Template free preparation and characterization of CuS nanoparticles in aqueous solutions of [EMIM][EtSO₄] as a low cost ionic liquid using ultrasonic irradiation

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This paper presents a facile, room temperature and environmentally benign green route for the production of nanocrystalline CuS at 7 min by ultrasonic irradiating in aqueous solution of room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium ethylsulfate, ([EMIM][EtSO₄]). The X-ray diffraction (XRD) studies display that the products are well crystallized in the form of hexagonal structure. Energy dispersive X-ray spectroscopy (EDX) investigations reveal that the products are extremely pure. The morphology of as-prepared nanoparticles was characterized by scanning electron microscopy (SEM). A possible formation mechanism for the production of nanoparticles in the aqueous solution of the RTIL with the aid of ultrasonic irradiation is proposed.

1. Introduction

Recently, there has been considerable interest in semiconductors of nanometer dimensions due to the quantum size effect they exhibit [1,2]. Nanometric semiconductor particles exhibit novel properties due to the large number of surface atoms and the three-dimensional confinement of electrons. Altering the size of particle changes the degree of confinement of electrons, and affects the electronic structure of the solid, in particular the band edges, which are tunable with particle size. Copper sulfides with various stoichiometries are important p-type semiconductors and have been extensively used in solar cells [3,4]. Also copper sulfides can be used as optical filters and superionic materials [5], which show metallic conductivity and transform into a superconductor at 1.6 K [6]. In addition, copper sulfides still exhibit fast-ion conduction at high temperature and some other special properties [7-9]. It is imaginable that combining such useful properties and the prominent characteristics of nanosized structures will inevitably bear broad applications in an even wider range.

Many methods have been developed for synthesis of copper sulfides including solid-state reaction [10], self propagating high temperature synthesis [11], sonochemical route [12], microwave irradiation techniques [13,14], pyrolysis of single source precursors [15], hydrothermal/solvothermal synthesis [16-20] and so on. Generally, these reactions require high temperature (500°C), long reaction time and use of toxic and highly sensitive compounds. The most straightforward way to synthesis copper sulfides is the direct combination of elements Cu and S. Unfortunately, traditional element direct reaction route needs high temperature and lead to

powders of relatively large grain size. A direct and simple method seems to be required.

The utilization of ultrasonic irradiation (USI) for production of nanomaterials has been a research topic of great interest. This is in consequence of the simplicity of sonochemical method, the inexpensive price of the equipment and that in many cases the as-prepared material is obtained in the crystalline phase. The chemical effects of ultrasound come from non-linear acoustic phenomena, primarily acoustic cavitation. This can be divided into three distinct stages: (i) formation, (ii) growth and (iii) implosive collapse of bubbles [21]. Stable and transient cavitations may occur simultaneously in the solution and a bubble undergoing stable cavitation may become a transient cavity. The formation of a bubble is explained by the presence of a nucleation process where the nuclei can be gas-filled crevices in small particles suspended in solution. Once the bubble is formed, it can grow as dissolved gas molecules enter during the expansion phase of sound wave, and shrinks during the compression phase. Thus, the bubble grows slowly over many acoustic cycles. In strong acoustic fields, the implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The extreme conditions attained during bubble collapse (transient temperature of ~ 5000 K, pressure of 1800 atm and cooling rates in excess of 10^{10} K/S [22]) has been exploited to generate metal sulfides [23-25].

Room-temperature ionic liquids (RTILs) have been accepted as a new green chemical revolution which excited both the academia and the chemical industries. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new

syntheses. They have a unique array of physico-chemical properties which make them suitable in numerous applications in which conventional organic solvents are not sufficiently effective or not applicable. The application areas of RTILs can be expressed as solvents for organic, organometallic synthesis and catalysis; electrolytes in electrochemistry, in fuel and solar cells; lubricants; stationary phases for chromatography; matrices for mass spectrometry; supports for the immobilization of enzymes; in separation technologies; as liquid crystals; in preparation of polymer–gel catalytic membranes and generation of high conductivity materials, etc.[26-30]. Furthermore, they readily dissolve many organic, inorganic and organometalic compounds. Room temperature ionic liquids (RTILs) have attracted increasing attention as the green, high-tech reaction media of the future [31] and they have recently received a great deal of attention as potential new media for nanomaterials synthesis [32-38].

