nanoparticles.² It is believed that the anisotropic growth of noble metal nanoparticles such as silver and gold were induced through site specific binding of ligands to some of the crystal facets of nanoparticles.³ The ligands can also form complexes with metal ions and change the nature of precursor metal complexes that subsequently affects the pH of the reaction medium, reaction kinetics and could influence on the resulting size and morphology of nanocrystals. Sodium dodecylbenzenesulfonate surfactant was used to prepare CuO nanoribbons in hydrothermal method.⁴ Qing *et al.* reported the synthesis of tunable morphologies of Cu₂O nanocrystals using different surfactants for structure dependent electrocatalytic studies.⁵ Citrate ions have been used extensively to alter the morphologies of ZnO nanostructures.⁶ ZnO nanocrystals with star and rose morphologies were obtained in presence of citric acid and citrate ions.⁷ Hui *et al.* utilized tartrate ions to obtain Cu₂O microcrystals with different morphologies.⁸ Monolithic CuO nanocrystals were synthesised from Cu(II)-1,10-phenanthroline complex.⁹ Recently, we have reported the synthesis of tunable

morphologies of Cu₂O nano/microcrystals using coordinating amino acid based reduced Schiff base phenolic chelating ligands and antimicrobial effects.¹⁰

Metal sulphide nanomaterials such as PbS, ZnS, CdS, CuS, Ag₂S, MoS₂ and Bi₂S₃ have attracted significant attention in the filed of materials science because of their unique properties and potential technological applications.¹¹ Particularly, copper sulfide (CuS) nanocrystals, a p-type semiconductor, have been found as one of the potential materials for application in catalysis¹² biosensor,¹³ tissue imaging,¹⁴ drug delivery¹⁵ and Li-ion battery.¹⁶ The shape, size, stoichiometric composition and crystal structure of CuS nanocrystals usually control the optical and electrical properties.¹⁷ Hence CuS nanostructures with spherical, nanotubes, nanowires, nanoplates, ball-flower, hollow cage and hollow sphere morphologies have been synthesised using different approaches.¹⁸ Surfactants or solvent ratio played important role in controlling the morphologies. For example, alkyl amine plays an important role in the synthesis of CuS with spheres, nanowire and nanotube morphologies.¹⁹ Joyjit *et al.* tuned the morphologies of CuS nanostructures by controlling organic and aqueous solvent ratio and studied the photocatalytic effects.²⁰ The organic coordination building blocks have been extensively employed as templates for the fabrication of ZnO with different structures.²¹ However, small organic coordination ligands that produced intriguing solid state structures have never been explored to control the nano/microstructure of CuS.

We have chosen alanine based reduced Schiff base ligands (Scheme 1) to investigate structure controlling agent for CuS

nano/microstructure preparation in view of its coordination versatility, simple synthesis and ability to exhibit topochemical transformation (single crystal to single crystal conversions).²² The topochemical conversion allows to explore the effect of precursors that differ in the ligand coordination mode and stability on the nanostructure formation. In this manuscript, we report the hydrothermal synthesis of CuS nano/microstructures with different morphologies using alanine amino based reduced Schiff base ligands (1-3, Scheme 1) as structure directing agents. Solid microspheres along with smaller sized nanoparticles and plates (1-CuS) were obtained using 1. 2 and 3 produced spherical nanocrystalline CuS (2-CuS) and microspheres made of nanoflakes (3-CuS), respectively. Interestingly, coordination polymers of 4 and 5 that was prepared using ligand 2 and differed subtly in the coordination produced completely distinct morphologies. Solid microcrystalline spheres of CuS composed of smaller nanocrystallites (4-CuS) were obtained from 4 and formation of powdered nanoparticles of CuS (5-CuS) were observed with 5. The surface functionality and crystalline structure of CuS nano/microstructures were confirmed using FT-IR and powder X-ray diffraction studies. Importantly, the as-prepared CuS nano/microcrystallites exhibited morphology dependent photocatalytic dye degradation property without using any specific light source.

2. Experimental Section

Alanine, salicylaldehyde, NaBH₄ and Cu(CH₃COO)₂·H₂O were obtained from Sigma-Aldrich and used as-received. Thiourea, ethanol and NaOH were obtained from Ranboxy India. Copper coordination polymers (4 and 5) from ligand 3 were prepared by following the reported procedure.²² All experiment was performed using Mill-Q water.

