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Short Communication

Rapid Synthesis of $CuFeS_2$ Nanoparticles Using Microwave Irradiation for Therapeutic Applications

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ABSTRACT

Nanoparticles (NPs) are a class of new materials, with less than 100 nm in diameter and exhibit enhanced size dependent properties as compared to larger particles of the same material. We describe the rapid microwave irradiation protocol for the synthesis of ternary $CuFeS_2$NPs, by reacting Cu, Fe, and S precursors in aqueous system. This one-pot facial synthesis strategy features shorter reaction time, easy process control, low energy consumption, and absence of a temperature gradient. The obtained NPs morphology and crystallite was characterized using TEM and XRD techniques, respectively. Furthermore, the obtained NPs, magnetic and fully water soluble, showed broad optical absorbance from the visible to the near infrared region could be applied for photothermal therapy and magnetic resonance imaging applications for future biomedical use.

Keywords: $CuFeS_2$, Microwave irradiation, Nanoparticle, Rapid synthesis, Phototheraml therapy.

There has been a wide interest in the synthesis of I-III-VI_2 group ternary chalcogenides, because of unique chemical and physical properties including high absorption coefficient, high conversion efficiency, and low toxicity. Chalcopyrite I–III–VI_2 semiconductors, such as $CuInS_2$, $CuInSe_2$, $AgInS_2$, and $AgInSe_2$,show significant roles in the fabrication of photovoltaic devices and in biomedical application (Coughlan et al., 2017; Girma et al., 2017; Kolny-Olesiak et al., 2013; Torimoto et al., 2014; Zhong et al., 2012). However, less attention has been paid to chalcopyrite $CuFeS_2$, which crystallizes in a tetragonal structure, with the space group I42d. It can be obtained by doubling the unit cell of a zinc blende structure, with the S atom residing in the tetrahedral void formed by the Cu and Fe atoms(Xie et al., 2017). $CuFeS_2$ is an n-type semiconductor that displays large thermoelectric power, low band gaps (~0.53eV for the bulk), and antiferromagnetic behavior, with a relatively high Neel temperature of 550 °C (Austin et al., 1956; Teranishi, 1961) and innovative electrical and optical properties. It is also unique among other Cu containing semiconductor owing to its unique broad intermediate bands formed by Fe 3d orbitals (Ghosh et al., 2016) exhibiting remarkable photothermal, thermo- and ferro-electrical properties (Lyubutin et al., 2013; Xie et al., 2017).

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Ghosh et al. reported a photothermal properties of $CuFeS_2$ NPs, synthesized using hot-injection method, in the first biological NIR spectral range (650–900 nm), avoiding the interference of endogenous chromophores within the body, which was implemented in the treatment of human epithelial carcinoma cells (Ghosh et al., 2016). In our recent study, we reported Cisplatin (IV) prodrug-tethered $CuFeS_2$ NPs, synthesized using heating-up method, with a high photothermal conversion efficiency and assessed their potential application for combined tumor-targeted chemotherapy and PTT of mouse melanoma and human cervical cancer cells (Girma et al., 2018). However, shared as an intrinsic drawback of hot-injection and heating up methods, both suffers from fast synthetic reproducibility and solvent mixing time, lack of large-scale production, problems related to temperature, pressure, and concentration gradient. During the past few years, a variety of methods has been explored to synthesize $CuFeS_2$ NPs, such as hot-injection (Ghosh et al., 2016), heating up (Girma et al., 2018), thermal decomposition (Ding et al., 2017), and hydrothermal methods (Li et al., 2015).

Herein, we report a synthesis protocol that delivers a therapeutic agent $CuFeS_2$NPs. $CuFeS_2$ NPs synthesized by simple microwave irradiation, with many unique characteristics (e.g., shorter reaction time, easy process control, low energy consumption,

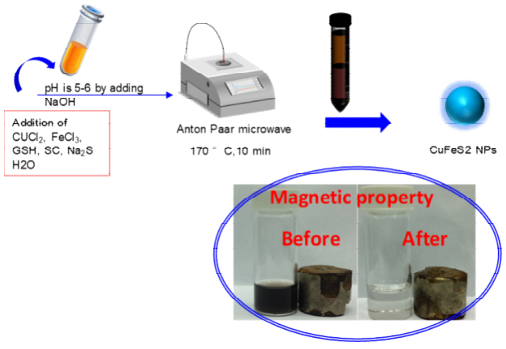
and absence of a temperature gradient) that are important in reactions with multiple precursors.

The chemicals used in this study were anhydrous iron (III) chloride ($FeCl_3$, 98%, Alfa-Aesar), sodium sulfide nonahydrate (Na_2S*9H_2O,98%) were obtained from Acros Organics (New Jersey, USA). Copper (II) chloride dihydrate ($CuCl_2*2H_2O$, 99.99 %,), Glutathione (GSH, 98%), and citric acid trisodium salt (SC, 98%) were acquired from Sigma-Aldrich (Milwaukee, USA).All other chemicals and reagents used were analytical grade.