The most commonly used RTILs have PF_6^- and BF_4^- ions [39]. RTILs with these ions are known to be decomposed in the presence of water and as a result toxic and corrosive species such as hydrofluoric and phosphoric acids are formed [40,41]. The RTILs with alkyl sulfate anions are halogen-free and relatively hydrolysis-stable compounds and they could be an interesting alternative for industrial application due to the fact that they avoid the liberation of toxic and corrosive materials into the environment [42]. One of the largest barriers to the application of RTILs in various fields arises from their high cost relative to conventional solvents [39]. In order to overcome this problem, also better tune and tailor the physicochemical properties of the RTIL of interest in a favorable fashion, researchers have started to focus on RTIL-based mixed green molecular solvent systems [43].

In continuing our investigations about nanomaterials preparations and RTILs [23-25, 44], [27,28, 45], ultrasonic-assisted aqueous room temperature ionic liquid (UARTIL) method was applied for the preparation of copper sulfide nanoclusters. For above mentioned reasons, halide-free and low cost RTIL, 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]), was used in this work [46,47].

2. Experimental details

2.1. Materials

Copper acetate (Cu(CH₃COO)₂ .H₂O extra pure), thioacetamide (TAA, CH₃CSNH₂ GR for analysis) and absolute ethanol were obtained from Merck, and employed without further purification. The ionic liquid was 1-ethyl-3-methylimidazolium ethyl sulfate, [EMIM][EtSO₄], and simply synthesized according to the literature [47].

2.2. Instruments

Surface morphology and distribution of particles were studied via LEO 1430VP scanning electron microscope (SEM), using an accelerating voltage of 15 kV. The purity

and elemental analysis of the products were obtained by energy dispersive analysis of X-rays (EDX) on the same LEO 1430VP instrument with the accelerating voltage of 20 kV. The sample used for SEM and EDX observations was prepared by transferring the particles, which at first was dispersed in the ethanol to glass substrate attached to the SEM stage. After allowing the evaporation of ethanol from the substrate, the particles on the stage were coated with a thin layer of gold and palladium. The X-ray diffraction (XRD) pattern was recorded on Philips Xpert X-ray diffractometer with Cu Kα radiation λ= 0.15406 nm), employing scanning rate of 0.02°/s in 2θ range from 15° to 75°. The ultrasound radiation was performed using Dr. Heilscher high intensity ultrasound processor UP200H Germany (0.7 cm diameter Ti horn, 140W, 23 kHz).

2.3. Preparation of CuS nanoparticles

At room temperature, 0.379 g copper acetate (Cu(CH₃COO)₂ .H₂O) and 0.150 g of TAA (CH₃CSNH₂) were added to 1 ml of the ionic liquid, [EMIM][EtSO₄], and 1 ml of double distilled water in a small beaker imposed to ultrasonic irradiation for 7 min. The titanium tip of the horn was immersed directly in the reaction solution. The formed dark brown color suspension was centrifuged to get the precipitate out and washed two times with double distilled water and ethanol respectively to remove the unreacted reagents. In order to investigate the effect of both solvents and irradiation of ultrasound on the properties of the products, two more comparative samples were prepared, keeping the reaction parameters constant except that in one of the samples, the solvent is 2 ml of water and in the other, the solvent is again the mixture of 1ml ionic liquid and 1 ml of water and the products are prepared at continuous stirring for 24 h without the aid of ultrasonic irradiation. Therefore, synthesis procedure was similar to the typical process described above, except for some changes in the solvents and elimination of ultrasound irradiation. Comparing the yield of the samples, the production yield of the sample prepared in ionic liquid and water that imposed to ultrasound irradiation is considerably higher.

3. Results and discussion

The XRD pattern of the as-prepared CuS nanomaterials arranged in three different ways, (i.e. ionic liquid and water (uppermost curve), in ionic liquid and water with the aid of USI (middle curve) and in water (downmost curve)) is depicted in Fig.1. The diffraction peaks correspond to (102), (103), (006), (105), (110), (108) and (116) planes of hexagonal covellite type CuS crystal system (ICSD reference code: 75-2234). It is clear from the figure that all products have the same cubic crystal structure and the peak broadening in the pattern indicates the CuS nanoclusters formed are very small in size. Very weak diffraction peaks appeared in synthesis of CuS samples in water as solvent demonstrates that as-

prepared nanostructures in absence of the RTIL hardly form the well-layered structure. Then, presence of the RTIL for formation of crystalline CuS is essential. In addition to identify the crystalline phase, the XRD data were also used to estimate the size of the constituent crystallites by the Scherrer's method. The average particle size, D, was determined using Scherrer's equation [48]