2.1 Synthesis of reduced Schiff base ligands 2 and 3

The reduced Schiff base ligands were synthesized by following the reported synthetic procedure.²³ Alanine (0.445 g, 5 mmol) was dissolved in 20 ml hot water using 1:1 equivalent of NaOH and ethanol solution of salicylaldehyde/2-hydroxynaphthaldehyde (1 equivalent, 10 ml) was added drop-wise at room temperature under vigorous stirring. The solution turned bright yellow for salicylaldehyde and dark red for 2-hydroxynaphthaldehyde. The solution was allowed to stir at room temperature for another 20 minutes. Then the reaction mixture was cooled in ice-bath and NaBH₄ (1.5 equivalent) was added portion-wise. The bright yellow colour was slowly disappeared (salicylaldehyde) and dark red was changed to light colour for 2-hydroxynaphthaldehyde. After stirring for another 30 minutes, the reaction mixture was neutralized using dil HCl which produced white precipitates. The formed precipitate was filtered, washed and dried under vacuum. Yield = 80-85 %. **2.** ¹H NMR (d₆-DMSO) δ 7.16-7.27 (m, 2H (aromatic)), 6.77-6.87 (m, 2H (aromatic)), 3.92-4.03 (q, 2H (CH₂)), 3.19-3.26 (q, 1H (CH)), 1.31 (s, 3H (CH₃)). ¹³C NMR (d₆-DMSO) δ 170.97, 156.39, 130.63, 129.69, 119.98, 118.81, 115.57, 56.12, 45.42, 15.79. C₁₀H₁₃NO₃ (195.22): calcd. C 61.53, H 6.71, N 7.18; found C 61.37, H 6.51, N 7.37. **3.** ¹H NMR (d₆-DMSO) δ 7.65-7.84 (m, 2H (aromatic)), 7.40-7.48 (m, 1H (aromatic)) 7.22-7.27 (m, 1H (aromatic)), 7.04 - 7.12 (m, 2H

(aromatic)), 4.23 (s, 2H (CH₂)), 3.17-3.22 (b, 1H, (CH)), 1.25 (s, 3H (CH₃)). C₁₄H₁₅NO₃ (245.20): calcd. C 68.56, H 6.16, N 5.71; found C 68.48, H 6.31, N 5.62.

2.2. General method of 1- to 3-CuS nanomaterials synthesis

Cu(CH₃COO)₂ (0.1 M) was added into 0.1 M aqueous solution of ligand (1-3, 25 ml) and stirred at room temperature for five minutes. It is noted that ligand 2-3 was dissolved in water using 1:1 equivalent of NaOH. Then two equivalent of thiourea was added and stirred at room temperature for another ten minutes. The reaction mixture was transferred to a hydrothermal Teflon-vial and heated in hot-air oven at 180 °C for 6 h. The reaction mixture was cooled to room temperature. The black precipitates of CuS (1-, 2-, 3-CuS) were filtered, washed with water and dried in vacuum. The dried samples were used for characterization and photocatalytic studies.

2.3. General method of 4- and 5-CuS nanomaterials synthesis

Copper coordination polymer (4 and 5) and thiourea in 1:2 ratio were taken in the hydrothermal Teflon vial and 25 ml of water was added. The mixture was gently stirred for 5 min and heated in oven at 180 °C for 6 h. The solution was cooled to room temperature and black precipitates (4-CuS and 5-CuS) formed were filtered, washed with water and dried. The dried 4-CuS and 5-CuS samples were used for characterization and dye degradation studies.

2.4. Characterization

The particle size and morphology of the products were studied by field emission scanning electron microscopy (FE-SEM) (Q400 SEM). The phase and the crystallographic structure were identified by X-ray diffraction (XRD, Bruker, Cu-Kα: λ= 0.1540598 nm) at a scanning rate of 0.07° s⁻¹ with 2θ ranging from 20° to 80°. FT-IR spectra were recorded for studying the functional groups using KBr disks on a Shimadzu affinity spectrophotometer.

