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ORIGINAL ARTICLE **OPEN ACCESS**

CuS/Graphene Composite for Water Purification through Advanced Oxidation Process

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ABSTRACT
In the present case A has been adopted for synthesis CuS and its graphene composite has been synthesized through low temperature mediated simple wet chemical technique. Various characterizations has been carried out which indicte phase purity as well as monodispersity of sample with particle type morphology. Also graphene composite of the product has been explored for environmental remediation in terms of removal of harmful industrial dye, through advanced oxidation process. Results indicate that the material is an efficient adsorbant as well as a photocatalyst with 75% degradation efficiency the for methyl orange (MO) dye in the presence of sun-light for an exposure time of about 2.5 hours in comparison to pure material (CuS).
Keywords*; Nanoparticle, semiconductor, graphene, copper sulphide, photocatalytic properties.*

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INTRODUCTION

Semiconducting materials have been receiving considerable attention for wide range of applications in different field. Such materials have an energy gap which is in between that of conductors and insulators. They do not conduct electricity at low temperature but conductivity increases as the temperature increases

Among different semiconducting materials Copper sulphide (CuS) is one of such materials which is extensively studied in past few years due to semiconducting and non toxic nature, making their use in wide range of application ranging from energy to biomedical field. The synthesis and studies of the optical and structural properties of CuS nanoparticles that make them useful in light emitting diodes,solar cells,fuel cells, drug delivery and as catalyst for industrial transformations [1]. CuS nanoparticles are also attractive because they exist in different stoichiometric compositions with varying crystalline phase [2-6]. CuS are known to be a very important p-type semiconductor due to its versatility, availability and low toxic nature. It exists in different phases ranging from copper rich (Cu_2S) to sulphur -rich (CuS) ,which exhibit wide variation of their direct/indirect band gaps. The electrical conductivity of CuS very much rely on its compositions and decreases from copper poor to copper rich compounds. Considerable attention has been focused on the fabrications of nanostructure CuS with different size, shape and morphologies due to quantum confinement effect. A variety of physical as well as chemical methods has also been employed in fabricating different nano dimensional 0,1 and 2-D CuS [7-9]. It has been well known that,the nature and different physical and chemical property of nanomaterials largely depend upon their morphology. In the last few years, the synthesis of CuS has become an interesting area of research because of its morphologies like nanospheres, nanowires, nanotubes, nanorods, hollow spheres and especially some complex structures.

During last few decades nanocomposites have been introduced due to their structural characteristics like machinery parts, coatings in scratch resistant and flame retardant cables. Generally, composites refers the materials formed by combining two or more different material possessing different properties to produce a end material having unique properties [10-13]. The nanocomposites coatings are engineered to provide attractive and cost effective functional surface coatings with superior properties for anticorrosion, antimicrobial, antifogging and adhesive applications. The unique characteristics of nanocomposite coatings include enhanced mechanical strength, weight reduction, improved barrier properties, and increased heat, wear and scratch resistance for lifelong performance. Regarding this various innovative and advanced research in graphene based composite is going on in recent times. Graphene –based materials and their composite posses different applications in wide range of fields such as, electronics,

biomedical aids, flexible wearable sensors, membranes ,and actuators. The presence of graphene can enhance the conductivity and strength of bulk material and help to create composites with superior qualities [16-18]. That's why Graphene can added to metals ,polymers and ceramics to create composites that are conductive and resistant to heat and pressure .Graphene composite applications seems endless,as it has many potential applications like one graphene polymer proves to be light ,flexible and an excellent electrical conductor ,while another dioxide graphene composites was found to be of interesting photocatalytic efficiencies, with many other possible coupling of materials to create all kinds of composites. The potential of graphene composites includes medical implants, engineering materials for aerospace and renewable and much more like researchers from the university of Toronto have shown that graphene is highly resistant to fatigue and is able to withstand more than a billion cycles of high stress before it breaks [14] .

In view of this present work is focused on formation of different phases of nano dimensional copper sulphide in terms of their crystal structure and synthetic methods. Development of improved methods for the synthesis of copper nanoparticles is of high priority for the advancement of material science and technology. A variety of synthetic strategies have been employed to prepare nanodimensional CuS of different compositions and phases such as hydrothermal,hot injection,thermolysis, microwave irradiation, electrodeposition and wet chemical methods etc. Among them we have used simple and cost effective wet chemical method to fabricate different nano structures of CuS in a controlled way. Thus, based upon above discussions, we aim at synthesis of CuS and CuS-graphene composite in simple wet chemical technique and test its efficacy in removal of industrial dye from contaminated water by the process of photocatalysis in presence of solar radiation.