$$D = K \lambda /(B \cos \theta)\qquad(1)$$

where λ is the wavelength of X-ray radiation (0.15406 nm), K the Scherrer constant ($K = 0.9$), θ the characteristic X-ray radiation ($\theta = 24.16^\circ$ or $2\theta = 48.32$) and B is the full-width-at-half-maximum of the (110) plane (in radians). The particle size obtained accordingly is 12 nm.
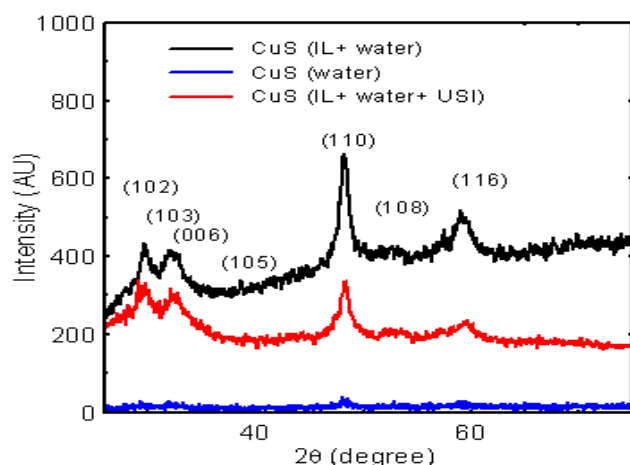

Fig. 1. The powder XRD pattern of as-prepared CuS nanoclusters prepared in the ionic liquid and water (1:1 in volume) (uppermost curve), in ionic liquid and water with the aid of USI (middle curve) and in water (downmost curve).
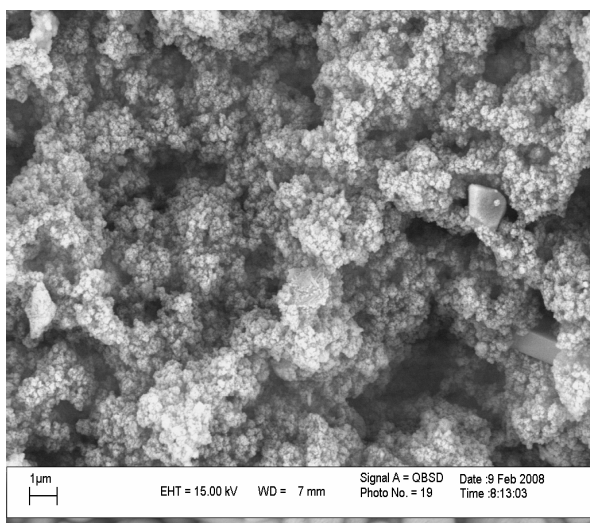

Fig. 2. The SEM image of the as-prepared CuS nanoclusters prepared in water without USI at magnification of 12 k.
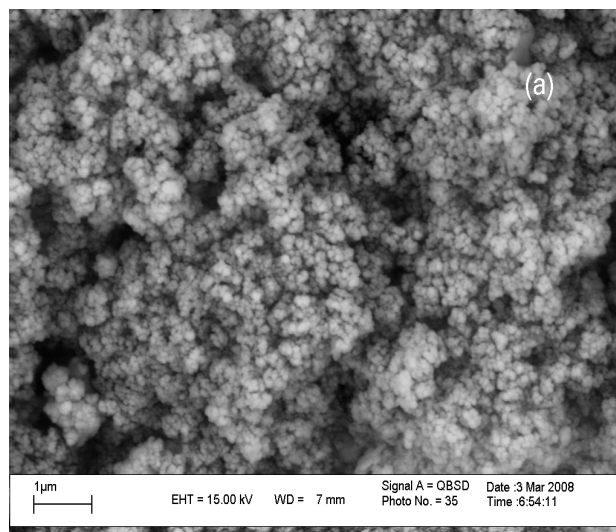

Fig. 3(a). The SEM image of the as-prepared CuS nanoclusters prepared in the ionic liquid and water (1:1 in volume) without USI at magnification of 30 k.
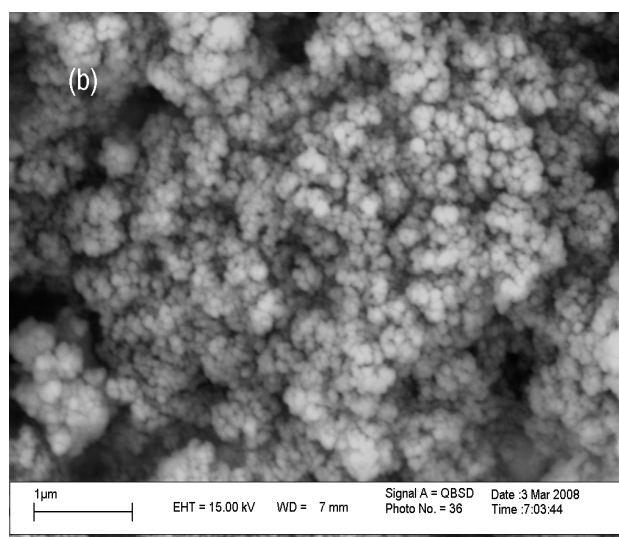

Fig. 3(b). The SEM image of the as-prepared CuS nanoclusters prepared in the ionic liquid and water (1:1 in volume) without USI at magnification of 50 k.