$CuFeS_2$ NPs were prepared according to previously reported methods (Gedda et al., 2017). In a typical synthesis, 20 mL deionized water, 0.50 mL of $CuCl_2$ (0.02 M), 0.75 mL of $FeCl_3$ (0.08 M), 12.3 mg of GSH (used as a stabilizer) and 41.30 mg SC (used as a stabilizer) were loaded in a 30 mL reaction vessel. Next, 0.50 mL of fresh prepared Na_2S solution (0.2 M) was added in drop wise into the mixture solution as the $CuFeS_2$ precursor. The pH value of the solution was amended to 5.0-6.0 by the drop wise adding 5.0 M NaOH solution. Afterward, $CuFeS_2$ NPs were prepared at a controlled reaction temperature of 170 °C using a single-mode microwave reactor. Further, the reaction was irradiated for 10 min. subsequently the reaction solution was allowed to cool to room temperature. Finally, resulting $CuFeS_2$ NPs were subjected to centrifugation at 6000 rpm for 15 min using 2-propanoland the supernatant discarded. The obtained product was dried and labeled as $CuFeS_2$ NPs.

The characterizations of as prepared sample were performed using the following techniques. Absorbance spectra were recorded using UV-visible spectrometer (JASCO V-630). Transmission electron microscopy (TEM) images were captured using FEI Tecnai G2 F20 microscope (Philips, Holland). X-ray diffraction (XRD) patterns were obtained by using Bruker D8 X-ray diffractometer.

The optical properties of water soluble $CuFeS_2$ NPs were investigated using UV-vis absorption



Scheme 1: Schematic representation for synthesis $CuFeS_2$ NPs using Microwave-irradiation approach.

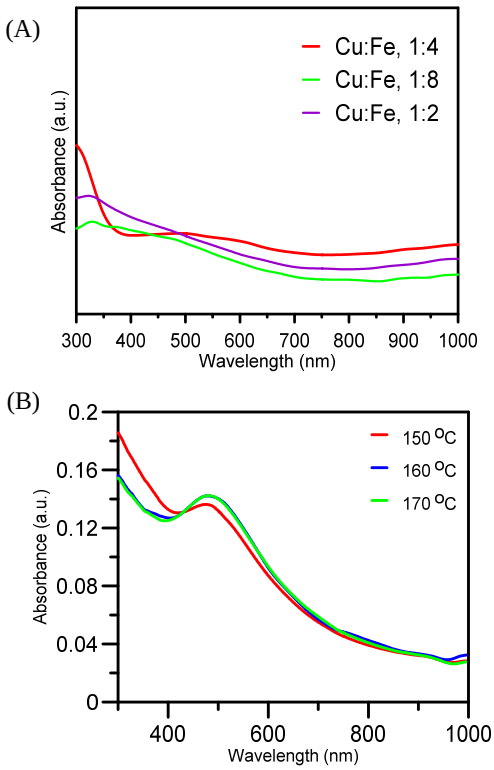


Fig. 1: The absorbance spectra of $CuFeS_2$ synthesized at different Cu:Fe ratio (A) and at different reaction temperature (B).

spectroscopy. Fig. 1(A), displays the absorbance spectra of $CuFeS_2$ NPs at different Cu:Feratio. As the absorbance, spectra displayed 1:4 ratio selected for further reactions. As shown in Fig.1(B) the absorbance spectra were carried out at different synthesis temperature, and shows good absorption profile in the NIR absorption windows from 700-1000 nm. From the absorbance profile 170 ºC were chosen for further characterization. Therefore, best reaction conditions which selected from absorbance spectra was 1:4 Cu:Fe ratio at 170°C for our facial synthesis protocol.

The prepared soluble $CuFeS_2$ NPs morphology was characterized by TEM. As shown in Fig. 2(A), TEM image showed a qusi-spherical dispersed particle. The HR-TEM image in Fig. 2(B), results clearly displayed that the distance between the adjacent lattice fringes was 0.31 nm, which corresponds to the d-spacing of $CuFeS_2$ NPs (112). The EDS analysis (Fig. 2(C)) was carried out using gold gird due to the presence of magnetic iron.

Furthermore, $CuFeS_2$ NPs were characterized by XRD (Fig.3), which clearly showed four-diffraction pattern that can match well with (112), (200), (204), (312) lattice planes of chalcopyrite $CuFeS_2$ (JCPDS no 37-0471).