MATERIAL AND METHODS

Chemicals used

Copper chloride ($CuCl_2$), Sodium sulphide (Na_2S), Disodium salt of Ethylene diamine tetra acetic acid (EDTA),sodium dodecyl sulphate, $CuCl_2$ and Na_2S, EDTA were purchased from Loba chemicals. Distilled water was used as solvent for all synthesis purposes.

All chemicals were used as such without any further purification.

Synthesis of CuS nanoparticles

In a typical procedure, 3 mmol of $CuCl_2$ (0.4030 g) was dissolved with 40 mL distilled water taken in a 100 ml. round bottom flask. A green colour solution is formed (indicates formation of a complex). A magnetic bead was put into the flask and after that 3 mmol. (0.87672 g) of EDTA was added to the solution. It is dissolved by constant stirring with the help of the magnetic bead. (0.4030 g) of Na_2S was added to the above solution. A dark green colouration was obtained. A reflux condenser is then attached to the round bottom flask and the setup was placed on an water bath was put on a hot plate provided with magnetic stirrer. The reaction was carried out for 4 hours with temperature 50^0C. with RPM 200. On vigorous stirring a dark green coloured precipitation was formed which was filtered with the help of a Buchner funnel provided with suction pump. The precipitation was washed for several times for hot water followed drying in the oven for 2 hr in 60^0 C. The powder was taken for further characterization.

The same process was repeated under temperatures 70^0C. and 90^0C. respectively keeping other experimental parameters same. The above procedure again repeated with the sodium dodecyl sulphate in place of EDTA.

Synthesis of graphene composite

About 12.5 mL of conc.H_2SO_4 was taken in a 500ml of beaker and 0.5g of graphite powder added to it .Then the addition of 0.25g of $NaNO_3$ in to it..It will place in an icebath with continuous stirring for 10 minutes .After that 1.5g of $KMNO_4$ is slowly added .Then stirred the solution for 40minutes fallowed by addition of 40 mL of hot water to it .After that 3-4 mL of 30% of H2o2 was added to it .The contents will allow to settle for 12hours.The final mixture will be centrifugated in the presence of hot water to remove excess acids and soluble impurities (several times).The black pasty mass is allowed to dry in oven at 60°C for 5-6 days.Now we get graphene oxide. About 0.5g of graphene oxide was taken in a round bottom flask then 50mLof water added to it .Stirred the solution well 0.25g of SDS, 0.2g of Na2S ,0.20g of cucl2 was added to it .then 2mLof hydrazine added to it.Then heat and stir in 90°Cunder reflux condition .after 3-4 hours collect the composites sample by filtration method and dry in oven about 70°C temperature.

Determination of dye degradation efficiency

The photocatalytic degradation of methyl orange (MO) was carried out in order to evaluate the photocatalytic activity of the as prepared nanoparticles and nanocomposites. 10 mg of prepared samples was dispersed in 50 mL of an aqueous solution of MO with an initial concentration of 10 mg/L. The above mixture was first stirred for 30 min in the dark to ensure that the adsorption-desorption equilibrium was

reach. Then, the photocatalytic degradation reaction was carried out under the irradiation of sun light. At every 10 min interval during sun light irradiation, 3 mL of the suspension was collected and subsequently centrifuged. The degraded solution supernatants was measured using a colorimeter by using blue-green filter.

RESULTS AND DISCUSSION

The XRD pattern of as-synthesized CuS nanoparticles with different temperature and different templating agent are shown in Figure. The lattice parameters indicate hexagonal structure [JCPDS file No. 04-0464] having lattice parameters, a = 3.79 Å and c =16.34 Å. all XRD patterns show peaks at 2= 28.519, 33.6, 47.358, 56.397, 59.9, 69.406, and corresponds to planes (101), (103), (107), (202), (116) and (207) respectively. The prominent peaks were seen to be broadened indicating the nanocrystallinity of all the samples.

