PHOTO-THERMAL AND OPTICAL PROPERTIES OF VARIOUS SAMPLES PREPARED AS CANDIDATE OF NIR ABSORBING MATERIAL

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Abstract - As demand for energy saving increases, interest in window films with solar energy shielding performance is increasing. Window film performance required in the market is high visible light transmittance and infrared ray blocking performance. Near-infrared (750 to 1400 nm) energy is considerable in the infrared region of the solar spectrum. So, it is most efficient to block near infrared rays for shielding solar energy. Plate-like CuS and Ag nanoparticles were prepared by a facile aqueous solution method and characterized by transmission electron microscopy, field emission scanning electron microscopy, powder X-ray diffraction, UV-Vis-NIR spectroscopy, and energy-dispersive X-ray spectroscopy. The CuS films showed strong absorbance in the NIR region and moderate visible transmittance when mixed with PVA. Plate-like CuS nanoparticles were thus found to display great potential as NIR-shielding materials and good photo-thermal efficiency.

Keywords - Nanoplate, CuS, Silver, Visible-NIR.

I. INTRODUCTION

The development of solar-shielding thin films for windows of buildings and automobiles is highly desirable in order to reduce the energy consumption since windows are the main sources of light and heat losses in buildings and automobiles. Solar energy from the invisible solar spectrum comprises more than 50% of the solar energy. Materials and coatings able to shield invisible NIR radiation and allow the transmittance of visible light are consider ideal for glazing and coating window glass. Recently, copper sulfide nanocrystals have been shown to possess strong NIR absorption due to their localized surface plasmon resonance (LSPR) arising from the oscillation of the valence band free carriers (positive holes) of this material.[1] Copper sulfide is a cost-effective material composed of earth abundant elements, making it a suitable alternative for Cs_xWO_3, noble metals, indium tin oxide (ITO), antimony-doped tin oxide (ATO), and gold for solar shielding and photo-thermal applications.

CuS nanomaterials can by synthesized with various morphologies, such as nanoflakes, nanotubes, nanowires, or nanoplates , by different synthetic strategies employing reagents such as Triton-X 100, dodecanethiol, or ammonium O,O' -dialkyldithiophosphate.[2-8] Aqueous reactions are the most desirable ones, as they can be performed at low temperature and are easy to scale-up. Recently, the development of copper sulfide synthetic procedures with biomolecules as stabilizers has gained increasing attention. These synthetic methods provide high efficiency under mild reaction conditions.

We report the facile aqueous synthesis of CuS nanoplate-like particles using Radix Puerariae extract. The solar-shielding properties of CuS nanoplate-like particles were investigated by coating glass slides with thin films of these particles. The solar-shielding properties of thin films of CuS mixed with a PVA matrix were studied. The photo-thermal efficiency of the copper sulfide nanoparticles was also examined.

II. EXPERIMENTAL

2.1. Synthesis of CuS nanoparticles

In a typical reaction, 2 mL of a 50 mM copper sulfate ($CuSO_4 \cdot 5H_2O$) solution and 1 mL of Radix Puerariae root extract were mixed together in a vial. The mixture was magnetically stirred for 5 min at room temperature. An ammonia sulfide solution (50 µL, 20 wt%) was added to the vial and mixed thoroughly. Then, the pH of the solution was increased to 9 by adding a 100 mM sodium hydroxide solution. The reaction was maintained at 60 °C under magnetic stirring for 10 h. After cooling the glass vial, the solution was centrifuged at 12,500 rpm for 9 min three times and then washed with distilled water. The separated solid was dried at 60 °C for 5 h, and the dry powder was stored for further use.

2.2. Preparation of CuS thin films

For the preparation of CuS thin films, 2 mL of distilled water and 1 mg of additive BYK 2000 were mixed in a glass vial and magnetically stirred for 5 min. Then, different amounts of CuS nanoparticles (10, 20, 30, and 40 mg) were added. The mixtures were sonicated for 10 min and stirred magnetically for 20 min. The solutions were used as 0.5, 1.0, 1.5, and 2 wt% coatings on glass

slides (76 × 26 × 1 mm^3). The glass slides were washed several times with distilled water, then with acetone, and left to dry. Copper sulfide was coated on the glass slides with a bar coater and, after coating, the glass slides were placed in an oven for 10 min at 60 °C. The optical characteristics of the CuS thin films were analyzed by UV-Vis-NIR spectroscopy.

2.3. Preparation of CuS/ PVA thin films

CuS/PVA thin films were prepared similarly by adding PVA. In a glass vial, the required quantity of distilled water was heated to 80 °C for 30 min, 5 wt% PVA was added, and the mixture was then stirred for 3 h at the same temperature. For the preparation of films, 10, 20, 30, and 40 mg of CuS was added to 2 g of water.