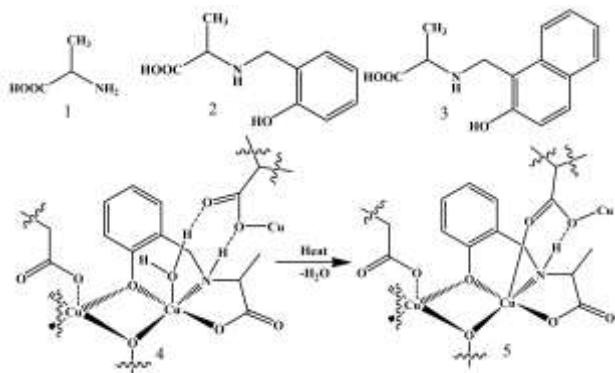
2.5 Photocatalytic studies

To 20 ml (10⁻⁴ M) of dye solution (Rhodamine Blue (RB), Methylene Blue (MB) and Methyl Orange (MO)), 5 mg of photocatalyst CuS nanomaterials synthesised using different structure directing ligands was added. The aqueous suspension was stirred at room temperature in the hood without any light under ambient conditions. At different time intervals a aliquot was taken out into 3ml eppendorf tube and centrifuged (5000rpm/5min) to remove the suspended CuS particles. The supernatant was collected and absorption spectra were recorded. The change of optical absorption (λ_{max}) intensity of dyes was taken as a measure of dyes degradation.

3. Results and Discussion

The structure of coordinating ligands (1-3) and copper coordination polymers (4 and 5) that are used for the synthesis of CuS nano/microcrystals is shown in scheme 1. The synthesis of ligands are shown in scheme S3. Ligand 1 could exhibit bidentate mode of interacting with Cu²⁺ whereas 2 and 3 can act as tridentate ligands (Scheme S4). Single crystal analysis of copper coordination polymer of 2 showed square pyramidal geometry with ligand occupying the square planar positions and a water molecule coordinated at the apical position.²² Hence copper with other ligands also expected to adopt similar coordination

geometry. Hydrothermal treatment of ligands, thiourea and $\text{Cu}(\text{CH}_3\text{COO})_2$ in water produced black precipitate. The morphology of as-synthesised CuS nanostructured materials was explored using FE-SEM. CuS obtained using alanine, 1 (1-CuS) showed the formation of different morphologies, solid spheres, plates and smaller nanoparticles, together (Fig. 1a, b). The size of the solid spheres and smaller nanoparticles are approximately 1 μm and less than 100 nm, respectively. However, 2 that has phenolic hydroxyl functionality with alanine produced completely different morphologies of CuS nanostructures (Fig. 1c,d). Unlike with 1, SEM studies showed the formation of spherical CuS nanoparticles in the size range of 50-100 nm. It is noted that solid spheres as well as rod morphologies could not be observed with 2-CuS. Interestingly use of 3 that consist of alanine with naphthyl phenolic hydroxyl functionality as structure directing ligand resulted in the formation of nearly uniform microspheres of CuS with size range of 1 μm (Fig. 2a,b). Compared to the CuS microspheres obtained using 1, 3-CuS microspheres did not have very smooth surface. 3-CuS microspheres have rough surface with many smaller crystalline nano-flakes with size range of 100 nm were grown on the surface. The higher magnification of 3-CuS microspheres suggest that the CuS spheres are completely composed of nano-flakes. The size of the CuS microspheres is in the range of 1 μm .



Scheme 1. Molecular structures of coordination ligands 1 – 3 and copper coordination polymers 4 and 5.

The modulation of CuS morphologies by use of structure directing ligands, 1-3 in the hydrothermal reaction prompted us to prepare copper coordination polymers of 2 and use as precursors for CuS formation. The ligand 2 (N-(2-hydroxybenzyl)-l-alanine) is known to form helical coordination polymeric structure with Cu^{2+} and Zn^{2+} ions.²² The exciting phenomena of topochemical conversion (single crystal to single crystal) have been demonstrated using these two metal coordination network structures. 2 with Cu^{2+} exhibited helical coil coordination polymer structure formation with water molecule coordinated in the apical position of copper metal ion (4). Heating of 5 loses the water molecule and converts helical coil structure to anhydrous 3-D chiral framework (5). Hydrothermal reaction of 5 with thiourea in water produced microspheres of CuS with nearly uniform size (Fig. 2c,d). However, the microspheres are completely different from one obtained from structure directing ligands 2 and 3. 4-CuS microspheres were made of many smaller spherical nanocrystals of CuS. The size of CuS spheres is in the range of 700 nm to 1 μm and the smaller crystallites in the sphere are in