XRD

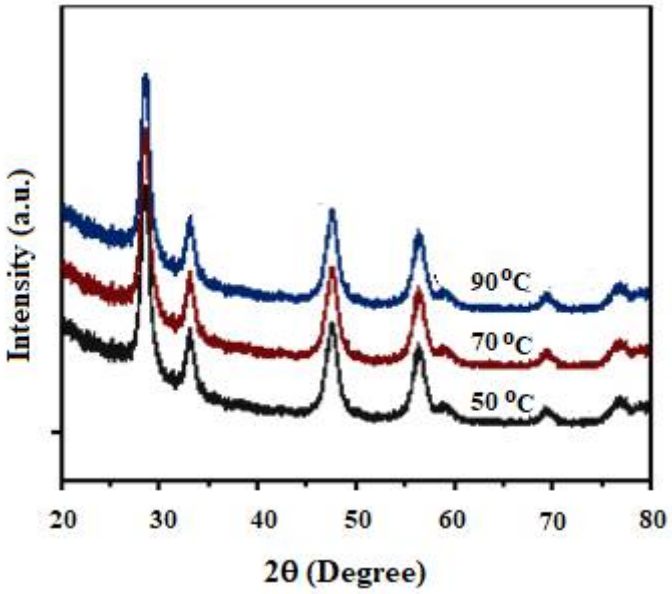

Figure 1 *XRD pattern of synthesized CuS particle prepared at different temperatures*

The analysis of XRD pattern stated that CuS nanoparticles possess the average crystallite size determined using Debye Scherrer's equation,

$D=K\lambda/(\beta \cos \theta)$

Where K, λ, β, and θ are Scherrer constant, wavelength of X-ray radiation target used, maximum peak width in half height and angle of diffraction respectively The presented data shows the samples synthesized with EDTA at 90°C, 70°C, 50°C have crystallite size 76, 55 and 44 nm respectively.

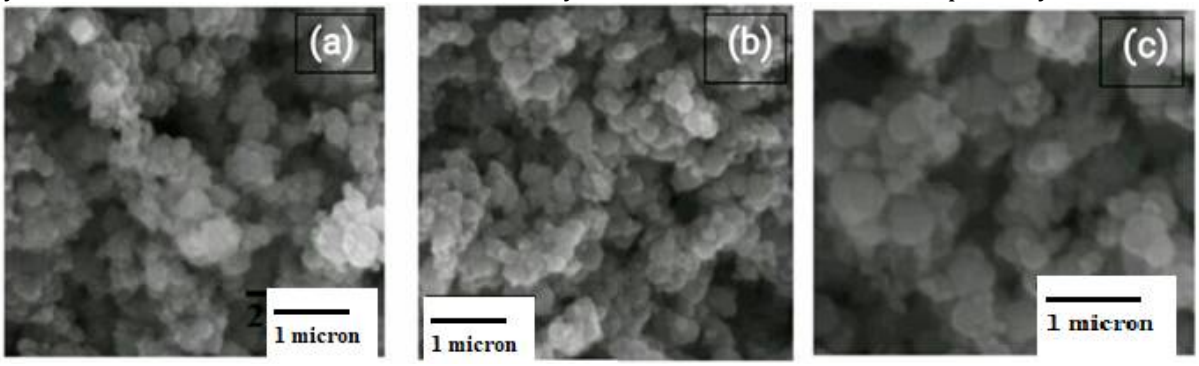

Figure 2 SEM images of CuS synthesized under reflux condition at (a) 50⁰ C., (b) 70⁰C. and (c) 90⁰C.

The surface morphology of the as synthesized CuS nanoparticles prepared at different temperatures was studied with the help of SEM and has been shown in Figure 2. From the SEM images it is clearly revealed that the CuS has particle type morphology with uniform size distribution in the range of 500-700 nm. In

addition it has also been observed that the particle size increases with rise in temperature from 50 to 90 ^{o}C. From the figures, it can be seen that nanostructures with different morphology is obtained by varying temperatures. Based on the results, the below mechanism was postulated. EDTA which was taken as a templating agent also act as a complexing agent, binds with Cu^{2+} and forms a complex [15]. In this process the release and availability of Cu^{2+} was reduced for which the reaction is slowed down favouring crystallisation and separating the growth step from the nucleation step [14-16]. So, Cu^{2+} ions from Cu-EDTA complex are released slowly and reacts with S^{2-} ions of Na_2S.

At lower temperatures ($50^0$and 70^0), there is slow releasing of Cu^{2+} ions from the complex which reduces the speed of reaction. Hence, the formation of CuS become slow and the growth on the nucleating center is less, so that the size of the particle is lesser. When the reaction temperature increased to 90^0 C., the complex becomes unstable and nearly breaks to generate higher concentration of Cu^{2+} ions in the solution leading to faster growth of CuS nanocrystals to bigger particles.

So, the observed particle size of CuS nanoparticles are 75, 90 and 115 nm at temperatures of 50^0, 70^0 and 90^0 C. respectively.

