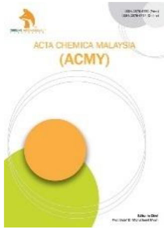
ZIBELINE INTERNATIONAL™ PUBLISHING

ISSN: 2576-6724 (Print)
ISSN: 2576-6732 (Online)
CODEN: ACMCCG

Acta Chemica Malaysia (ACMY)

DOI: http://doi.org/10.26480/acmy.02.2023.68.72



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RESEARCH ARTICLE

SYNTHESIS OF CuS NANOPARTICLES AND STUDY OF ITS PHOTOCATALYTIC ACTIVITY

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ARTICLE DETAILS

Article History:

Received 06 June 2023
Revised 15 July 2023
Accepted 22 August 2023
Available online 29 August 2023

ABSTRACT

Advancement in nanotechnology has been revolutionary in various filed of life including environment and energy related application. For removal of organic and inorganic pollutants from water bodies, photocatalysis is promising phenomenon and it has been highly effective against textile pollutants such as methylene blue- a commonly used one of azo dyes in textile industry. Dye polluted water bodies are highly hazardous for aquatic life and there are numerous health risks for human beings and animals. To provide a possible solution for removal of dyes from textile wastewater, Copper sulfide nanoparticles offer various advantages over other photocatalyst such as suitable band gap, large surface area and unique electronic structure. Hydrothermal route was employed for synthesis owing to it easiness, cost effectiveness and the control it offers in structural modification of product. Synthesized photocatalyst is capable of degrading 100% methylene blue in 250 minutes indicating its capability for industrial scale application in environmental remediation. This research focuses on the synthesis of CuS nanoparticles via hydrothermal method and its photocatalytic activities were observed on different methylene blue dye.

KEYWORDS

Cetyltrimethylammonium bromide, Methylene Blue, Nanoparticles, Photocatalyst

1. Introduction

Since Michael Faraday in 19th century extensive research has been made on nanoparticles and this subject has been evolved tremendously. In 1980s a process of revitalization was started by Henglein and Kreibig (Luis and Marzen, 2006; Whitelider, 2005). First of all, the scientist aimed to identify and quantify the size effect in nanoparticles. With the development of different techniques involving colloidal chemistry, now synthetic techniques are main purpose of research devising such method that can be used as tool to manipulate and control novel features of nanoparticles (Murphy et al., 2005; Yattinahalli et al., 2016).

The prefix "nano," derived from the Greek "nanos," signifying "dwarf," is being considered widely accepted in scientific literature. Nanoparticles are particles with at least one dimension smaller than 1 nm, and potentially as small as atomic and molecular length scales (~0.2 nm). Nanoparticles can have amorphous or crystalline form, and their surfaces can act as carriers for liquid droplets or gases (Buzea et al., 2007). Significant modifications are required for the manipulation of properties of nanoparticles, these modifications may be structurally and compositionally (Singh et al., 2016).

Nanoparticles are not only synthesized in laboratory but also abundantly present in nature. Examples of naturally occurring nanoparticles are present in moth's anti-glare and anti-reflective eyes and Namibian desert beetle. Nanoparticles are not totally new inventions; these were also available to human in prehistoric time such as Lycurgus cup found in 1600s which changes its colour from natural green to spectacular red in bright light (Smith, 2006). Nature always helps the researchers to develop these nanomaterials by producing examples such as skeletons are self-assembling nanostructures. Nanoparticles are categorized as metal and non-metal NPs that can be found naturally or can be synthesized in laboratory.

Now a day, number of methods are used to synthesize these nanoparticles such as low-pressure spray pyrolysis, surfactant - mediated method, simple liquid phase process, hydrothermal synthesis and other techniques. Different methods are applied to produce nanoparticles, complying the required features for applications in diverse field (Rahdar et al., 2015). Nanoparticles are versatile materials and can be used widely in diverse field of life. Some of the applications of these materials in the field of medicine such a drug delivery agent, food for preserving and flavoring, cosmetics such as sunscreen lotions, electronics like LED, catalysis as photocatalyst, construction to strengthen the concrete, Renewable energy such as solar cells and in environmental remediation are being used to treat or decontaminate the air, water and soil (Ealia and Saravanakumar, 2017; Abiodun_Solante et al., 2014; Manjunatha et al., 2016; Koo et al., 2005).

