

## Preparation and Optical Absorption Property of Poly(acrylic acid)/Copper Sulfide Nanocomposite Films

Yasuo GOTOH, Yutaka OHKOSHI, and Masanobu NAGURA

*Faculty of Textile Science and Technology, Shinshu University,  
3-15-1 Tokida, Ueda, Nagano 386-8567, Japan*

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Solar control materials are required in architectural glazing to reduce the heating of building interior under solar radiation in hot weather. In particular, blocking infrared ray properties are desirable to save energy during air conditioner use in buildings or cars.

Some copper compounds exhibit near-infrared absorption useful for solar control materials.<sup>1–5</sup> Copper sulfide, a p-type semiconductor in which copper atom vacancies act as acceptors,<sup>6</sup> has been frequently investigated due to its attractive optical and electrical properties.<sup>2,3,6–12</sup> Copper sulfide is generally represented as  $\text{Cu}_x\text{S}$  ( $x = 1–2$ ) because there are numerous stable and metastable species which have various compositions ranging between  $\text{Cu}_2\text{S}$  (chalcocite) and  $\text{CuS}$  (covellite).<sup>2,8</sup> The near-infrared absorption of  $\text{Cu}_x\text{S}$  significantly depends on composition as well as on electrical properties.<sup>2,6,7</sup> Most earlier papers have dealt with  $\text{Cu}_x\text{S}$  thin films coated on a glass substrate by vacuum evaporation<sup>2,7,8</sup> and chemical deposition.<sup>3,9,12</sup> However, with regard to practical application, these techniques are limited to the preparation of  $\text{Cu}_x\text{S}$  film on an industrial scale because the formation of  $\text{Cu}_x\text{S}$  layers on glass substrate requires large scale facilities.

Studies on organic–inorganic nanocomposites consisting of polymers doped with metal and semiconductor nanoparticles have increased because of optical properties; *e.g.*, nonlinear optical and laser amplification properties.<sup>13–16</sup> Matrices of organic polymers have the advantage of processability of composite materials in the forms of film and fiber compared with inorganic matrices such as glass or ceramics. We prepared such nanocomposites, *i.e.*, the poly(acrylic acid) (PAA)/copper metal nanoparticle composite films by reduction of the copper(II) salt of PAA in an  $\text{H}_2$  flow above 230°C.<sup>17</sup>

The present study describes a simple procedure for preparing composite films consisting of PAA and  $\text{Cu}_x\text{S}$  nanoparticles, and discusses optical absorption in terms of application of these films as solar control materials.

### EXPERIMENTAL

#### *Preparation of PAA- $\text{Cu}_x\text{S}$ Composite Film*

Acrylic acid (AA) and trimethylolpropane triacrylate (TMPTA) were used as monomers. TMPTA, which has three acryloyl groups in the molecule, functions as a crosslinking agent. The reason for using TMPTA is de-

scribed in the section of RESULTS AND DISCUSSION. 1-Hydroxycyclohexyl phenyl ketone was used as initiator. Composite films consisting of PAA and  $\text{Cu}_x\text{S}$  were prepared as follows: AA 6.840 g (90 mmol) and TMPTA 2.963 g (10 mmol) were mixed, and the initiator was added to the mixture. The mixture solution was spread on a glass plate and polymerized by UV irradiation at room temperature. The thickness of the PAA film was *ca.* 10  $\mu\text{m}$ . PAA films were subsequently immersed in 2 wt% copper(II) acetate aqueous solution at room temperature for 6 h and then placed in 5 wt% sodium sulfide nonahydrate aqueous solution at room temperature for 2 h. The composite obtained was represented by PAA- $\text{Cu}_x\text{S}$ .

#### *Measurements*

X-Ray diffraction (XRD) measurement was performed using a Rigaku Geigerflex 2028 diffractometer with Ni-filtered  $\text{Cu-K}\alpha$  radiation. Voltage and current of the X-Ray source were 40 kV and 150 mA, respectively. The ultraviolet-visible-near infrared (UV-VIS-NIR) absorption spectrum was recorded using a Hitachi U-3500 UV-VIS-NIR recording spectrophotometer. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2010 transmission electron microscope operated at 200 kV.

### RESULTS AND DISCUSSION

PAA is an anionic polymer and complexes with various metal ions. After immersing crosslinked PAA films in copper(II) acetate solution, the films changed from colorless to blue-green, indicating the formation of copper(II) salt of PAA.<sup>17</sup> PAA film 1 g reacted with 0.103 g copper(II) ions under the present conditions. Sulfuration of copper(II) ions by sodium sulfide proceeded quickly in solution. The color of the films changed to dark yellow within 30 min by immersion in sodium sulfide solution. In the absence of TMPTA, PAA films immersed in the sodium sulfide solution dissolved in water. Thus, some crosslinking agent is needed for the method in the present study.