III. RESULTS AND DISCUSSION

3.1. Characterization of CuS nanoparticle

CuS nanoparticles were synthesized in aqueous solution by reacting copper sulfate and ammonia sulfide in the presence of Radix Puerariae root extract at 60°C for 10 h. The TEM and SEM images of a CuS sample after 10 h of reaction are presented in Fig. 1, showing irregular plate-like structures ranging from 10 to 250 nm in size. In the SEM image, it can be observed that the plate-like structures are assembled and interlaced with each other.

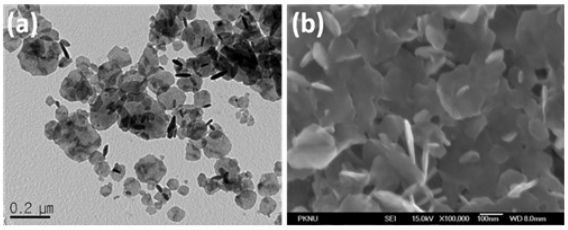


Fig. 1. (a) TEM and (b) SEM images of CuS sample.

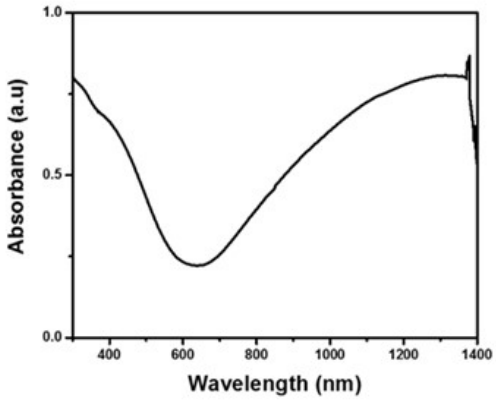


Fig. 2. UV-Vis-NIR spectrum of CuS sample.

The UV-Vis-NIR spectrum of the as-synthesized copper sulfide was recorded on a UV-Vis spectrophotometer, as shown in Fig. 2. The absorption spectrum shows low absorption in the visible region, suitable for the transmittance of visible light. An absorbance peak is located near 1300 nm. The absorption of the CuS sample is high in the NIR region, arising from the localized surface plasma resonance of valence-band free carriers. The transmittance of visible light and the absorbance in the NIR region spectrum makes the CuS material a suitable candidate material for NIR-shielding thin films and as a photo-thermal agent for cancer therapy.

3.2. NIR-shielding characteristics of CuS thin film

Copper sulfide thin films were prepared by coating different amounts of plate-like CuS nanoparticles on glass slides by the simple doctor-blade method. This method is easily scalable for the mass production of thin film-coated glass and is also highly cost-effective. Fig. 3(a) shows the transmittance spectra of the CuS thin films prepared with different amounts of CuS nanoparticles. The 0.5 wt% CuS thin film transmits more than 50% of the visible light in the range of 400–750 nm and presents slightly lower transmittance in the region of 800–1400 nm and of ~60% in the range of 1400–2500 nm. This indicates negligible shielding of NIR radiation. The 1 wt% CuS thin film presents low transmittance of about 40–50% in the region of 800–1400 nm. The transmittance in the 1400–2500 nm region is slightly higher. This indicates moderate shielding of NIR radiation but the transmittance of visible light is also low. The thin films with 1.5 wt% and 2 wt% CuS exhibited a similar tendency with transmittance values below 0.05% and 1%, respectively. From the spectral transmittance, it can be concluded that the CuS nanoplate-like structures display reduced transmittance in the region of 800–1400 nm. However, above 1500 nm, the transmittance of NIR radiation is high, indicating that the shielding properties of CuS nanoplate-like structures are not suitable for coating windows, although they can significantly shield NIR radiation in the range of 800–1400 nm, compensating thus the visibility.

CuS/PVA thin films were then prepared on glass slides with a PVA coating and different amounts of plate-like CuS nanoparticles. The transmittance spectra of the CuS/PVA films are shown in Fig. 3(b), which are clearly different that those of the CuS thin films. The transmittance spectrum of the 0.5 wt% CuS/PVA thin film shows a transmittance of 80% in the NIR region. The transmittance spectrum of the 1 wt% CuS/PVA thin film shows a transmittance of ~60% in the range of 800–1500 nm and of ~70% at 2000–2500 nm. The transmittance spectrum of the 1.5 wt% CuS/PVA thin film shows transmittance values of 40–50% in the 800–1500 nm range and below 20% in the 800–1500 nm range, indicating good solar-shielding properties and moderate transmittance of visible light. In conclusion, this CuS/PVA thin film meets the optimal conditions for solar shielding. The transmittance spectrum of the 2 wt% CuS/PVA thin film shows very good shielding properties below 10% in the NIR region

of 800–2500 nm. However, the visible transmittance of the film is very low, 20–30% in the 480–800 nm region.