Photocatalytic activity

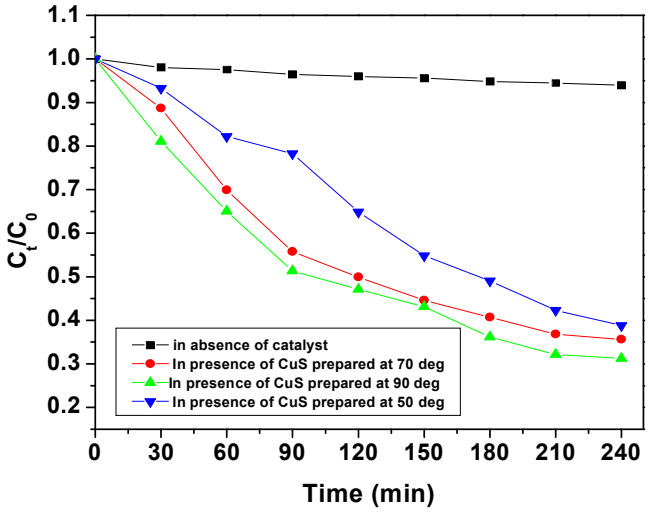

Figure 3: Percentage of photo degradation of MB vs solar irradiation time in presence of CuS nanoparticles synthesized at different temperatures.

The photocatalytic decomposition of aqueous MB solution has been carried out in absence/presence of CuS, acting as catalysts, under dark/UV radiation. These studies show no appreciable degradation of MB either in absence (or presence) of catalysts in absence sunlight even after 4 h. On the contrary, MB dye degraded very fast in presence of catalysts and sunlight.

These data have been used to calculate the fraction of MB left undegraded at different interval of time, from which % degradation of MB has been calculated using the relationship: $D = (C_0-C_t)/C_0 \times 100$. The observations have been shown in Figure 3. These observations suggest that ~ 70% degradation of MB in 240 minute take place in presence of CuS. The same catalyst has also been used for studying the reusability and has been found that the reusability of the CdS drastically decreases after 2nd use. This is possibly because photocorrosion of CuS nanoparticles. The further exposure to UV radiation up to 300 min showed no further sign of any appreciable degradation.

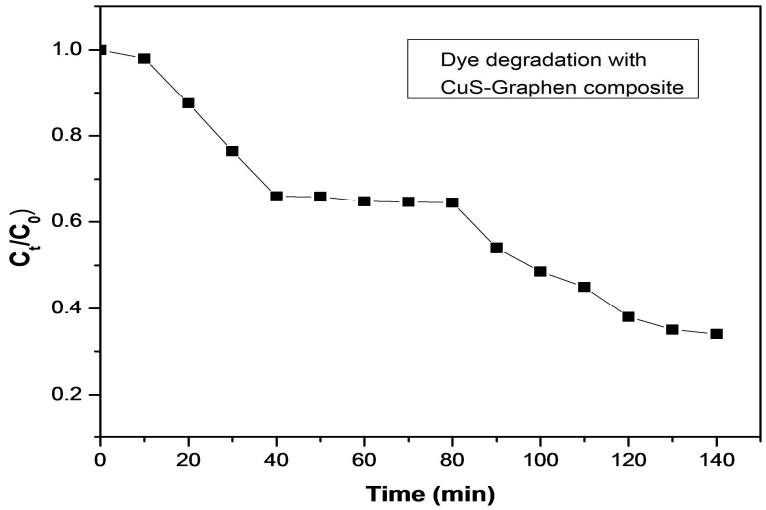

Figure 4: Percentage of photo degradation of MB vs solar irradiation time in presence of graphene composite of CdS nanoparticles synthesized at 90 ^{0}C.

Figure 4 indicates the photodegradation efficiency of the graphene composite of CuS nanoprticles. According to which, for a similar degradation (up to 70%) a time period of 140 minutes required (against 240 minutes for CuS nanoparticles), clearly suggesting that the graphene composite do have greater photocatalytic activity in comparison to pure CdS. The higher catalytic activity of composite in comparison to the CuS nanoparticles is because of greater mobility of charge carriers of graphene nanosheets [18]. Reportedly Graphene is a good electron acceptor, which which resists the recombination of the electron-hole pair in CdS due to enhancement of the electron transfer at the interface [26-30]. Moreover, the two dimensional nanosheets of graphene having very high surface-to-volume ratio and and very high specific surface area, disperses the CdS nanoparticles easily and allows enhanced light absorption on the surface of the catalyst [19]. For reusability assessment, the same photocatalytic study was carried with the used CdS-graphene composite and the observations indicate that the dye absorption on the surface of the catalyst decreases gradually. The percent degradation of the dye decreases by 8 and 17% with subsequent runs, in comparison to the initial run. This also indicates the reusable efficiency is not that much low, due to which the composite can be effective up to 3rd run for a photocatalysis.

