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BRIEF COMMUNICATION

Fabrication of titania nanocoatings on ZnS-type phosphors using the titanium diethanolamine as the precursor in an aqueous solution

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Abstract The titania nanocoatings on ZnS: Ag, Cl phosphors were successfully obtained by the sol–gel process in an aqueous solution using the titanium diethanolamine complex as the precursor. The titanium diethanolamine complex was prepared with diethanolamine (DEA) and titanium butoxide at the temperature of 120 °C. The nanocoatings synthesized by this technique were uniform and continuous with a thickness of about 10–15 nm, and the photoluminescent (PL) spectra showed that no other luminescent center was introduced. The titania coatings with an appropriate thickness were expected to prevent the degradation of ZnS phosphors in field emission displays (FEDs).

Keywords Sol–gel · Nanocoatings · Phosphors · Titania · Diethanolamine

1 Introduction

Recently, field emission displays (FEDs) have been developed as the next-generation flat panel displays to replace cathode-ray tubes (CRTs). But worldwide attempts to develop new, durable, and high-efficiency phosphors have not yet been successful so far. ZnS-type phosphors which have been widely used in CRTs have been considered to be applied in FEDs because of their high luminescence efficiency. However, they undergo fast degradation under high current densities in the FEDs environment because FEDs operate at much lower voltage excitation, which requires higher current densities in order to maintain the same output luminance. The poor ageing performance is believed to be associated with the surface recombination of phosphors [1, 2]. Because of the existence of traces of oxygen in the vacuum, ZnS surfaces will be oxidized into ZnO dead layers which reduce cathodoluminescence intensity significantly.

Surface coating is an effective way to prevent the surface oxidation. Many coating materials have been investigated, such as SiO_2 [3–6], ZnO [7, 8], TiO_2 [9, 10], In_2O_3 [11, 12], and Y_2O_3 [13]. However, so far none of those coatings has been put into practice.

Titania coatings are expected to inhibit fast degradation of ZnS phosphors applied in FEDs due to their chemical, thermal stability and wide band-gap. There are many methods for the fabrication of titania coatings, eg. chemical vapor deposition [14], chemical spray pyrolysis [15], electro-deposition [16], and sol–gel methods[17]. Among them, the sol–gel technique is efficient, cost-effective, and simple to manipulate, which is frequently applied in approaching of coating particles [18–20]. The titania coatings are fabricated by sol–gel method generally using titanium alkoxides as the precursor. However, due to the strong hydrolysis of them in the aqueous solution, the sol–gel process can not be carried out in an aqueous solution, but in an alcohol solution, which causes organic pollution.

The inhibitors such as acetic acid (HAc) [21] and acetylacetone (acac) [22, 23] are usually introduced even though the the hydrolysis and polycondensation of titanium alkoxides are conducted in an alcohol solution. Due to the formation of the chealating complexes, $Ti(OR)_x(Ac)_y$ or $Ti(OR)_x(acac)_y$, the hydrolysis and polycondensation rate decreases. Sometimes, diethanolamine (DEA) [24] is used to inhibit the strong

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hydrolysis of alkoxides by forming the complex such as $(DEA)_yTi_2(OC_2H_5)_{8-x-y}(OC_3H^i{}_7)_{x-y} \cdot 2C_2H_5OH$ in ethanol.

In the present work, the uniform, continuous and smooth titania coatings have been successfully obtained on ZnS-type phosphors using the titanium diethanolamine complex as the precursor via a sol–gel route in an aqueous solution.

2 Experimental

ZnS-type phosphors used in this work were green-light emitting ZnS: Ag, Cl phosphors with the mean particle size of about 4–5 μm (Beijing Chemical Factory, P. R. China). Titanium butoxide (CP) and cetyltrimethylammonium bromide (CTAB, AR) were obtained from No. 1 Tianjin Chemical Reagent Factory, P. R. China. Diethanolamine (DEA, AR) was purchased from Tianjin Bodi Chemical Company, P. R. China.

The titanium diethanolamine complex was synthesized with DEA and titanium butoxide. 2.1 g DEA and 3.4 mL titanium butoxide were mixed completely under continuous stirring, and then heated up to 120 °C. The translucent solid complex was obtained after cooling, which was stable enough to be preserved for a long time at room temperature.