Figure 1a shows the XRD of PAA- $\text{Cu}_x\text{S}$ . The pattern of  $\text{CuS}$  powder obtained by mixing aqueous solutions of copper(II) acetate and sodium sulfide is shown in Figure 1b for comparison. The compound in Figure 1b could be

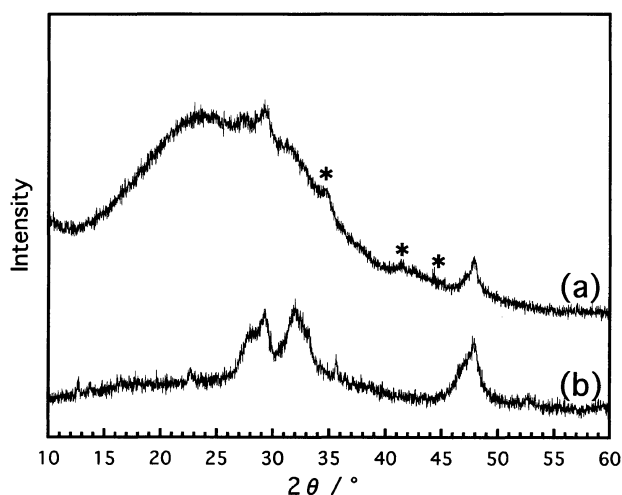


Figure 1. XRD of PAA-Cu<sub>x</sub>S (a), and CuS powder (b).

concluded covellite<sup>18</sup> based on 17 JCPDS files of copper sulfide allotropic forms. In Figure 1a, the large broad peak at 24° is shown, which is originated from scattering of amorphous PAA. Some crystalline peaks are observed between  $2\theta = 27$  and  $49^\circ$ . Most of the peak positions well agree with those of CuS powder. The peaks with asterisks could not be assigned to CuS. Therefore, some copper sulfides with different compositions may coexist in the composite. The phase diagram of the Cu-S system is very complicated,<sup>8</sup> and that copper sulfides having various compositions exist.<sup>7,8</sup> Peaks with asterisks could not be assigned based on 17 JCPDS files of copper sulfides, and thus accurate determination of the composition of the copper sulfide in the specimen from XRD measurement is extremely difficult.

Figures 2a and 2b show absorbance and transmittance of UV-VIS-NIR for PAA-Cu<sub>x</sub>S film, respectively. In Figure 2a, the composite film exhibits strong absorption in UV (below *ca.* 500 nm) and near-infrared (around 1250 nm) regions. The transmission curve in Figure 2b indicates UV below 400 nm to hardly be transmitted in the film, while over 90% of near-infrared between 900 and 2100 nm is absorbed. The wavelength of the transmittance maximum at *ca.* 600 nm is very close to 565 nm, which corresponds to maximum spectral sensitivity of the human eye.<sup>19</sup> PAA-Cu<sub>x</sub>S film is sufficiently transparent to the human eye in daylight, although transmittance at 600 nm is only 45%. Thus, PAA-Cu<sub>x</sub>S film is very useful and effective as a blocking filter of UV and near-infrared rays in sunlight. Absorption in the shorter wavelength region is due to interband transition from the valence band toward the conduction band in Cu<sub>x</sub>S, whereas absorption in the higher wavelength region is attributed to free carriers.<sup>2,7</sup> The wavelength of the absorption maximum for PAA-Cu<sub>x</sub>S at 1250 nm is almost consistent with that of the solid covellite calculated from diffuse reflectance data by Silvester *et al.*<sup>20</sup> The peak intensity of the phase which is different from covellite in the XRD profile of Figure 1 is relatively low. Thus, most of the Cu<sub>x</sub>S components in the composite may be considered covellite.

The dispersion state of Cu<sub>x</sub>S in composite film was observed directly by TEM. Figure 3 shows the TEM image

