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Effects of the Coating Process on Nanoscale Y_2O_3:Eu^{3+} Powders

Qiang Li,* Lian Gao, and Dongsheng Yan

State Key lab, Shanghai Institute of Ceramics,
Chinese Academy of Sciences, Shanghai 200050,
P. R.China

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Coated powders are used in many different areas. Nowadays, the coating process is an important technology in industry for the production of pigments having special optical properties or other physical properties.[1,2] Because of the large specific surface, the characteristics of nanoscale materials are apparently determined by the appearance structure. Many defects exist in the surface of nanoscale particles. Unfortunately, the efficiency of luminescent materials is sensitive to those defects.[3] However, the coating process is useful in amending the appearance structure of powders and decreasing surface defects. So it is possible to improve luminescence intensity of nanoscale materials by the coating process.

We prepared nanoscale Y_2O_3:Eu^{3+} powders by the polyacrylamide gel method.[4] Figure 1 is a TEM photograph. The grain size is about 20 nm. However, the degree of aggregation is serious.

To improve luminescent efficiency, the powders were coated. The process is described in detail as follows: At first, nanoscale Y_2O_3:Eu^{3+} powders were dipped in a solution of $KAl(SO_4)_2$ for 15 min, and Al^{3+} was absorbed on the surface of nanoscale powders. After being separated by centrifugation, the powders were dipped in a solution of Na_2SiO_3 for 15 min. So on the surface, this reaction was proposed:

$$2Al^{3+} + 3SiO_3^{\ 2-} + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2SiO_3\downarrow$$

After being washed and separated by centrifugation, the powders were calcined at 400 °C for 3 h. Figure 2 is a TEM photograph of coated nanoscale Y_2O_3:Eu^3 powders. The dispersity of nanoscale powders was obviously improved.

In the coating procedure, Al^{3+} absorbed on the surface of nanoscale Y_2O_3:Eu^{3+} powders is very important. After the nanoscale powders were dipped and separated, the Al^{3+} concentration in the solution of $KAl(SO_4)_2$ was determined by compleximetry. The Al^{3+} concentration decreased from 0.06715 M to 0.02326 M. The Al^{3+} content on the surface of the nanoscale Y_2O_3:Eu^{3+} powders is 6.4 mol %. After the powders were calcined, the Al^{3+} content of the coated powders was analyzed by X-ray fluorescence methods. This result (6.8 mol %) is close to the former (6.4 mol %).

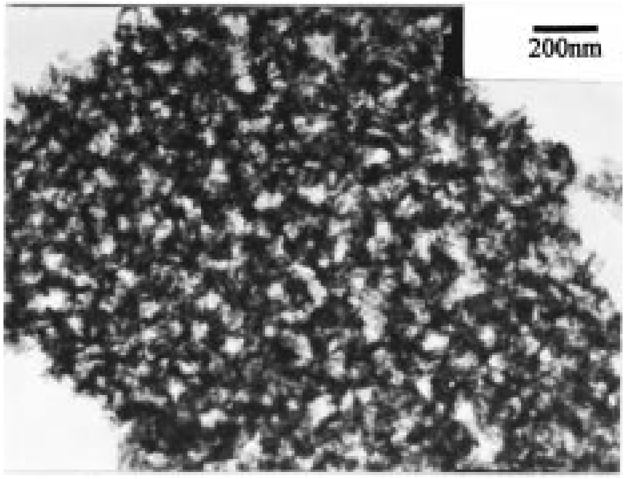

Figure 1. TEM photograph of a noncoated nanoscale Y_2O_3:Eu^{3+} powder.