The resulted titanium diethanolamine complex was dissolved into 50 mL deionized water to get the precursor solution. 1.6 g ZnS: Ag, Cl phosphors were dispersed in 200 mL deionized water with the addition of 0.07 g CTAB. Then 10 mL precursor solution was slowly added to the ZnS suspension (the weight ratio of titania to ZnS was 1:10) at a rate of one drop per second under continuous stirring. The sol–gel reaction proceeded for 12 h at room temperature. Finally, the solids was filtered off, dried at 100 °C for 24 h and calcined at 500 °C for 4 h. Thus, the titania coated phosphors was obtained.

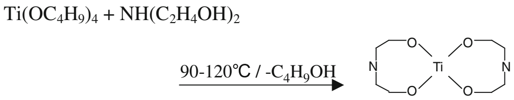
The titanium diethanolamine complexes were analyzed by Fourier transform infrared spectroscopy (FTIR, NEXUS 8700, Thermo Electron Corporation). The samples were synthesized by the same method as described above, with the various molar ratio of DEA to titanium butoxide (1:1, 2:1, 3:1, and 4:1).

The morphology of the uncoated and titania coated ZnS phosphors was investigated by the high resolution transmission electron microscopy (HRTEM, JEOL-3010, JEOL) and the field emission scanning electron microscopy (FE-SEM, S-4700, Hitachi). The selected area electron diffraction (SAED) pattern was carried out by the high resolution transmission electron microscopy (HRTEM, JEOL-3010, JEOL), using an accelerating voltage of 300 kv. The surface elements were analyzed by the X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo Electron Corporation). The photoluminescent spectra of the uncoated and titania coated ZnS phosphors were measured by fluorescence spectrometer (F-4500, Hitachi).

3 Results and discussion

The titanium diethanolamine complex was synthesized by heating the mixture of DEA and titanium butoxide up to 120 °C under continuous stirring. After cooled to room temperature, its phase state was changeable with the increase of DEA content. When the molar ratio of DEA to titanium butoxide was 1:1 or 2:1, the complex turned into translucent yellowish solid. However, at the ratio of 3:1 or 4:1, it exhibited a semisolid mixture. The reason was that the excessive DEA couldn't volatilize from the reaction system below its boiling point (268.8 °C). The FTIR spectra results (Fig. 1) showed that the absorption band for $-CH_3$ groups (at 2954.5 cm^{-1}) still remained at the ratio of 1:1. However, it disappeared at the ratios of 2:1, 3:1 and 4:1. That indicated that the byproduct butanol was removed from the reaction system, and there were unreacted $-CH_3$ groups at the ratio of 1:1, which should be from the excessive titanium butoxide. At the ratio of 1:1, the product could strongly hydrolyze in an aqueous solution and a white precipitation was formed immediately; however, it had high stability at the ratio of 2:1–4:1.

According to the above results, the possible reaction of DEA and titanium butoxide was described below (Eq. 1), and the similar reaction were seen in the study of Bickmare et al. [25, 26].



(1)

The titania coatings on ZnS-type phosphors were fabricated by the hydrolysis and condensation of the titanium

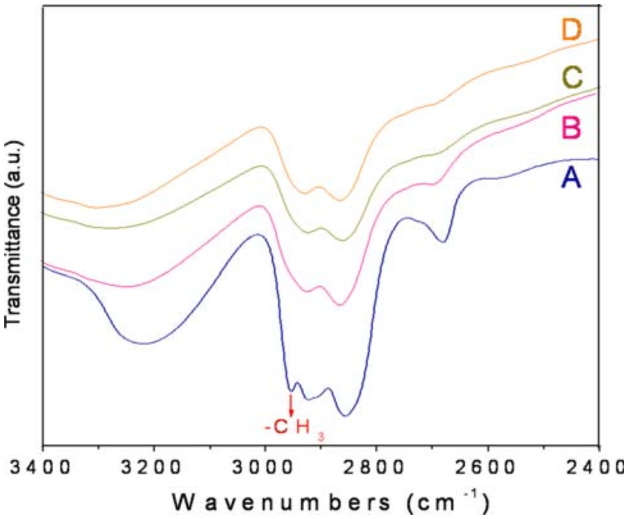


Fig. 1 FTIR spectra of the titanium diethanolamine complexes prepared with various molar ratios of titanium butoxide to DEA: (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4