A Photocatalyst is a substance which accelerate the chemical reaction after absorbing a photon and is not consumed itself in the reaction. The reaction which are speed up by the use of photocatalyst are called photocalysis. The photocatalyst basically are semiconductors. These photocatalyst absorb the photon and transfer its energy to the reacting materials and contribute in their activation energy (Umar and Abdul Aziz, 2013). "Nanoscience" is the rising science of objects that are intermediate in size between the bulk molecules and the tiny structures that can be fabricated by current photolithography; i.e. the science of objects with smallest dimensions

Quick Response Code	Access this article online	
	Website: www.actachemicamalaysia.com	**DOI:** 10.26480/acmy.02.2023.68.72

Cite the Article: Usman Mureed, Zohaib Saddique, Kiran Asad (2023). Synthesis of CuS Nanoparticles and Study of Its Photocatalytic Activity. *Acta Chemica Malaysia, 7(2): 68-72.*

ranging from a few nanometers to less than 1000 nanometers (Wang et al., 2022). One of the most popular field of applied science is nanotechnology (Adams and Barbante, 2013). Nanotechnology refers to the exploration and evaluation of an applied science at nanoscale particles like atomic or molecular level (Roco, 1999). Nanotechnology is the controlling and understanding of matter at dimensions of roughly 1 to 100 nanometers (Ananda et al., 2022). Nanotechnology involves in the science and engineering of design, synthesis, applications and characterization of on nanometer scale i.e. one billionth of a meter (Silva, 2004; Dasgupta et al., 2017).

In agriculture, Nanotechnology capable the improving quality of soil with supply of nutrients that plants demand, influence the improvement of genetic traits of plants, delivery of genes, control and monitoring the pathogenic activities (Rai and Ingle, 2012). The ability to detect and quantify the presence of toxic agents in the environment is a first step towards taking helpful action and nanotechnology can help in providing improved systems for environmental analysis (Rickerby and Morrison, 2007; Zand, 2011). Nanoparticles are defined as particulate dispersions or solid particles with a size in the range of 10-1000nm. Nanoparticles are not only produced by modern synthesis laboratories, but have evidently present in nature for a long period of time, and therefore their use can be traced back to ancient times (Heiligtag and Niederberger, 2013). NPs are classified into two types based on dimension of the nanoparticles and origin of the nanoparticles. Depending upon the dimension, Nanoparticles could be zero dimensional, one dimensional and two dimensional etc. On the basis of origin, nanoparticles are further classified into natural or synthetic. Nanoparticles are also categorized on material basis i.e. organic and inorganic nanoparticles.

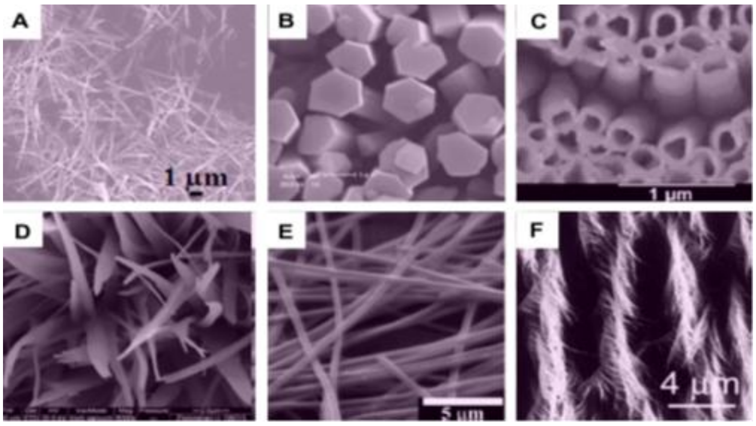


Figure 1: Typical SEM image of different types of 1D NPs, (A) Nanowires, (B) nanorods , (C) nanotubes , (D) nanobelts , (E) nanoribbons, and (F) hierarchical nanostructures (Tiwari et al., 2012)

