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Hydrothermal synthesis of nanostructured CuS for broadband efficient optical absorption and high-performance photo-thermal conversion

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ABSTRACT

Solar photo-thermal conversion is the simplest way to utilize solar energy by using nanofluid as the working medium. In this paper, we aim to investigate the broadband optical absorption and high-performance photo-thermal conversion via CuS nanofluids to realize the efficient solar energy utilization. Nanostructured CuS nanospheres and nanotubes were successfully synthesized by using simple hydrothermal reaction. The crystal structures, element compositions and surface properties of the obtained CuS nanostructures were characterized. And the formation mechanisms of the nanostructured CuS were discussed. The optical absorption and photo-thermal conversion performances of the CuS nanofluids based on water were studied. The UV/Vis/NIR absorption spectra tests show that the CuS nanofluids prepared have strong optical absorption in both visible light and near infrared light regions. The photo-thermal conversion results indicate that the CuS nanofluids possess good photo-thermal conversion performances, and the maximum temperature of the nanofluid reaches about 72.15 °C only with the volume fraction of 0.02% related to the nanotube nanofluid. Moreover, at the same volume fractions, the nanotube nanofluids show better photo-thermal conversion performances than those of the nanosphere nanofluids. This implies a simple approach to enhance photo-thermal conversion for efficient solar energy utilization.

1. Introduction

Energy is the basis for survival and development of the human beings. However, the combustion of traditional fossil fuels not only aggravates the energy crisis but also causes serious environmental pollution. Therefore, the exploration of clean and renewable energy and the improvement of energy utilization efficiency have become important development strategies for many developed countries [1]. Among so many energy sources, solar energy is the most ideal energy due to its simple and extensive source and without any harm to the environment. Thus, how to efficiently absorb and utilize solar energy has become a focus for many researchers [2–4].

Solar photo-thermal conversion is the simplest way to utilize solar energy by using absorption device to convert solar energy directly into the heat energy [5–7]. In 1970s, Abdelrahman et al. [5] proposed a black liquid solar collector, and different from traditional surface-type absorption, the collector absorbed solar radiation directly by means of the working fluid, thus the heat loss which transferred from the absorbing surface to the heat working medium could be greatly reduced. As for nanofluid formed by the stable dispersion of nanoparticles in base liquid, the capture and absorption ability on the incident light will be enhanced due to the enhancement of light scattering from the nanoparticles and the increment of light path of the photon [8,9]. Moreover, the direct solar absorption via nanofluid makes the heat transfer process simplified, the thermal resistance reduced, and is conducive to the uniform distribution of temperature. Therefore, the direct absorption technology based on nanofluid as a new type of heat collection method has attracted widespread attentions [8,10,11]. For example, Wang et al. [9] studied the optical absorption and photo-thermal conversion properties of the CuO/H_2O nanofluid, and they found that the CuO/H_2O nanofluid showed good photo-thermal performance under the 635 nm visible light irradiation. Otanicar et al. [12] examined the photo-thermal conversion performances of three different nanofluids (carbon nanotubes, graphite and silver), and by controlling the sizes, shapes and volume fractions of the nanoparticles, an efficiency improvement up to 5% was obtained by using nanofluids as the absorption media. Amjad et al. [13] investigated the volumetric solar heating and steam generation via gold nanofluids under a concentrated solar flux of 280 suns, and they found that an enhancement in the energy efficiency of about 95% over the base fluid was achieved for only 0.04 wt% gold

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nanofluids. Chen et al. [14] studied the effect of the mass fractions on optical absorption and photo-thermal conversion performance of the graphene oxide/water nanofluids, and the results showed that the photo-thermal performance of the graphene oxide/water nanofluids increased with the mass fractions of graphene oxide increasing from 0.001% to 0.02%, but decreased with the further increase in mass fractions from 0.02% to 0.1%.

It should be noted that the optical absorption of the most reported mono-component nanofluids is mainly in the visible light region, and it is difficult to achieve broadband spectrum utilization of the solar energy. However, as is known to all, the near infrared light takes about 42% of the total solar radiation energy [7], thus it is attractive to regulate the absorption of the nanofluids in both visible and near infrared regions so as to more effectively improve the photo-thermal conversion performance. To achieve this goal, great efforts have been carried out to prepare nanofluids containing nanoparticles with special compositions, morphologies and structures. Duan et al. [15] numerically simulated the light absorption and the photo-thermal performance of a direct solar thermal collector containing SiO_2 @Au nanoshell-based nanofluid. They found that the light absorption could be effectively enhanced via the plasmonic effect, and the nanoshells nanofluid achieved an equal temperature rise at very low volume fraction, which was only 1/5 of the Au nanofluid. Wang et al. [16] prepared an composite combining hedgehog-like hierarchically structured ZnO particles (HPs) and plasmonic gold nanoparticles (Au NPs). By using the composite ZnO-Au/oil nanofluid, the broadband-absorbing was realized and the photo-thermal conversion efficiency reached 58% at the concentration of 1.0 mg/mL under a solar irradiation power of 10 kW/m^2. Rativa et al. [17] studied the linear optical absorption in the visible and near infrared spectral region of aqueous nanofluids containing Au and Ag nanoellipsoids (NEs), and the results showed that a solar weighted absorption coefficient close to the ideal solar radiation absorber condition could be obtained by tuning the geometry of the metallic NEs. Fan et al. [18] presented a strategy to enhance the solar absorption properties of graphene nanofluids utilizing the Sn@SiO_2 @Ag core-shell nanoparticles, and they found that the solar absorption performance could be enhanced 2.9 times by only using the 0.4 mg/mL graphene-embedded Sn@SiO_2 @Ag nanofluids. Chen et al. [7] investigated the complementary optical absorption and enhanced solar thermal conversion of CuO-ATO nanofluids, and the combination of CuO and ATO nanoparticles endowed the two-component nanofluids with broadband absorption across the visible and near infrared regions.