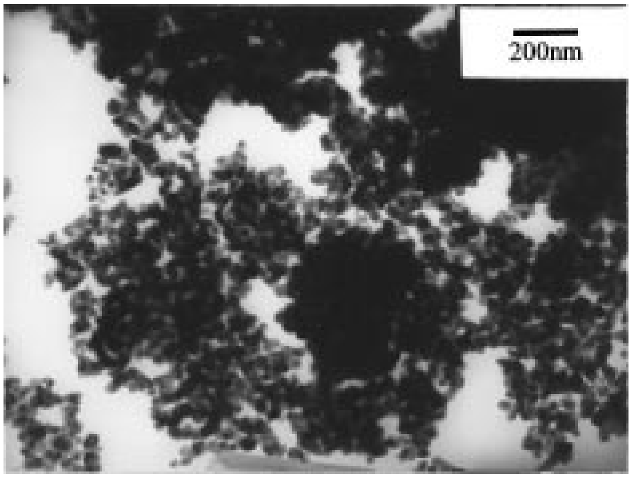

Figure 2. TEM photograph of a coated nanoscale Y_2O_3:Eu^{3+} powder.

AES (Auger electron spectroscopy) was employed to study the effects of the coating procedure. As indicated in Figure 3, after the powders were coated, the elementary composition of the surface had been changed. In the AES of coated nanoscale Y_2O_3:Eu^3 powders, there are obviously peaks for Al_2O_3 and SiO_2. Furthermore, the peaks (1738 and 1811 eV) of Y in the high-energy section of Auger electron spectra remained, but those in the low-energy section disappeared. The intensity of the remaining peaks were much lower than those of the noncoated nanoscale powders. The composite oxide layer prevents Auger electrons of Y from escaping from the surface of the powders.

The escape depth of Auger electrons is determined by the nature of the materials and by the energy (Figure 4).[5] Generally, the limit of escape depth is no more than 5 nm. The observation that only a few high-energy electrons of Y can escape indicated that the thickness of the coating layer is near this limit. It confirms that

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* To whom correspondence should be addressed. E-mail: liq@ihw.com.cn.

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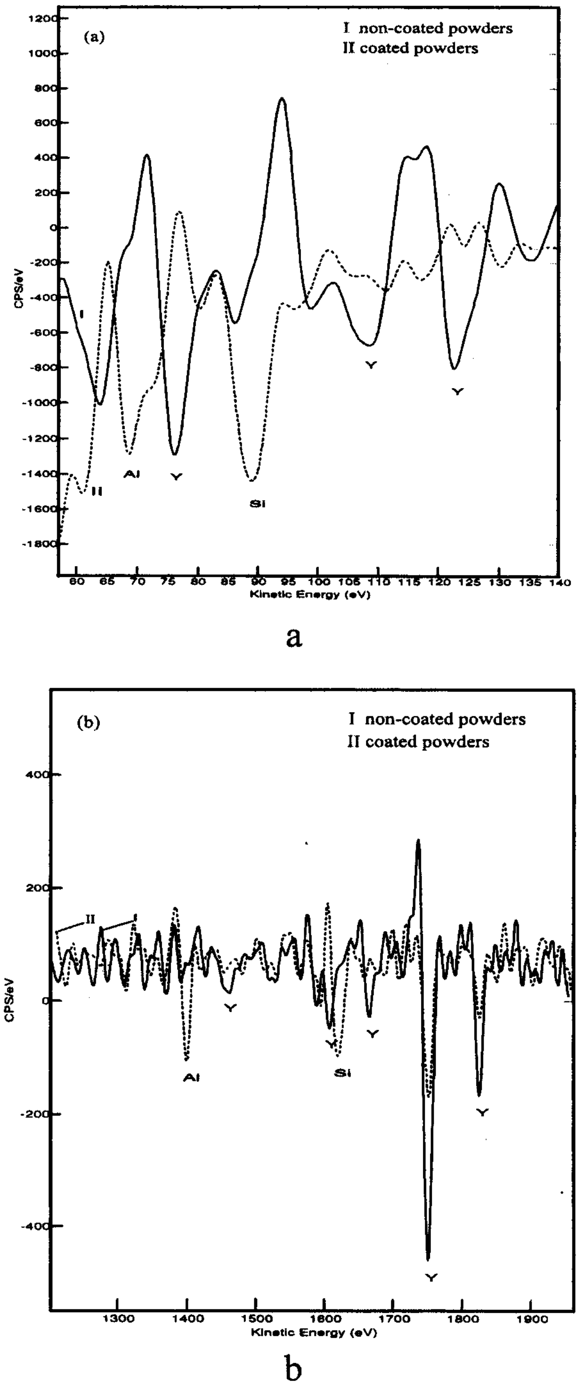

Figure 3. Auger electron spectra of noncoated (I) and coated (II) nanoscale Y_2O_3:Eu^{3+} powders: (a) low-energy section; (b) high-energy section.

nanoscale Y_2O_3:Eu^{3+} powders were properly covered by composite oxide layer of about 2~3 nm.