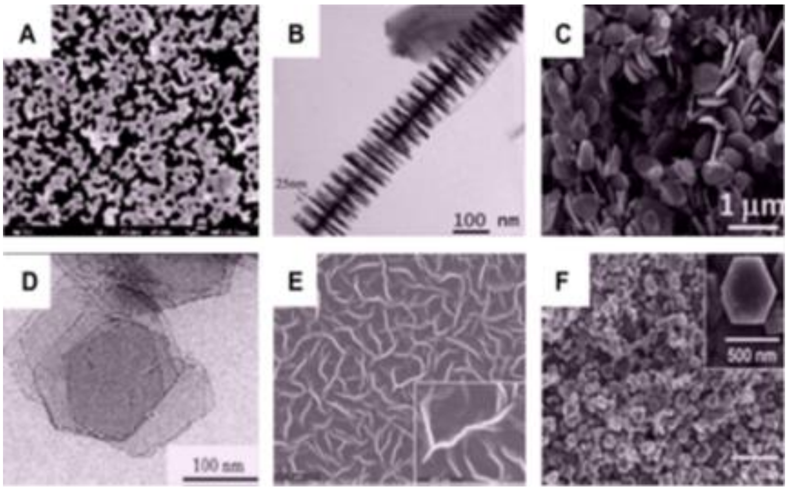


Figure 2: Typical SEM and TEM image of different kinds of 2D NPs, (A) Junctions (continuous islands), (B) branched structures, (C) nanoplates, (D) nanosheets, (E) nanowalls, and (F) nanodsks (Tiwari et al., 2012)

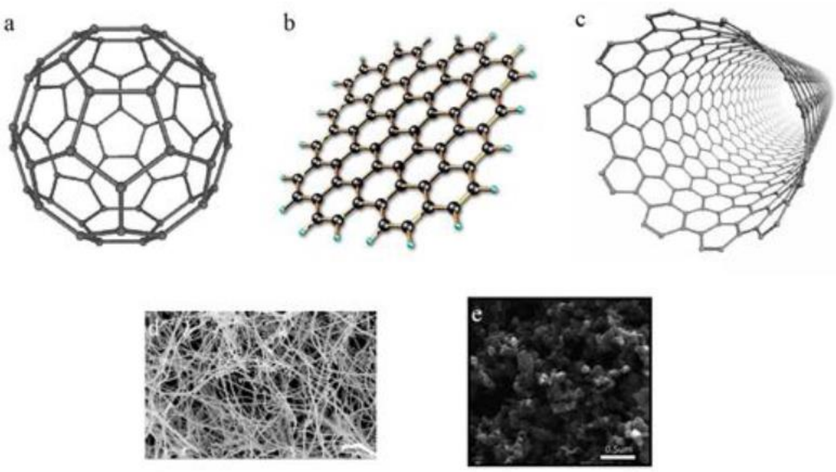


Figure 3: Carbon based nanoparticles: (a) fullerenes, (b) graphene, (c) carbon nanotubes, (d) carbon nanofibers and (e) carbon black (Smith, 2006)

CuS belongs to the unique class of group I-V multifunctional chalcogenide metal sulphide semiconductors. Due to eccentric properties and wide spread range of electrical potential, CuS nanoparticles are used as cathode material in Li-ion batteries, high temperature thermistors, photocatalyst, photothermal conversion, gas sensors and other metal organic reactions (MOR) (Megashwari et al., 2011). Wavelength absorption of CuS NPs is not effected by size, Shape and surrounding environment. This feature helps in the fabrication of nanoshells, hallow nanospheres and nanorods shaped CuS nanoparticles (Xiao, 2014). Different methods are used for the preparation of CuS nanoparticles. Some of them are discussed in this research.

In a typical hydrothermal method, $CuCl_2 \cdot 2H_2O$ and CTAB are dissolved in deionized water. The $CuCl_2$ solution is then added drop by drop into Na_2S solution with continues stirring until black slurry is formed. After few, the slurry is transferred into a Teflon-lined stainless steel autoclave. The autoclave is sealed and maintained at 180 °C for 24 h, and then temperature is reduced to room temperature naturally. Finally, the as-formed precipitate is centrifuged, washed sequentially with deionized water and absolute ethanol, dried at 60 °C for 5 h in vacuum.

CuS nanoparticles can also prepared by using co-precipitation method (Pejjai et al., 2020). P123 dissolved in DMF while stirring, followed by the addition CuAc at room temperature. Then, the temperature slowly increased. Equivalent molarity of ThU dissolved in DMF is added drop wise to the above solution and stirred for 2 hours. The pH is sustained at 10 by using NH_4OH to precipitate CuS. The as-produced precipitates collected and washed several times with ethanol and hot deionized water. Subsequently, the obtained precipitates are dried in a heating chamber at 100 °C for 12 hours. The above procedure is repeated with different molar ratios of ThU to CuAc at 2.51, 3.77, and 5.03 g for 2:1, 3:1, and 4:1, respectively.