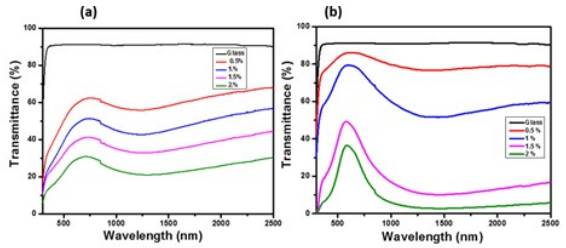


Fig. 3. UV-Vis-NIR spectra of (a) CuS thin films and (b) CuS/PVA thin films.

3.3 Photo-thermal properties of CuS nanoparticle

The photo-thermal conversion efficiency of solutions containing different amount of CuS plate-like nanoparticles was investigated under laser irradiation (530 nm, 16.5 mW/cm^2). Fig. 4 shows that the temperature of a 20 wt% CuS solution under irradiation increased from 23 to 42°C in 600 s, while the temperature change for pure water was minimum, i.e., 2.8°C, under the same conditions. The changes in the temperature increased with the increasing amount of CuS in the solution. These results demonstrate that the CuS plate-like nanoparticles can effectively convert laser energy into heat.

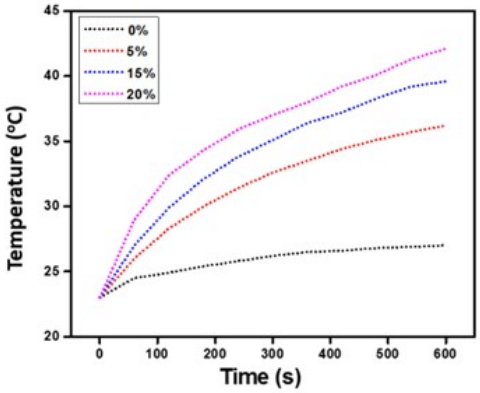


Fig. 4. Temperature change of solutions containing different amounts of CuS nanoparticle under laser irradiation at 530 nm and power of 16.5 mW/cm^2.

3.4 Solar-shielding efficiency of CuS/PVA films in a sealed box

To analyze the solar shielding properties of the CuS/PVA thin films, a simulated solar irradiation experiment was performed. A sealed box was irradiated with simulated solar light through a glass window and the inner temperature was monitored with a digital thermometer. Fig. 5 shows the increment of the temperature in the sealed box upon irradiation. When blank glass was used as the window material, the temperature in the sealed box increased sharply from 22 to 47°C after 10 min. Conversely, when a CuS/PVA thin film-coated glass was used in the window, the temperature increased slowly to 35.2°C after 10 min. Such a difference in the temperature increase inside the sealed box suggests that CuS/PVA thin film-coated glass exhibits superior solar-shielding ability.

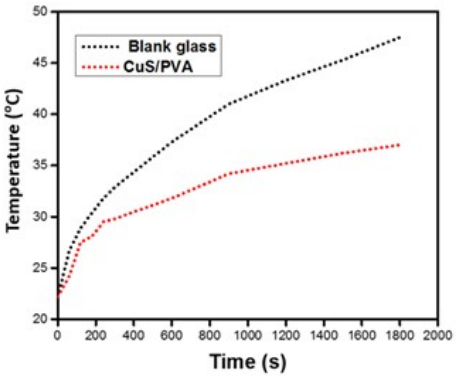


Fig. 5. Temperature variation in a sealed box upon irradiation with simulated solar light.

IV. CONCLUSION

In summary, we developed a simple low-temperature aqueous solution method to synthesize CuS nanoplate-like structures. The optical studies of the as-synthesized CuS nanostructures mixed with PVA coated on glass revealed excellent NIR-shielding properties. The high absorption of NIR light by the CuS nanoplate-like structures endows them with photo-thermal efficiency, and thus the nanostructures exhibit remarkable photo-thermal properties. A sealed box with a window coated with CuS/PVA showed low temperature elevation under simulated solar light irradiation. In conclusion, the as-synthesized CuS nanoplate-like structures are a promising candidate for low-cost solar-shielding semi-transparent materials and photo-thermal materials for cancer therapy.

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