

Preparation of uniform titania nanocoating on ZnS-based phosphors by a sol–gel process

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Abstract

A sol–gel process has been developed to coat micron-sized ZnS:Cu,Au,Al phosphors with a smooth and uniform layer of amorphous titania having nanosize thickness. The titania nanocoating is based on the hydrolysis and condensation of titanium tetrabutoxide $\text{Ti}(\text{OBU})_4$. Acetylacetone was used to decrease the reactivity of $\text{Ti}(\text{OBU})_4$. The experimental variables such as water concentration, the amount of ZnS particles, and reaction time were investigated. The thickness of the titania nanocoating was homogeneous and can easily be controlled from 20 to 54 nm by adjusting the experimental variables. The as-prepared titania nanocoating was amorphous phase and could be crystallized to anatase phase upon heating at 500 °C in Ar atmosphere.

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1. Introduction

In recent years, ZnS-based materials have been studied for use in field emission displays (FEDs) because of their high cathodoluminescent properties [1,2]. FEDs operate at low voltages and high current densities [3–5]. At low applied voltages, the electron penetration depth into phosphor particle is shallow and the phosphors exhibit lower luminescent efficiency due to the energy loss processes associated with the surface recombination. Thus it is necessary to use higher current densities to maintain the output luminance. However, the ZnS-based phosphors easily degenerate under high current densities, forming ZnO on the surface and releasing sulfur-based volatile gas into the vacuum.

In order to overcome these drawbacks, a possible way is to coat the surface of ZnS phosphor particles with a very thin oxide layer. The coating has to be transparent, hard, and highly resistant to moisture and chemical deterioration. In addition, the

photoluminescence intensity of phosphors has to decrease as little as possible. Although several coating materials such as SiO_2 [6,7], BaTiO_3 [8], In_2O_3 [9], Al_2O_3 [10], Y_2O_3 [11], etc. have been investigated, materials practically applicable to FEDs are still to be found. Titania is expected to be one of the candidates for the coating materials because it is a chemically stable, wide-band-gap semiconductor material [12–14]. A thin, uniform titania coating can offer stable protection to the ZnS cores from degradation and can passivate surface recombination centers to keep luminescent efficiency. In addition, by being invested with some electron conductivity, the semiconducting titania coating possibly reduce the charge-up damage of the phosphors during electron beam irradiation.

Up to now, titania has been coated on the surfaces of very small, nanosize colloidal particles of gold [15,16], silica [17,18], zinc oxide [19], Mn–Zn ferrite [20,21], etc. However, most of these titania coatings were irregular in shape and the coating thickness was difficult to control. Further, it seems to be quite difficult to synthesize a smooth, uniform titania nanocoating on relatively large, micron-size particles, because the titania species such as titanium alkoxides are highly reactive, easily resulting in precipitation of bulk titania from solution [22]. Thus, there have

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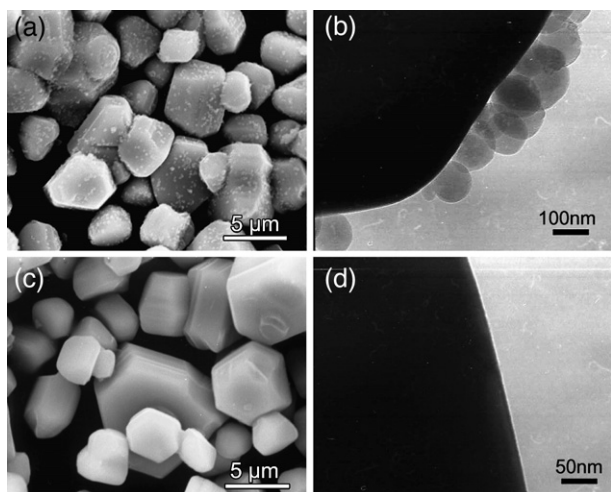


Fig. 1. SEM and TEM images of (a, b) untreated and (c, d) pretreated ZnS particles.

been few reports on preparation of a smooth titania coating on micron-size particles of ZnS-based phosphors. In the present study, we present a simple process to obtain a smooth and uniform titania nanocoating on the micron-size particles of ZnS-based phosphors. The effects of the concentration of reactants and ZnS core on the titania nanocoating have been investigated in detail.