the range of 100 to 150 nm. Interestingly, hydrothermal reaction of anhydrous coordination polymer, 5-CuS did not show any microspheres rather it showed the formation of powdered CuS without any specific morphology (Fig. 2e,f). Hence same coordination polymer with different coordination network structure yielded completely different morphologies of CuS. The energy dispersive X-ray analysis (EDX) of 2-CuS confirmed the presence of both Cu and S (Fig. 3, S5). Compound 2-CuS was chosen as a representative example of CuS samples. Further the purity of 2-CuS was confirmed by XPS analysis (Fig. S6). The full XPS spectrum of 2-CuS suggests the presence of Cu, S, as well as C, N and O peaks. The observation of C, N and O peaks further support the organic ligand surface functionalization of CuS nanoparticles. Cu2p peaks, Cu2p3/2 and Cu2p1/2 appeared at 932.5 and 952.5 eV, respectively. This is perfectly matches with the binding energies of Cu2p orbital of Cu(II).²⁴ Whereas two peaks observed in the S2p region at 162.3 and 162.5 eV indicates the S presence in CuS.²⁵

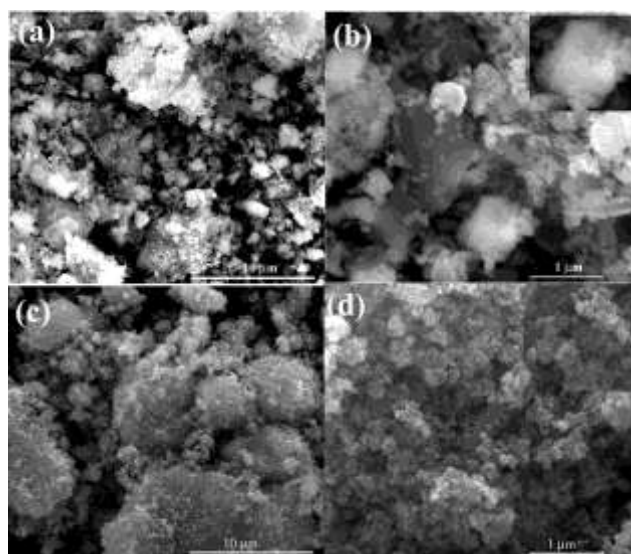


Fig. 1. SEM images of (a, b) 1-CuS and (c, d) 2-CuS.

The crystal structure of as-synthesized CuS nano/microcrystals was investigated by powder X-ray diffractogram (PXRD). Figure 4 shows the XRD pattern of the CuS nano/microstructures of CuS prepared using different coordinating ligand and coordination polymers. The XRD pattern shows diffraction peaks corresponding to 101, 102, 103, 006, 008, 110, 108 and 116 plane that matched a pure hexagonal CuS structure (JCPDS card no. 006-0464). FT-IR studies were performed to analyse the organic surface functionality of ligands on the CuS surface. FT-IR spectra of pure organic ligand as well as 1- to 5-CuS is shown in Fig. 5. All ligands showed characteristic symmetric and asymmetric stretching of carbonyl group and N-H stretching. The strong intense C=O asymmetric stretching appeared between 1550 to 1650 cm^{-1} . 1 to 5-CuS also exhibited similar IR spectra of the corresponding ligand that suggest the presence of organic ligands on the surface of CuS (Fig. 5). The N-H stretching appeared between 3200 – 3350 cm^{-1} moved upwards slightly upwards to 35500 – 3550 cm^{-1} with CuS nanoparticles. It is noted that small change of peak position could be due to the interaction of the ligands with CuS surface.

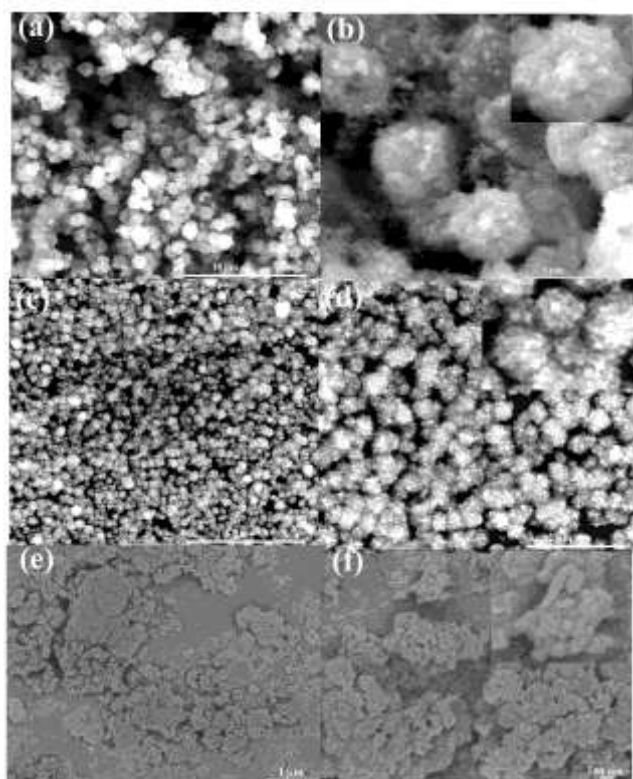


Fig. 2. SEM images of (a, b) 3-CuS, (c, d) 4-CuS and (e, f) 5-CuS.