The morphology of the CuS nanoclusters prepared in the three different ways was investigated by scanning electron microscope (SEM) which their records at different magnifications are shown in Fig. (2-4). It is evident from the Fig. 2 that the structure of the particles produced in water as solvent, is highly polydispersive nanoclusters possessing irregular shapes and the range of cluster dimensions are broad. In comparison, the sample prepared in ionic liquid and water (Figs. 3(a) and 3(b)), is somehow monodispersive nanoclusters possessing approximately regular spherical shape. In comparison to the previous samples, the CuS nanocrystallites formed in aqueous solution of the ionic liquid with the aid of USI is highly monodispersive of spherical nanoclusters (Figs 4a

and 4b). The purity and composition of the products was studied by energy dispersive X-ray spectroscopy (EDX) and is displayed in Fig. 5. The curve reveals the presence of Cu and S peaks and the average atomic percentage ratio of Cu:S are about 39:61, 14:86 and 64:36 for the structures prepared in water, ionic liquid plus water and ionic liquid plus water with the aid of USI, respectively. Other peaks in this figure correspond to gold, palladium and silicate which are due to sputter coating of glass substrate on the EDX stage and were not considered for elemental analysis of Cu and S.

presented. TAA has a strong coordination ability to combine with transition metal ions; metal complex consequently forms and then dissociates to form metal chalcogenide [49, 50]. The formation of CuS nanoparticles may be expressed by the following equations:

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3COONH_4 + H_2S\uparrow \qquad (2)$$

$$Cu(CH_3COO)_2 . H_2O + H_2S \rightarrow CuS\downarrow + 2CH_3COOH + H_2O \qquad (3)$$
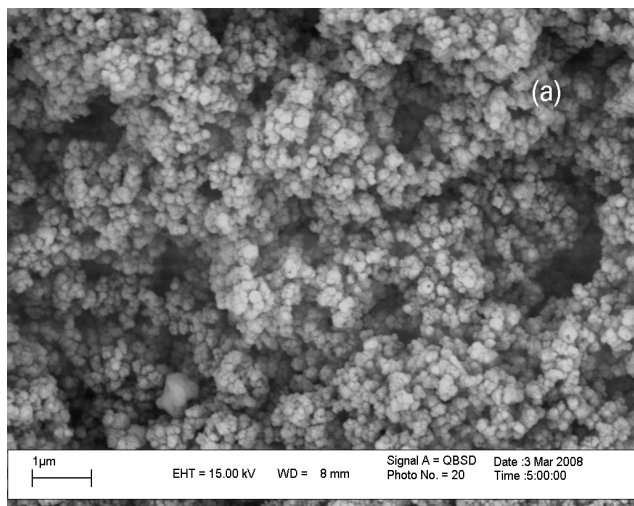

Fig. 4(a). The SEM image of the as-prepared CuS nanoclusters prepared in the ionic liquid and water (1:1 in volume) with the aid of USI at magnification of 30 k.
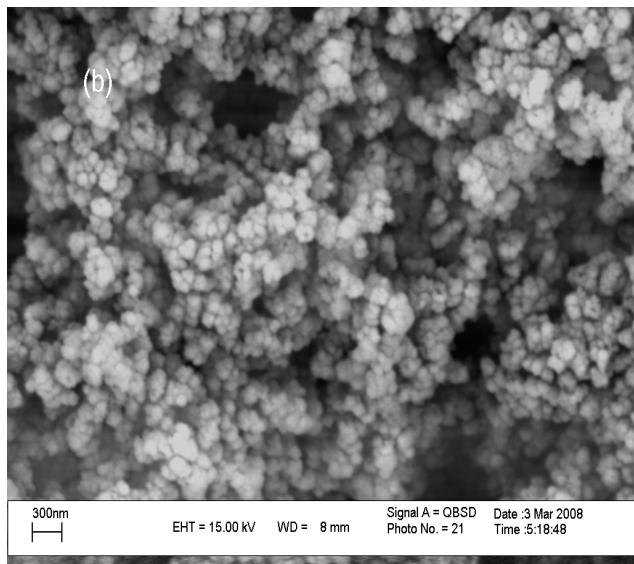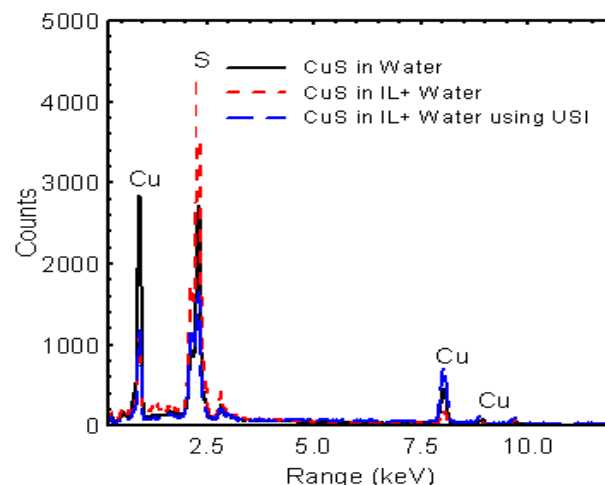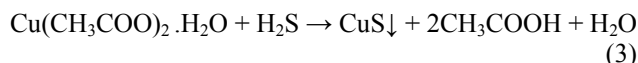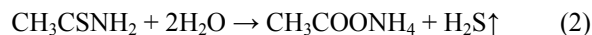

