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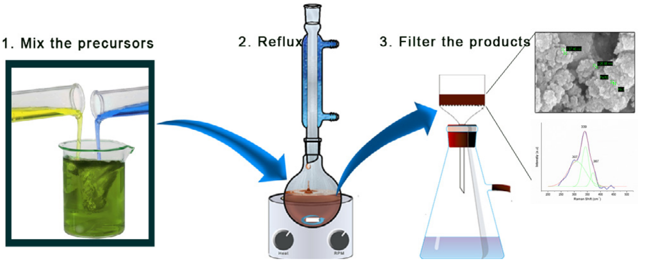
Aqueous based reflux method for green synthesis of nanostructures: Application in CZTS synthesis

Sai Kiran Aditha *, Aditya Dileep Kurdekar, L.A. Avinash Chunduri, Sandeep Patnaik, Venkataramaniah Kamisetti

Nanoscience Laboratory, Department of Physics, Sri Sathya Sai Institute of Higher Learning, Prasanthinilayam, 515 134 AP, India

GRAPHICAL ABSTRACT



ABSTRACT

The aqueous based reflux method useful for the green synthesis of nanostructures is described in detail. In this method, the parameters: the order of addition of precursors, the time of the reflux and the cooling rate should be optimized in order to obtain the desired phase and morphology of the nanostructures. The application of this method is discussed with reference to the synthesis of CZTS nanoparticles which have great potential as an absorber material in the photovoltaic devices. The highlights of this method are:

- Simple.
- Low cost.
- Aqueous based.

* Corresponding author.
E-mail address: saikiranaditha@sssihl.edu.in (S.K. Aditha).

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A R T I C L E I N F O
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Method overview

There exist many methods to prepare nanostructured materials with various sizes and shapes. These methods can be broadly categorized into vacuum based and non-vacuum routes. The vacuum based methods include sputtering [1], vacuum deposition [2], thermal evaporation [3], etc. The non-vacuum routes that are employed are electrodeposition [4], solution processing [5]. The vacuum based techniques are energy intensive requiring high vacuum and temperatures, thereby indirectly increase the effective cost. Most of these non-vacuum methods use toxic chemicals and organic solvents that are harmful to the environment. Therefore aqueous based methods that are easily scalable are highly desired.

The aqueous based reflux method is a simple, low cost method that gives the desired product with precise control over reaction parameters. This method has been used to synthesize various nanostructured materials such as nanoparticles [6], nanowires [7], nanorods [8], nanourchins [9], core–shell nanostructures [10], hierarchical nanostructures [11]. In this method the energy necessary for the reaction is supplied by heating the reaction solution over long periods of time. Through this method one can control the size, morphology and crystallinity of the materials by varying parameters such as the reaction time, concentration of precursors and the type of solvent employed [12,13]. In this method, the parameters: the order of addition of precursors, the time of the reflux and the cooling rate should be optimized in order to obtain the desired phase and morphology of the nanostructures.

The order of the addition of precursors: In the case of reactions where multiple precursors are involved the order of reaction plays an important role. If the product is quaternary like CZTS then the chance of formation of secondary phases is very high. Therefore it is necessary to identify the various secondary phases that could form, find out the reactivity's and their formation energies. If one of the binary compounds is more stable than the others then such a reaction should be avoided. Thus the desired phase can be obtained by carefully choosing the order of the precursors.

The time of the reflux: After the initial nucleation, grain growth takes place and simultaneously the phase formation also takes place. If the reaction is stopped early, then there will be incomplete phase formation. On the other hand the increase in the time of reaction leads to a larger grain size and hence bulk crystals will be obtained. Therefore the time of reflux should be optimized in order to obtain a pure phase nanostructure.

The cooling rate: Many times this parameter is overlooked but it is an important factor. A reaction could be arrested by a rapid decrease in the temperature. At higher temperatures the kinetic energies of the molecules is high and the nucleation species are very mobile in the reaction system. As the reaction cools down, the mobility decreases and the product becomes stable. Slow cooling rate leads to defect free particles whereas rapid cooling of the solvated ions will end up in the formation of defective crystals.

CZTS (Copper Zinc Tin Sulfide), a quaternary chalcogenide, is an upcoming material with applications in photovoltaics as an absorber. It has an optimum bandgap of about 1.5 eV, and a high absorption coefficient of the order $10^4\,cm^{-1}$ [14]. The raw material costs of leading solar cell technologies are presented in Table 1. Clearly CZTS is an order of magnitude lesser in price compared to the other materials [15].

In this article we report the use of reflux method for the synthesis of CZTS nanoparticles.

The equilibrium equation of CZTS formation as reported in the literature [16] is

$$Cu_2S + ZnS + SnS_2 \leftrightarrow Cu_2ZnSnS_4$$

The formation of the binary sulphides is favourable at higher temperatures whereas at lower temperatures the equilibrium shifts towards the right hand side. Therefore the recrystallization of CZTS depends on the cooling rate.