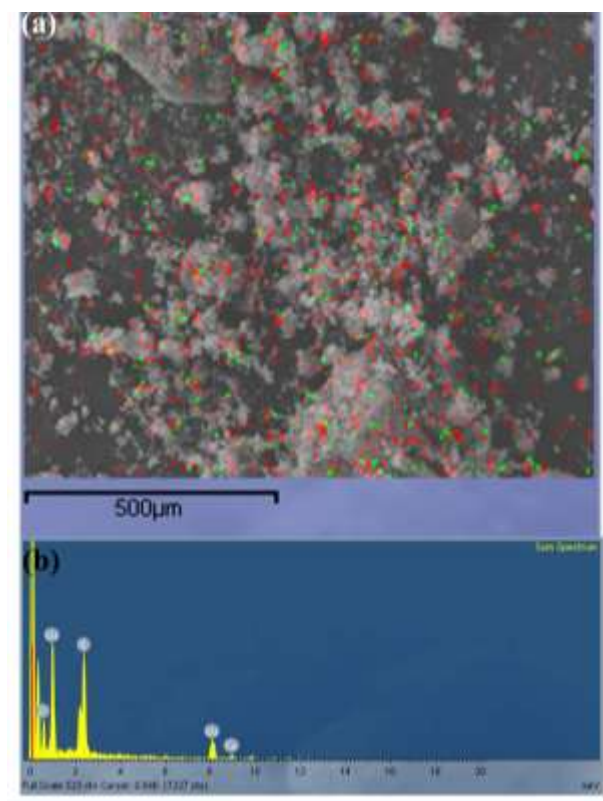


Fig. 3. (a) SEM EDX images and (b) EDX spectrum of 2-CuS.

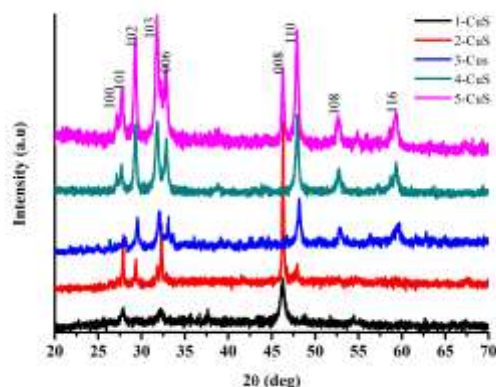


Fig. 4. PXRD pattern of different CuS nano/microstructure samples.

The modification of CuS nano/microstructures using different coordinating ligand and coordination polymers might be due to the difference in the reaction kinetics upon interaction or formation of metal-ligand complex. The ligand interactions with metal precursors or formation of metal-ligand complexation are known to alter the reaction kinetics and the resulting size and morphology of nanostructures.²⁶ The change of ligand structure (1-3) could have influence on the metal-ligand interactions (Scheme S4). The simple alanine ligand, 1, without phenolic hydroxyl might have only weak interaction with copper metal ions. The uncontrolled reaction of sulphur from thiourea under hydrothermal condition produces different morphologies of CuS. However, introducing hydroxyl group in the phenyl ring (2) lead to the formation of nearly uniform nanospheres. The phenolic hydroxyl group is known to form strong coordination with metal ions.²⁷ Increasing hydrophobicity by introducing extra phenyl ring in the ligand (3) leads to the formation of uniform microspheres made of nanoflakes. Thus increasing the coordination character of the ligand produced more uniform sized CuS nano/microstructures. This could be due to the regulated reaction of metal ions from the metal-ligand complex. The weak interaction of ligand with metal ions might not be able to regulate the reaction kinetics and produce different shaped nano/microstructures. The different morphologies of CuS nano/microstructures obtained from copper coordination polymers of ligand 2 further support the hypothesis. Hydrothermal reaction of 5 gave completely CuS microspheres of small crystallites. Thus, using already prepared coordination polymer (4) produced microspheres with small crystallites whereas separate addition of Cu^{2+} and 2 and hydrothermal