diethanolamine complex in an aqueous solution. The green emitting ZnS: Ag, Cl phosphors used in this work had smooth surfaces (Fig. 2a). The SEM micrograph showed that the coated phosphors also had smooth surfaces (Fig. 2b), similar to the uncoated. However, HRTEM micrograph clearly showed, compared with the uncoated (Fig. 2c), a uniform, continuous and smooth titania coating was formed on the ZnS particle (Fig. 2d), rather than island-like titania particulates. The coating thickness was estimated to be 10–15 nm. Figure 3 shows clearly that the titania coating was composed of crystalline nanoparticles and each particle possessed identical lattice fringes (d = 0.350 nm). In addition, the electron diffraction pattern shown in the inset of Fig. 3 supported that the coating was anatase-type titania.

To further confirm the existence of titania coatings on the surfaces of ZnS phosphors, the XPS measurement was carried out (Fig. 4). In contrast with the uncoated, the XPS spectrum of the coated phosphors (Fig. 4b) showed that the Ti $2p_{3/2}$ peak appeared and the Zn $2p_{3/2}$ and S 2p peaks became weak. In addition, the Zn, S, O, and Ti peaks were at their normal binding energies, indicating that the coatings were in the form of titania. The formation of the Ti–O–Zn bonds could make the binding energy shift; however, there was no binding energy shift after coated. Therefore, the interaction force between titania coatings and ZnS phosphors could not be the chemical binding of Ti–O–Zn.

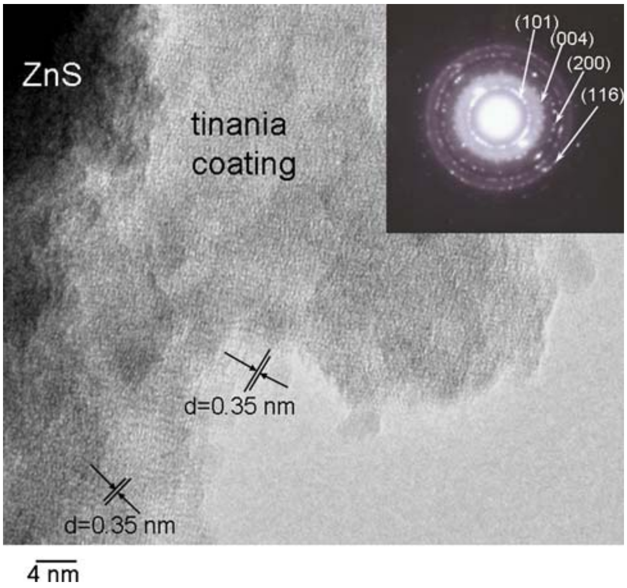
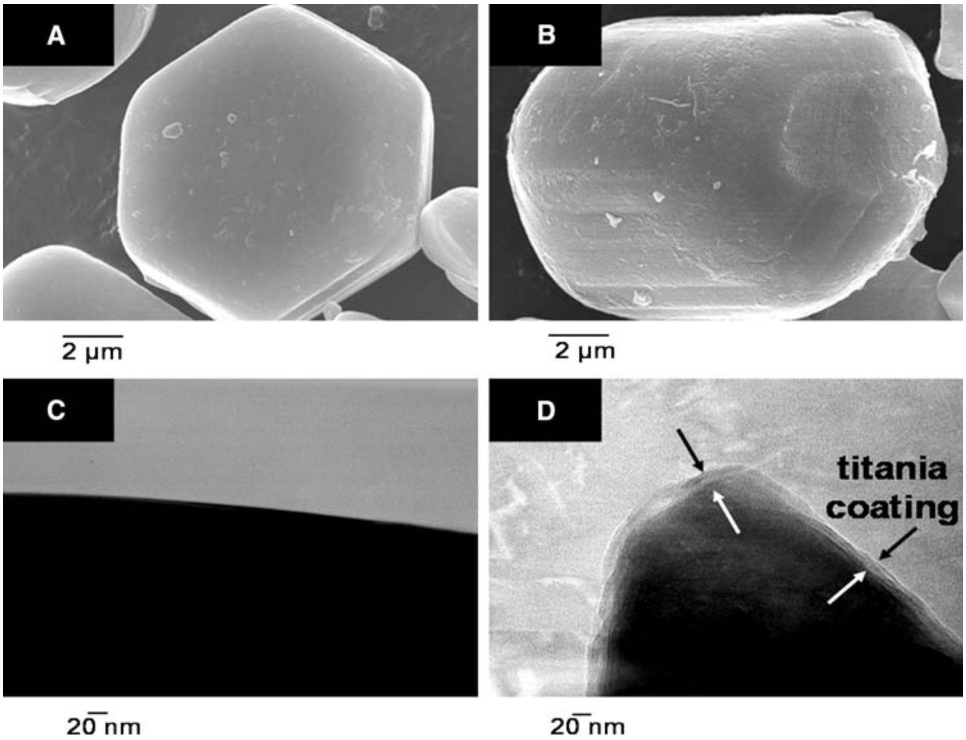