CONCLUSION

CuS nanoparticles was successfully synthesized by wet chemical processes. Subsequent characterizations confirms that the cubic phased particles with rise in particle as well as crystallite size with rise in temperature. When studied for photocatalytic activity, it indicated that the photocatalytic activity higher with particles synthesized at higher temperatures. A degradation of 70% achieved under irradiation time of 240 minutes. However, for the similar extent of degradation with graphene composite, 140 minutes required indicating clearly the better efficiency of the graphene composite.

REFERENCES

1. A. Sánchez, A., Recillas, S., Font, X., Casals, E., González, E., Puntes, V. (2011). Ecotoxicity of, and remediation with, engineered inorganic nanoparticles in the environment. Trends Anal. Chem., 30(3), 507–516.
2. J Tian, J Xu, F Zhu, T Lu, C Su, G Ouyang (2003). Application of nanomaterials in sample preparation J Chromatogr A. 1300:2-16. doi: 10.1016/j.chroma.2013.04.010.
3. Jacak L., Hawrylak P. and Wojs A.(1997). *Quantum Dots*, Springer, Berlin Heidelberg New York.
4. Davis J. H., (1998). *Physics of Low Dimensional Structures*, Cambridge.
5. AM Morales, CM Lieber. (1998). A laser ablation method for the synthesis of crystalline semiconductor nanowires. Science, 9;279(5348):208-11. doi: 10.1126/science.279.5348.208.
6. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman. (1994). Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid–Liquid system. J. Chem. Soc., Chem. Commun 7, 801
7. Weck, M.: (1997). Machine tools and manufacturing systems 2: Design and calculation. Springer, Berlin.
8. North, Anna (2014). "Are Trophies Really So Bad?". *The New York Times*. Retrieved 17 November 2016.
9. Wang, X.; Li, Qunqing; Xie, Jing; Jin, Zhong; Wang, Jinyong; Li, Yan; Jiang, Kaili; Fan, Shoushan (2009). "Fabrication of Ultralong and Electrically Uniform Single-Walled Carbon Nanotubes on Clean Substrates". *Nano Letters*. 9 (9): 3137–3141.
10. S. Park, R. S. Ruoff, (2009). Chemical methods for the production of graphenes, Nature Nanotechnol. 4, 217-224

11. T. Kuila, S. Bose, A. K. Mishra P. Khanra, N. H. Kim, J. H. Lee, (2012). Chemical functionalization of graphene and its applications. Prog. Mater. Sci. 57,) 1061-1105.
12. S. Kaveri, L. Thirugnanam, M. Dutta, J. Ramasamy, N. Fukata, (2013). Thiourea assisted one-pot easy synthesis of CdS/rGO composite by the wet chemical method: Structural, optical and photocatalytic properties, Ceram. Int.l DOI: 10.1016/J. ceramint. 05.025
13. K. Zhang, X. Liu, (2011). One step synthesis and characterization of CdS nanorod/graphene nanosheet composite, Appl. Surf. Sci. 257, 10379-10383.
14. F. Liu, X. Shao, J. Wang, S. Yang, H. Li, X. Meng, X. Liu, M. Wang, (2013). Solvothermal synthesis of graphene-CdS nanocomposites for highly efficient visible-light photocatalyst, J. Alloys and Comp. 551: 327-332.
15. A. Ye, W. Fan, Q. Zhang, W. Deng, Y. Wang, (2012). CdS-graphene and CdS-CNT nanocomposites as visible-light photocatalysts for hydrogen evolution and organic dye degradation, Catal. Sci. Technol. 2, 969-978.
16. M. Feng, R. Sun, H. Zhan, Y. Chen, (2010). Lossless synthesis of graphene nanosheets decorated with tiny cadmium sulfide quantum dots with excellent nonlinear optical properties, Nanotecnology 21, 1-7.
17. H. Hu, X. Wang, F. Liu, J. Wang, C. Xu, (2011). Rapid microwave-assisted synthesis of graphene nanosheets-zinc sulfide nanocomposites: Optical and photocatalytic properties, Synth. Met. 161, 404-410.
18. L. Xue, C. Shen, M. Zheng, H. Lu, N. Li, G. Ji, L. Pan, J. Cao, (2011). Hydrothermal synthesis of graphene-ZnS quantum dot nanocomposites, Mater. Lett. 65, 198-200.
19. S. Pan, X. Liu, (2012). ZnS-Graphene nanocomposites: Synthesis, Characterization and optical properties, J. Solid State. Chem. 191, 51-56.

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