treatment produced spherical nanopowder. The coordination process is completed in 4 but might not completed in the separate addition of 2 into Cu^{2+} solution. This coordination kinetics differences might have lead to different morphologies of CuS. However, hydrothermal treatment of dehydrated coordination polymer, 5 gave powdered CuS nanoparticles. The crystal structure of 4 has labile water molecule that coordinated at the apical position of copper metal ions. Thermal studies showed the loss of water molecules in the temperature range of 70 -90 °C.^{22b} The structure was converted to anhydrous stable form of 5 which did not show any change of mass of up to 240 °C. The labile water molecules in 4 might have offered regulated reactivity with thiourea and produced nearly uniform spherical morphology.

Whereas 5 is highly stable and hence thiourea reaction might lead to complete break-up coordination network in uncontrolled way.

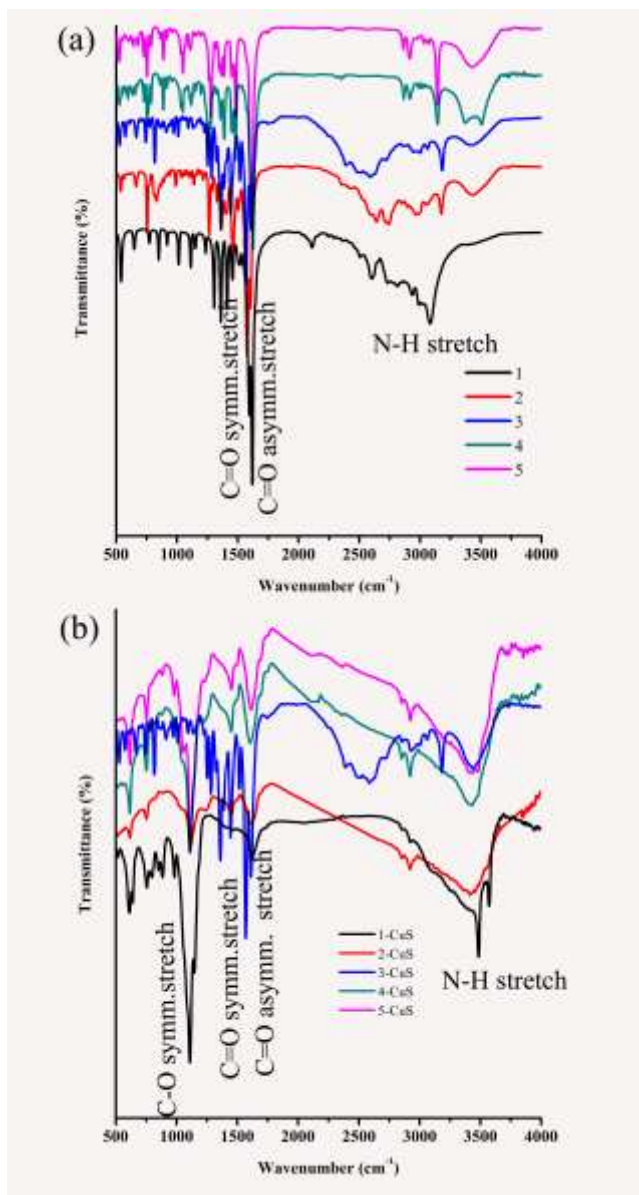
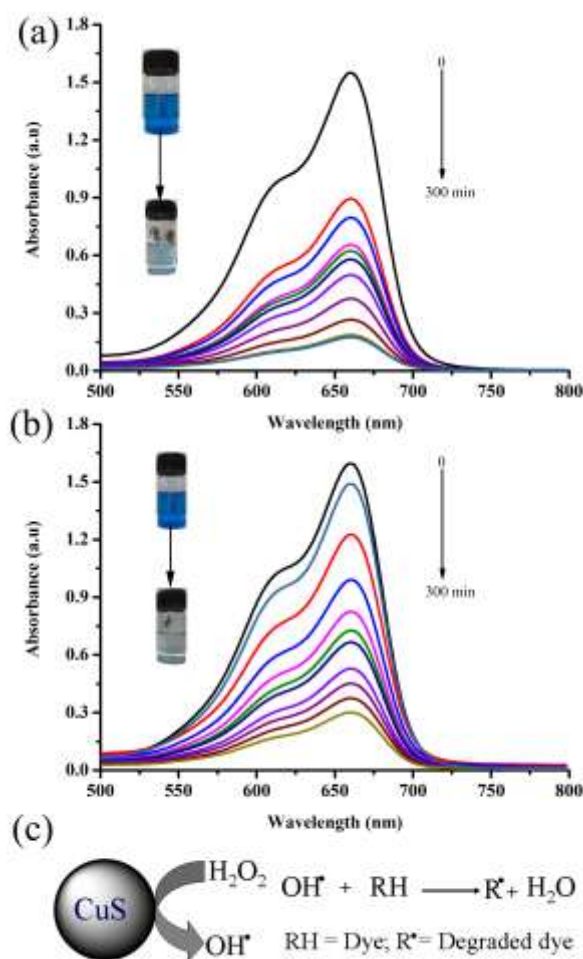