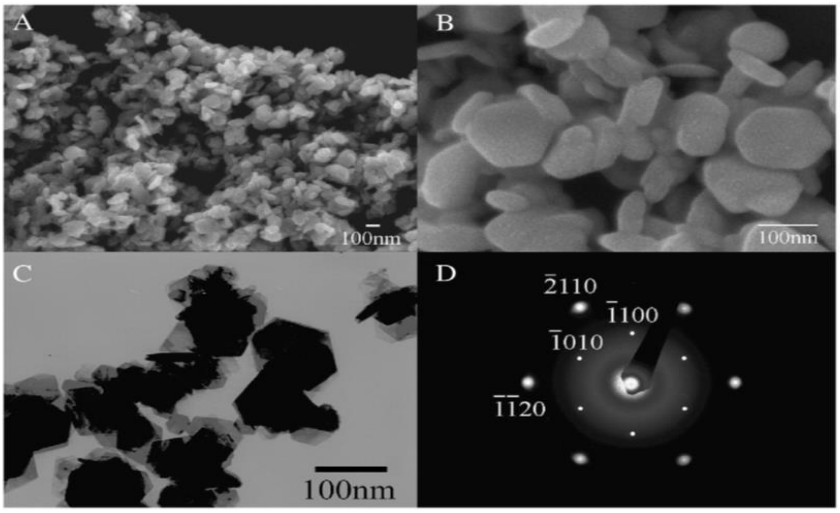


Figure 4: Images of as-prepared CuS NPs by hydrothermal method, (A) low-magnification SEM image; (B) high-magnification SEM image;(C) TEM image; (D) ED pattern taken from an individual nanoplate (Zhang and Zhang, 2008)

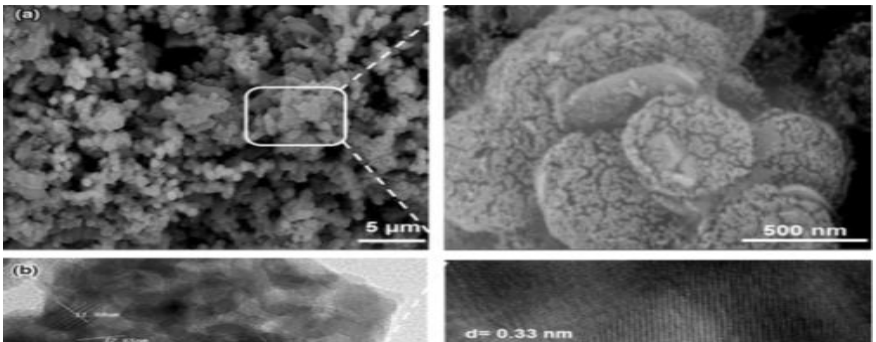


Figure 5: FE-SEM and corresponding TEM images in (b) for CuS photocatalyst; the right-side images are the high-resolution images showing the urchin-like structure in SEM and confirm the lattice parameters of hexagonal CuS in TEM (Pejjai et al., 2020)

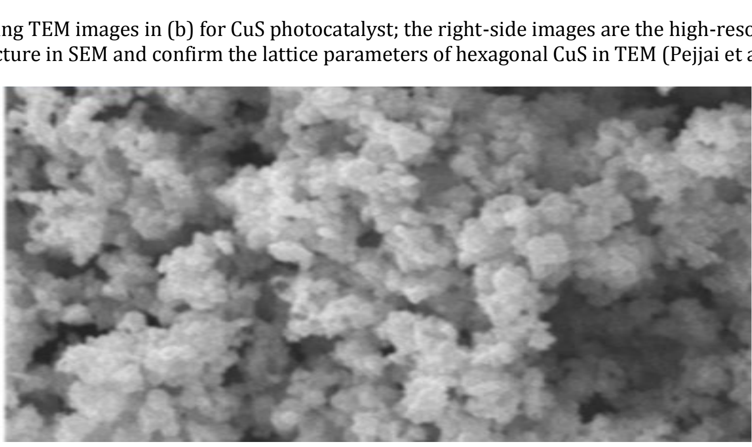


Figure 6: SEM image of phase controlled synthesized CuS nanoparticles (Shawky et al., 2020)