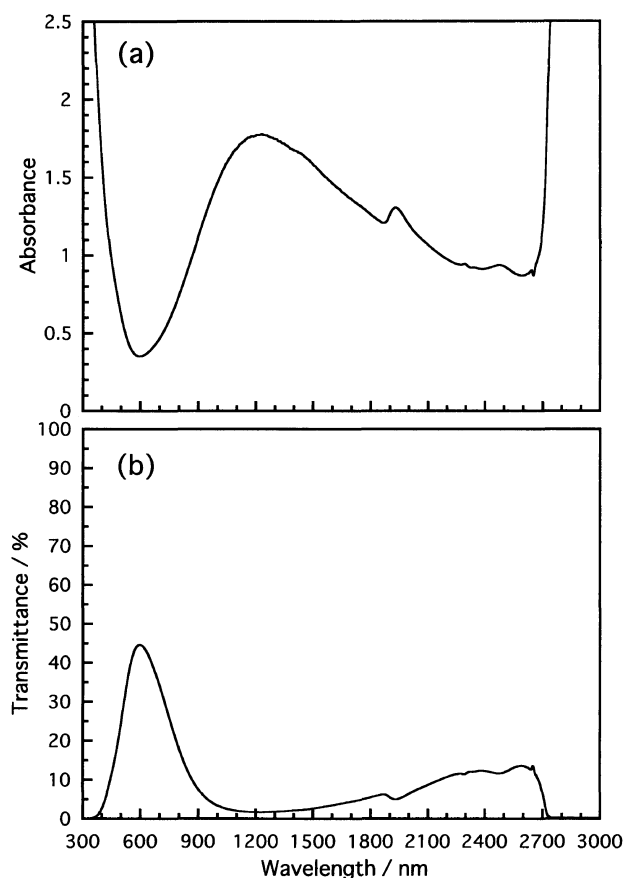


Figure 2. UV-VIS-NIR spectrum for PAA-Cu<sub>x</sub>S film ((a) absorbance, (b) transmittance).

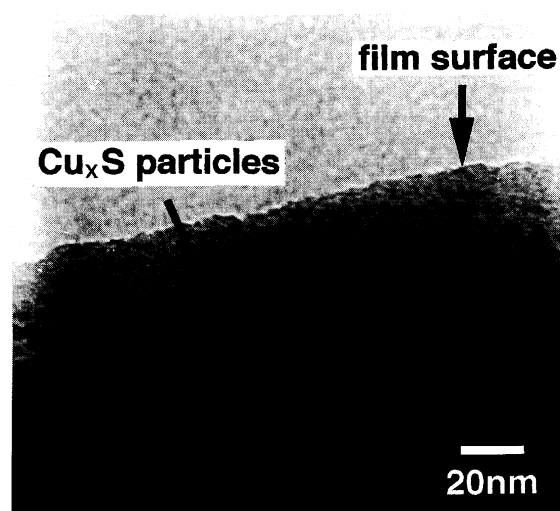


Figure 3. TEM image of a cross-sectional view of the edge of PAA-Cu<sub>x</sub>S film.

of the cross-sectional edge view of PAA-Cu<sub>x</sub>S film. Spherical Cu<sub>x</sub>S particles are dispersed in the composite film, and Cu<sub>x</sub>S particle diameter is from 2–5 nm, which is considerably small. Such small Cu<sub>x</sub>S particles do not scatter visible rays. Thus, PAA-Cu<sub>x</sub>S film is transparent in the visible region.

Semiconductor nanoparticles with radii smaller than the bulk exciton Bohr radius exhibit interesting size-

dependent optical properties.<sup>21,22</sup> The spectrum of copper sulfide is dependent on composition. The absorption maximum at NIR region shifts to the longer wavelength by reduction of copper(II) in Cu<sub>x</sub>S (*i. e.*, *x* of Cu<sub>x</sub>S increased).<sup>23</sup> Thus, optical absorption of PAA-Cu<sub>x</sub>S is affected by size and composition of copper sulfide particles. The spectra of PAA-Cu<sub>x</sub>S film was affected by certain treatments. The wavelength of the absorption maximum at 1250 nm increased with annealing temperature in air (*e. g.*, absorption maximum shifted to 1650 nm by annealing at 280 °C), and the absorption maximum at 1250 nm shifted to 1040 nm by storing in methanol at 60 °C, although the origin of the shift of the absorption maximum was not clarified. Optical absorption properties of PAA-Cu<sub>x</sub>S film may thus be controlled by changing the radius and composition of Cu<sub>x</sub>S particles, which is presently under investigation.

PAA-Cu<sub>x</sub>S is easily prepared and has sufficient absorbance to block most UV and near-infrared rays. The film is only 10 μm in thickness and is flexible, and thus can be easily handled (*e. g.*, transferred to a plate of glass or resin). Intensity and wavelength of optical absorption for PAA-Cu<sub>x</sub>S can be controlled by changing the thickness of PAA film, concentration of copper(II) acetate solution and immersion time, and heat treatment of PAA-Cu<sub>x</sub>S. PAA-Cu<sub>x</sub>S in this study was found effective not only for reducing interior heating under solar radiation but protecting human eyes against harmful near-infrared ray around 1000 nm.<sup>24</sup> PAA-Cu<sub>x</sub>S film thus has great potential as a solar control material.

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