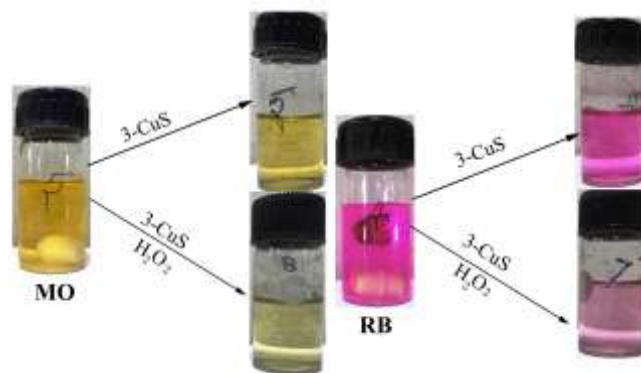
Fig. 5. FT-IR spectra of (a) organic ligands and (b) CuS with organic ligands.

5 The photocatalytic activity of the synthesized CuS nano/microstructures was explored for MB, MO and RB dye degradation with and without H₂O₂ in the absence of any specialised light source. Previously, it has been reported that CuS can act as a photocatalyst in the presence of H₂O₂ under light irradiation.²⁸ However, our studies of photocatalytic dye degradation with CuS nanostructure suggest that both light as well as H₂O₂ is not required to degrade the dyes. It is noted that CuS nanostructures showed slightly less efficiency of photo-degradation dyes in absence of H₂O₂ compared to the H₂O₂ presence. Absorption studies were used to monitor the dye degradation. For the photocatalysis study, 20 mL of 1 × 10⁻⁴ (M) MB or MO or RB dye solution was taken in a beaker and 5 mg of synthesized CuS nano/microcrystalline powder was added to it.



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Fig. 6. MB dye degradation studies using 2-CuS nanoparticles (a) without and (b) with H₂O₂. (c) Mechanism of dye degradation using CuS and H₂O₂. Digital images of colour change is shown the inset.



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Fig. 7. Digital images of MO and RB dye degradation using 2-CuS with and without H₂O₂.

The resulting solution was stirred at room temperature with and without H₂O₂ in the absence of any specialized light source. The solution was centrifuged to separate the CuS

nano/microstructures from the dye for the measurement of absorption spectra. The UV-Vis absorption spectra of MB