In the field of biomedical and photoelectricity research's, semiconductor chalcogenide compounds,

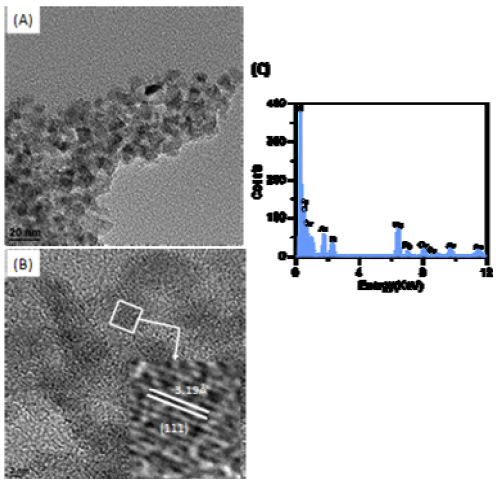


Fig. 2: The TEM image of $CuFeS_2$ (A) HRTEM image of $CuFeS_2$ (B) EDS spectra of $CuFeS_2$.

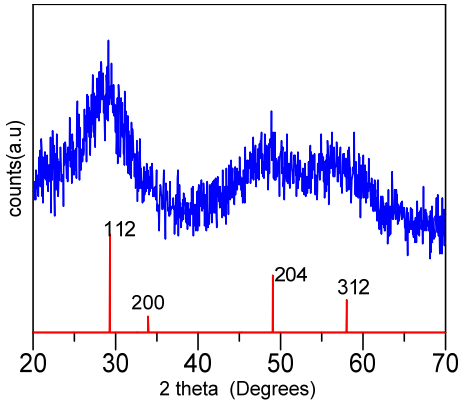


Fig. 3: XRD diffraction patterns of $CuFeS_2$

$CuFeS_2$, with near-infrared absorbance and good biocompatibility has attracted much attention. However, cost effective and facial mechanism of synthesis has been less reported. Compared to traditional method of synthesis of NPs microwave irradiation provides lower energy consumption, easy reproducibility and process control, absence of temperature and pressure gradient (Girma et al., 2017; Zhou et al., 2015). In the process, multiple precursors are heated with an aqueous medium to induce chemical reaction to yield nucleation and growth from monomers. The above results demonstrate that $CuFeS_2$ NPs successfully fabricated using rapid one pot synthesis approach using microwave-irradiation.

The synthesis protocol for $CuFeS_2$ NPs is illustrated as shown in Scheme 1, $CuCl_2$, $FeCl_3$ and Na_2S was used as a copper, iron and Sulphur sources, respectively. GSH and SC also serve as a stabilizer/capping agents and water was used as a reaction medium. Up on rising the temperature the color of the solution turns to dark indicates nucleation and growth (Jing et al., 2016). Further, after 10 min reaction time the reaction stops to cool at room temperature. After obtaining the NPs, it was dissolved in water and we assessed the magnetic properties of solution. Obviously, the growth of $CuFeS_2$NPs can be affected by the followings: (1) the nucleation and growth of$CuFeS_2$ nuclei are dependent on the producing speed of the free copper, iron and sulfur ions by reactants, (2) the properties of surfactants or solvents can affect the ion exchange and atom rearrangement during crystal growth (3) reaction temperature. Therefore, the composition, and the temperature was varied during the synthesis protocol (Zhu et al., 2014).

As shown in scheme 1, it showed a clear solution in contact with the bar magnet, which mean the magnetic NPs attracted by the magnet (Jiang et al., 2017).

The prepared water soluble magnetic nanoparticle showed a broad absorbance spectrum in the near infrared which is good to use for biological applications as revealed from the result Fig 1. The variations in composition of the reactants: as the ratio Cu:Fe (Fig.1(A)) varied from 1:2 to 1:8, 1:4 showed better absorbance in the near infrared region may be due to correctness of the proposed growth mechanisms of the NPs. Similarly, with varied reaction temperature the absorbance profile also checked and sated to 170°C.

The prepared soluble $CuFeS_2$ NPs morphology showed a qusi-spherical dispersed particle (Bhattacharyya et al., 2016), which is very desirable to use for bio-medical applications, confirmed by TEM. Furthermore, the crystallite of $CuFeS_2$ NPs with a clear four-diffraction pattern (112), (200), (204), (312) matched with lattice planes of chalcopyrite $CuFeS_2$ (JCPDS no 37-0471).

In conclusion, we have successfully synthesized $CuFeS_2$ NPs through non-injection rapid aqueous synthesis protocols. Notably, $CuFeS_2$ showed a broad absorbance spectrum in Near IR and magnetic properties, which could may exhibited higher photothermal conversion efficiency and magnetic properties, to be applied for biomedical purpose. Furthermore, the morphology of the synthesized NPs was a qusi-spherical and fully soluble in aqueous system which is important to be applied in biomedical applications. However, it is necessary to conduct zeta potential test, cytotoxicity study and checking the photothermal ablation properties of the material. Furthermore, conducting other properties of the obtained semiconductor nanoparticle will be useful to use as alternative clinical materials in future for therapeutic application.

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