Fig. 5. The EDX pattern of the as-prepared CuS nanoclusters prepared in three different conditions.

Fig. 4(b). The SEM image of the as-prepared CuS nanoclusters prepared in the ionic liquid and water (1:1 in volume) with the aid of USI at magnification of 50 k.

Based on the experimental results, a possible formation mechanism of the CuS nanoclusters in aqueous solutions of the ionic liquid using ultrasonic irradiation is

As the Gibbs free energy of the surface is usually very high due to the large surface/volume ratio and the existence of dangling bonds, freshly formed nanostructures have a tendency to randomly aggregate until they become stable. For this reason, the morphology of the nanostructures produced in water as solvent, is highly polydispersive nanoclusters possessing irregular shapes and the range of particle dimensions are broad. When aqueous solutions of an ionic liquid is used as a reaction medium, the solute can be solvated by ions, thus, the reaction proceeds in an environmentally different from that when water or ordinary organic solvents are used. RTILs form extended hydrogen-bond systems in liquid state and are therefore highly structured [51]. The RTIL, [EMIM][EtSO$_4$], consists of [EMIM]$^+$ cations and [EtSO$_4$]$^-$ anions. The imidazolum ring is an electron-withdrawing group and it can attract the electron pair shared by hydrogen and carbon of position 2 of imidazolum ring [27], thus the hydrogen-bonding between the RTIL and sulfide moieties of CuS nuclei is strong [52]. Also, [EMIM]$^+$ cations can combine with sulfide moieties of CuS nuclei through electrostatic attraction [52]. In aqueous solutions of the ionic liquid, dissociation of the copper acetate gives rise to solvated metal cations, along with the acetate anions. Reaction of the metal cations with the sulfide anions gives rise to metal chalcogenide. As soon as the metal chalcogenide nuclei are formed, they get

coated by the RTIL, thereby producing a control on the growth. Meanwhile, the activities of freshly generated CuS surface will be greatly inhibited by $[EMIM]^+$ ions, so the anisotropic growth of the CuS crystals will markedly be modified. In absence of RTIL, small CuS particles grow randomly and eventually form CuS aggregates with different size. When the experiments are performed in the presence of ultrasound, some active sites can be uniformly produced on CuS nanoparticles surrounded by $[EMIM]^+$ ions to enhanced mobility triggered by the irradiation of ultrasound [53]. Thus CuS particles can preferably grow on these active sites and finally lead to CuS nanoclusters. Then, hydrogen-bonding interactions formed between the hydrogen atoms at position-2 of the imidazolium ring and the sulfide ions of CuS crystal cores and electrostatic interactions between them, may act as an effective bridge to connect the produced nuclei of copper sulfide and cations of the ionic liquid, playing a crucial role for the monodispersed CuS nanoclusters growing.

4. Conclusions

Ultrasonic-assisted aqueous room temperature ionic liquid (UARTIL) method was proposed for preparation of small size and monodispersed pure crystalline CuS nanostructures. This room-temperature and environmentally benign green method is fast and template-free which remarkably shortens synthesis time and avoids the complicated synthetic procedures. The strategy presented in this work is expected to prepare other transition metal sulfide nanomaterials. In this method, aqueous solution of the RTIL can act as solvent for reactants and morphology templates for the products at the same time, which enable the synthesis of inorganic materials with novel and improved properties.

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