In phase-control synthesis, deionized water is taken in a beaker and CuCl is added into it and stirred well. To this solution, TEA and IPA are added and stirred vigorously for 30 min at 70 °C. This mixture is labelled as Cu-precursor solution. Next, CH_4N_2S was added directly into the Cu-precursor solution. Then, the total volume of this solution was made up to 200 ml by adding deionized water and the pH of the solution was maintained at ~10 by adding NH_4OH solution. The mixture was allowed to react for 2h at a constant temperature of 70°C. After the reaction, the solution is cooled naturally to room temperature. A greenish-black precipitate is obtained, which was collected by centrifugation at 3200 RPM for 10 min after successive washing steps by deionized water and ethanol for three times to remove the by-products and impurities. Finally, the obtained product was dried in an oven at 120°C for 2h under the open atmosphere and used in the characterization (Pejjai et al., 2019).

Photocatalysis is the process in which photon generated electron form a substance generally semi-conductor is used to catalyze reaction without being consumed. A semiconductor surface, on irradiation with light, generates an electron-hole pair. The attacking photon must have enough energy that can knock out electron from semi-conductor material. This can happen only when energy of photon is more than band gap of given material. That electron emitted from semi-conductor react with one of the reactant of reaction being catalyzed. If oxidation and reduction reaction both are happening simultaneously in photocatalyze reaction, then this process is considering sustainable.

Photocatalyst + hv→hvvb^{+}+hvcb^{-}

There are two types of photocatalysis

1. Homogeneous photocatalysis: When both the semiconductor and reactant are in the same phase, i.e. liquid, gas, or solid, such photocatalytic reactions are called as homogeneous photocatalysis.
2. Heterogeneous photocatalysis: When both the semiconductor and reactant are in different phases, such photocatalytic reactions are termed as heterogeneous photocatalysis (Ameta et al., 2018).

The term photocatalyst is a combination of two words: photo related to photon and catalyst, which is a substance altering the reaction rate in its presence. Therefore, photocatalysts are materials that change the rate of a chemical reaction on exposure to light. This phenomenon is known as photocatalysis. Photocatalysis includes reactions that take place by utilizing light and a semiconductor. The substrate that absorbs light and acts as a catalyst for chemical reactions is known as a photocatalyst. All the photocatalysts are basically semiconductors. Photocatalysis is a phenomenon, in which an electron-hole pair is generated on exposure of a semiconducting material to light (Chen et al., 2020).

CuS nanoparticle photocatalysts are low cost and abundantly available nanoparticles that can be used with ease in photocatalysis. They are p-type semiconductor with small band gap requiring less energy for excitation of electron that is emitted to photocatalyze. They enhance visible light absorption capacity of other catalyst by combining with them. CuS NPs combine with other low band gap semi-conductor and lessen its own band gap leading to higher photocatalytic efficiency. It is promising sun light sensitive material that makes it efficient photocatalytic material (Radhakrishnan et al., 2020; Malik et al., 2022).

2. Experimental Work

2.1 Synthesis of CuS Nanoparticles

0.17g copper chloride (Sigma Aldrich, 99.9%) and 0.10g CTAB were dissolved into 30ml of deionized water (Spelco, 99,98%). 0.1 M solution of copper chloride (Sigma Aldrich, 99.99%) was added into 30 ml of sodium sulfide (Sigma Aldrich, 98%) solution. This mixture was stirred continuously until black slurry is formed. After 15 min slurry was transferred to 80 ml capacity Teflon lined stain less steel autoclave. The autoclave was sealed tightly and place in heating oven. The temperature oven was 180 °C for 24 hours. It was cool down to room temperature gradually. Precipitates were removed from autoclave and then washed using deionized water and absolute ethanol. Then precipitates were dried at 60 °C for five hours in vacuum.

2.2 Photocatalytic activity of copper sulfide Nanoparticles

Distilled water (Sigma Aldrich) was taken in 200ml beaker in it and then added methylene blue (Sigma Aldrich, 99.99%) solution in this water about 10 mg in it. The ratio used for methylene blue (MB) aqueous solution was 50mg/L. This aqueous solution of methylene blue was added to photocatalytic reactor. In this solution 40 mg of self-prepare copper Sulfide nanoparticles were dispersed. UV lamp of 250 W was used as source of light in this experiment. In first hour, solution was kept in dark to measure activity in solution. Then it was placed in light and after every 30 minutes sampling was done during illumination and UV-Vis spectra of solution was obtained.