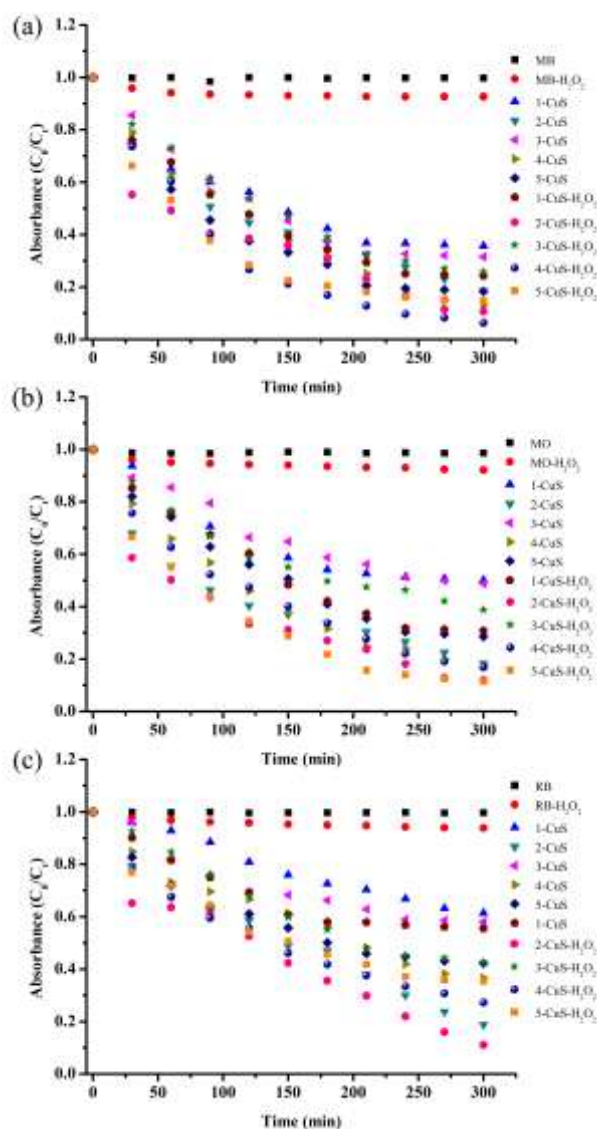


Fig. 8. Photodegradation studies of (a) MB, (b) MO and (c) RB with CuS nano/microstructures with and without H_2O_2 .

solution stirred with 3-CuS is shown figure 6. In absence of H_2O_2 , MB absorption at 660 nm exhibited gradual decrease of absorption over 5 h. After 5 h, MB dye was degraded nearly 82 % using some of the CuS samples (Fig. 6a). In presence of H_2O_2 , the MB dye solution showed a drastic decrease of absorption immediately and steady decrease of absorption afterwards (Fig. 6b). After 5 h, 3-CuS sample exhibited nearly 90 % of MB dye degradation. Similarly MO and RB dyes were also degraded nearly 80 – 90 % using CuS samples (Fig. 7, S7-8). As can be seen from the absorption spectra (Fig. 6, S7 and S8), absorption of MB, MO and RB dyes gradually decreases without showing any additive peak or shift (blue or red) in the peak position. This clearly indicates that dyes undergo photodegradation with CuS nano/microstructures in presence as well as absence of H_2O_2 .²⁹ CuS nano/microstructures produces hydroxyl radicals from H_2O_2

that reacts with organic dyes and degrade (Scheme 2, S9). In presence of H_2O_2 , hydroxyl radical are directly formed from hydrogen peroxide.³⁰ In the absence of peroxide, the absorption of visible light by CuS produces excited electron that reacts with hydrogen ions of water and produces hydroxyl radicals.³¹ This could be the reason for CuS in presence of H_2O_2 to exhibit drastic degradation of dye immediately.

Interestingly, the CuS nano/microstructures exhibited morphologies dependent dye degradation. 1-CuS and 3-CuS samples showed comparatively slow photodegradation of dyes with other samples (Fig. 8). The spherical nanoparticles of 2-CuS exhibited strong dye degradation compared to all samples both with as well as without H_2O_2 condition. 5-CuS that formed as powders and microspheres of nanocrystallites (4-CuS) also showed stronger dye degradation compared to 1-CuS and 3-CuS. This could be due to the enhanced surface area of CuS. However, the reason for the weaker dye degradation by CuS microspheres of nano-flakes is not clear. Thus the present study indicates that CuS nanomaterials could be used for photodegrading organic dye molecules without the use of any specialized light source as well as hydrogen peroxide. Further, the rate and extent of dye degradation could be optimized by tuning the morphologies.

4. Conclusion

CuS nano/microstructured materials with different morphologies were prepared using alanine and alanine based reduced Schiff base coordinating ligand (1-3) and subtle structural change in the MOF (MOF-4 and 5) by hydrothermal method. Solid spheres with smaller particles, only solid spheres, smaller spherical nanoparticles and spheres made of thin plates were obtained using 1-3 structure as directing ligand. Interestingly hydrothermal reaction MOF-4 and MOF-5, both are differ only by small coordination and water molecule, produced distinctly different nano/microstructures. MOF-4 produced spheres composed of smaller nanocrystals on the surface whereas MOF-5 produced nanocrystalline powdered materials. Photocatalytic dye degradation studies were performed at room temperature under ambient condition that revealed morphology dependent properties. Highly powdered smaller particles showed higher degradation effects than with the solid spheres. Thus simple coordinating ligands were demonstrated as potential structure directing unit in the synthesis of different morphologies of CuS nanomaterials for structure dependent photocatalytic studies.

Acknowledgments

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: 1H-NMR spectra, synthesis and coordination mode of ligand, and dye degradation scheme. See DOI: 10.1039/b000000x/

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