Fig. 3 HRTEM micrograph and the corresponding SAED pattern of the titania coated ZnS phosphors

Figure 5 showed the photoluminescent (PL) spectra of the uncoated and titania coated ZnS phosphors under 400 V. The spectral shape of titania coated samples was the same as the uncoated phosphors except for the overall reduction in the peak intensity. Both the uncoated and coated phosphors had the same peak emission at 522 nm.

Fig. 2 FE-SEM micrographs of (**a**) the uncoated, (**b**) titania coated ZnS phosphors, and HRTEM micrographs of (**c**) the uncoated, (**d**) titania coated ZnS phosphors



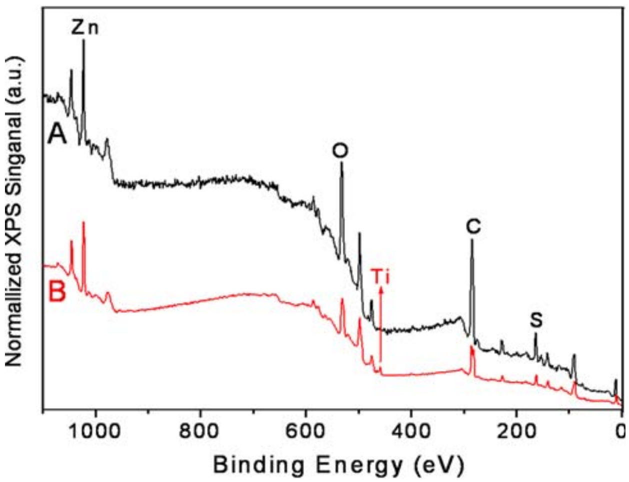


Fig. 4 XPS spectra of (a) the uncoated and (b) titania coated ZnS phosphors

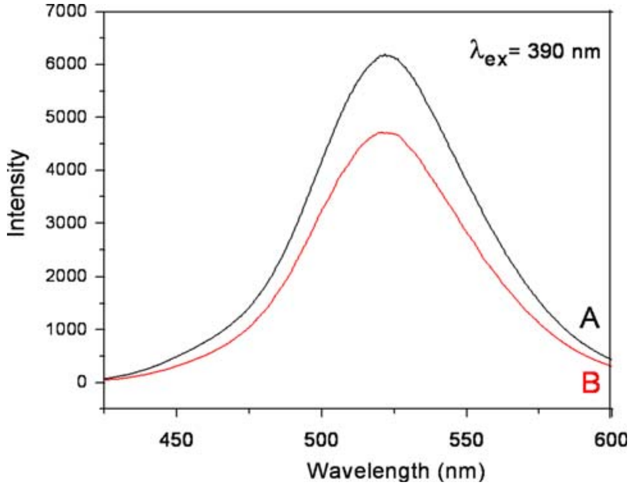


Fig. 5 PL spectra of (a) the uncoated and (b) titania coated ZnS phosphors under 390 nm excitation

Since no presence of side-peak was observed, titania nanocoatings on the phosphors didn't introduce any other luminescence center.

4 Summary

The titanium diethanolamine complex, synthesized from the mixture of DEA and titanium butoxide at the molar ratio of 2:1, could hydrolyze and polycondense in an aqueous solution at a lower rate compared to titanium butoxide. The uniform, continuous and smooth titania nanocoatings on ZnS phosphors were obtained by a sol–gel method using the titanium diethanolamine complex as the precursor. It would be expected that the thin titania coatings fabricated by this method could inhibit the surface oxidation of ZnS phosphors. Now we are trying to get thinner coatings with better ageing performance.

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