2. Experimental details

2.1. Starting materials

Titanium(IV) tetrabutoxide ($\text{Ti}(\text{OBU})_4$, 95%) and acetylacetonone (AcAc, 99%) were obtained from Wako Pure Chemical Industries, Ltd., Japan. All these chemicals were used without further purification. A commercial green-emitting ZnS:Cu,Au,Al phosphor with an average particle size of 6.5 μm was obtained from Nichia Co., Japan.

2.2. Pretreatment of ZnS particles

On the surface of the commercial green emitting phosphor, there were many small SiO_2 particles (Fig. 1(a) and (b)), which were added to improve the fluidity or dispersivity of ZnS particles in a sheet making process for ordinary cathode ray tubes which are to be operated at higher voltages [23]. However, these SiO_2 particles could decrease the cathodoluminescent property of the phosphor. Hence, the SiO_2 particles were removed from the raw ZnS phosphors before coating.

The ZnS powders of 10.00 g were dispersed in an ultrasonic bath containing 200 mL of diluted HNO_3 solution (pH 5). The mixture was then placed in an oven preheated at 80 $^\circ\text{C}$ and kept for 2 h. After aging, the pretreated particles were separated by centrifugation and washed 6 times with distilled water, followed by 2 times with ethanol, and then dried at 50 $^\circ\text{C}$ for 24 h. After the pretreatment, a fresh and even surface of ZnS particles was obtained (Fig. 1(c) and (d)).

2.3. Preparation of titania nanocoating

The titania-coated ZnS particles were prepared by the hydrolysis and condensation of $\text{Ti}(\text{OBU})_4$. In a typical coating procedure, 2.50 g of pretreated ZnS particles was dispersed in 50 mL of ethanol in an ultrasonic bath. The titanium solution was prepared by dissolving 0.50 mL of $\text{Ti}(\text{OBU})_4$ and 0.25 mL of acetylacetonone into 50 mL of ethanol. The titanium solution was subsequently added to the ZnS dispersion under vigorously stirring, followed by the addition of 2.00 mL of distilled water. The total amount of ethanol was maintained at 100 mL. The final mixture was then refluxed for 1 h. After refluxing, the resulting particles were centrifuged, washed several times with ethanol and dried in an oven at 60 $^\circ\text{C}$ for 24 h.

2.4. Characterization

The surface morphologies were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images were obtained using a Hitachi S-530 microscope operating at 25 kV and a JSM-5800 LV microscope with energy-dispersive X-ray spectroscopy (EDX, JED-2140) operating at 20 kV. TEM images were obtained using a Hitachi H-800 microscope at an acceleration voltage of 200 kV. The SEM-EDX specimens were prepared by fixing sample powders on metal holders with a conductive carbon tape. The TEM specimens were prepared by depositing sample suspensions in absolute ethanol onto copper grids coated with a carbon film. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku RTP-300RC diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$, 40 kV, 100 mA) with a graphite monochromator.

3. Results and discussion

3.1. Effect of AcAc on morphology

AcAc was found to be used to form a Ti-bearing complex that acts as a precursor for the formation of titania nanocoatings.

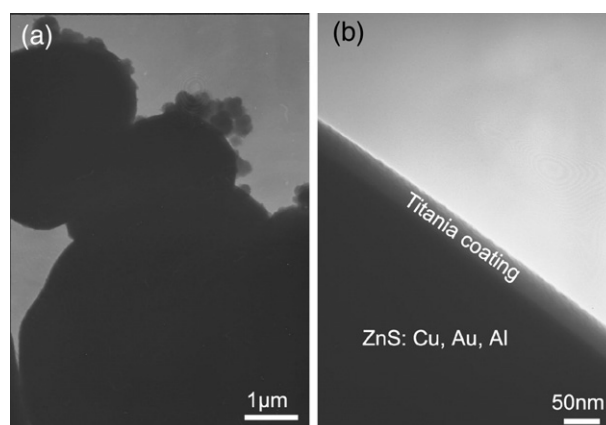


Fig. 2. TEM images of titania-coated ZnS particles (a) with AcAc and (b) without AcAc (0.25 mL) system. The amounts of $\text{Ti}(\text{OBU})_4$, H_2O , and ZnS were kept at 0.50 mL, 2.00 mL, and 2.50 g, respectively.

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