Nanofluids containing these multi-component sophisticated nanostructures have showed excellent broadband optical absorption almost close to the solar radiation spectrum. However, they still suffer so many difficulties in stability and large-scale production for the sophisticated structures. In addition, the high cost caused by the use of noble metals is also a drawback to be considered. Therefore, the new strategies to prepare nanofluids containing nanoparticles with stable structure and low cost have become so desired for the researchers.

Copper sulfide (CuS) is a kind of narrow band gap semiconductor material widely used in solar cell [19], solar thermal-conversion [20], lithium battery [21], non-linear optical material [22], and so on. Due to their unique microstructure and size effects, CuS nanocrystals show excellent electrical, optical and magnetic properties, thus the studies on preparation, structures and properties of the CuS nanocrystals have attracted wide attentions for the materials scientists [23,24]. Cu^{2+} can occur d-d energy level transition in a relatively independent environment and the localized surface plasmon resonance (LSPR) will arise from the oscillation of the valence band free carriers in CuS nanocrystals, which makes the CuS nanocrystals have strong absorption in both visible light and near infrared light regions [20,25,26], thus CuS nanocrystals can be expected to have excellent photo-thermal performance. Attractively, CuS also has the advantages of low cost, good chemical stability and low toxicity [20,27]. Therefore, it is of great significance to study the photo-thermal conversion properties of the CuS nanomaterials. CuS nanomaterials can be prepared by several methods, and they are including hydrothermal synthesis [23,27], solvothermal synthesis [28], template synthesis [29], electrodeposition synthesis [30], etc [31,32]. Since the nanomaterials obtained by hydrothermal synthesis possess high purity and good crystalline, and the preparation process is relatively simple, hydrothermal synthesis becomes the first choice to prepare the CuS nanomaterials for many researchers [23,27,33].

Therefore, this work attempts to investigate the broadband optical absorption and photo-thermal conversion properties of the CuS nanofluids based on water. Firstly, nanostructured CuS nanospheres and nanotubes were prepared via simple hydrothermal synthesis method. For the as-prepared CuS nanostructures, experimental measurements on crystal structures, element compositions and surface properties were conducted by using XRD, SEM, TEM, EDS and BET. And the possible formation mechanisms of the nanostructured CuS were discussed. Then the optical absorption and photo-thermal conversion of the CuS nanofluids with different volume fractions based on water were studied.

2. Experiment

2.1. Preparation of the CuS nanostructures

The nanostructured CuS nanospheres and nanotubes were prepared by using the simple hydrothermal synthesis reaction [23,33,34]. The preparation process was illustrated in Fig. 1, and the specifics were as follows. Firstly, accurately measured stoichiometric ratio of 1:1 of the sodium thiosulfate ($Na_2S_2O_3$) and copper sulfate ($CuSO_4$) aqueous solutions with molar concentrations of 0.125 M and 0.5 M in 80 mL and 20 mL deionized water was prepared, respectively. The resultant solutions were then transferred into 100 mL Teflon lined stainless steel autoclaves, sealed and maintained at 180 °C for 12 h. Subsequently, the obtained dark colored precipitates were washed respectively with deionized water and ethanol for 3 times. After centrifugation, the products were dried at 80 °C for 4 h, and finally the CuS nanospheres and nanotubes were obtained, respectively.

2.2. Preparation of the CuS nanofluids

The CuS/water nanofluids were prepared as follows [9,14]. At first, a certain amounts of the two different CuS samples were dispersed with 100 mL deionized water. To obtain stable fluids, the dispersant hexadecyl trimethyl ammonium bromide (CTAB) with an appropriate concentration was added to each of the nanofluids, followed by ultrasonically vibration for about 30 min. Then the nanofluids containing 0.02% volume fraction of the CuS nanomaterials were obtained. The

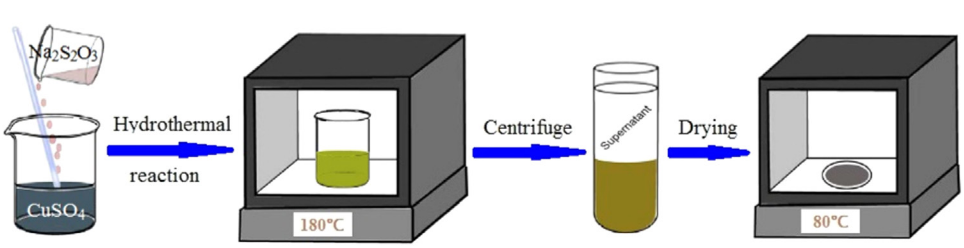

Fig. 1. The process flow for the preparation of nanostructured CuS.