3. Result and Discussion

This research has two functional parts along with basic information that is provided earlier. In first part experiment was preformed to synthesize copper sulfide nanoparticles using ecofriendly and cost-effective method and this targeted method was hydrothermal method of nanoparticles synthesis. In second part photocatalytic activity of this self-prepared copper sulfide nanoparticles studied.

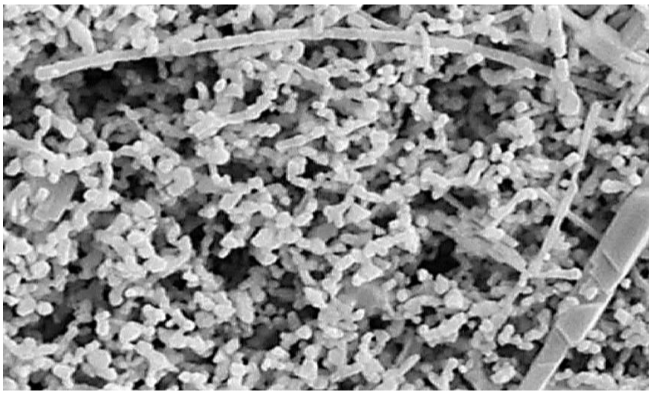
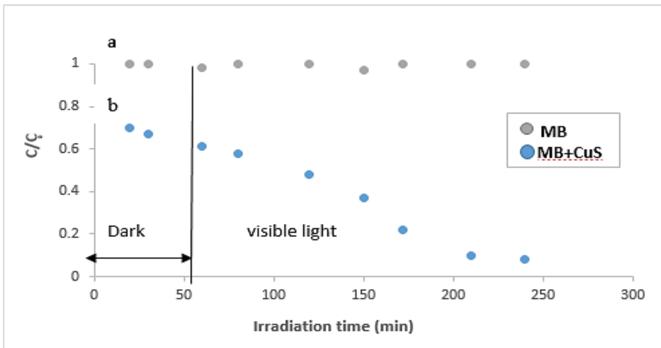


Figure 7: CuS nanoparticles synthesized though hydrothermal process

Figure 7 shows the transmission electron microscopic result of prepared copper sulfide nanoparticles by hydrothermal synthesis. These particles look like irregular rod scattered here and there. The method used for preparation was simple and easy to implement with flexibility of manipulating the result for purposed results. This hydrothermal approach is used to prepare every structural type of nanoparticles ultimately with different properties.



Graph 1: (a) Irradition time of only Methylen blue, and (b) irradtition time of methylene blue with copper sulphide nanoparticles

Graph 1 shows the result of photocatalytic activity of copper sulfide nanoparticle in given situations. To study photocatalytic activity methylene blue was used as organic agent that is being used for degradation. The results were promising and data shows maximum activity level in between wavelength of 600-700 nm. This maximum activity happened after about 90 minutes and continued gradually decreasing until 150 minutes. After this activity was minimal and not promising. Method used in this experiment proved very efficient and useful. There is hazardous effect of the nanoparticles on environment and life of human being but looking at greater good by reduction of organic waste material from environment is more worthy. Approaches and hypothesis are in line with previous researches and experiments on the topic.

We are unable to say with full confident that these methods are faultless because there is fault in these methods, there limitation in this method that are sometime halting factor for further research. Further researches are recommended with up-to-date and modern technology to explore new properties and make these substances beneficial for human being in particular and environment in general. Semi conduction activity is main factor that affect these properties of substance but we are leaving it here without any further comment because this is not scope of our research.

Further researches should be performed to understand this integration of properties so that we can manipulate these properties for our good use. Last but not least this research was a infinitesimally small step toward furtherance of understanding of science to use it for benefits of human being and hope this will be substantial step forward.

4. Conclusion

A pertinent and environment friendly approach of synthesis of copper sulfide nanoparticles was used that was also economic and this approach is called hydrothermal approach. This research obviously supports hydrothermal approach but there are some limitations of this approach that restrains our research at some point and in some far-flung areas. Prepared nanoparticles were used to study photocatalytic activity of given substance and in this regard methylene blue was used as organic agent to be degraded. In this research it can be concluded that hydrothermal technique is good technique to prepare copper sulfide and these nanoparticles are promising photocatalyst.

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