The luminescence intensities of all samples were studied with a 850 spectrofluorophotometer. These samples were exited by 254 nm radiation, which is absorbed by the change-transfer transition of the Eu^{3+} ion. In the emission spectrum of Eu^{3+}, the main peak (610 nm) belongs to the $^5D_0-^7F_2$ transition of 4f energy levels. Figure 5 shows the luminescence intensity of coated and noncoated nanoscale Y_2O_3:Eu^{3+} powders with different Eu^{3+} concentrations. This shows that the luminescence intensity was apparently improved after being coated. This evolution benefits from surface changes of the coated nanoscale powders. The luminescence intensity is decreased due to defects. Without a doubt, the large surface of nanoscale powders can afford these kinds of defects.

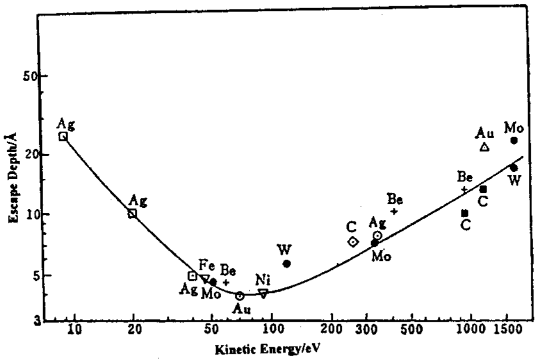

Figure 4. Dependence of escape depth on electron energy in different materials.

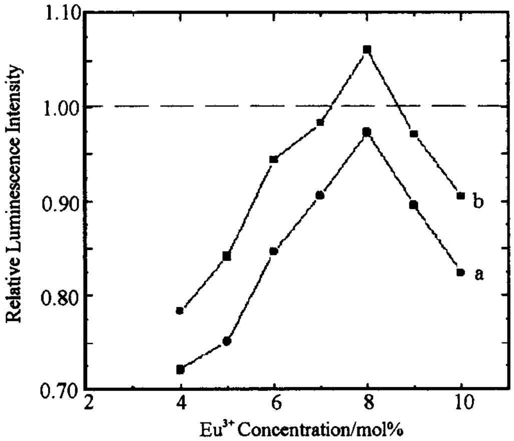

Figure 5. Luminescence intensity (the main peak at 610 nm) of nanoscale Y_2O_3:Eu^{3+} powders with different Eu^{3+} concentration: (a) noncoated powders; (b) coated powders.

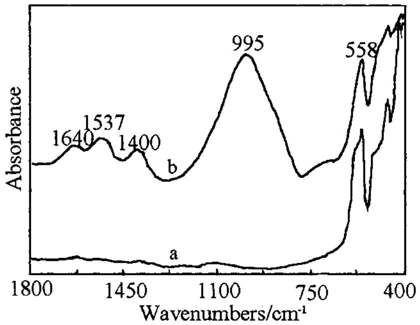

Figure 6. FT-IR spectra of uncoated nanoscale Y_2O_3:Eu^{3+} (a) and coated nanoscale Y_2O_3:Eu^{3+} (b).

To examine chemical bonding, FT-IR spectroscopy was used. Figure 6 shows the FT-IR spectra of coated and noncoated nanoscale Y_2O_3:Eu^{3+} powders. In the FT-IR spectra of noncoated nanoscale Y_2O_3:Eu^{3+} powders, there is a shoulder peak near 558 cm^{-1}. The peak at 558 cm^{-1} is due to a stretching vibration of Y(Eu)−O.[6] This shoulder peak may belong to defects connected with Y(Eu)−O on the surface of nanoscale powders.[7,8]

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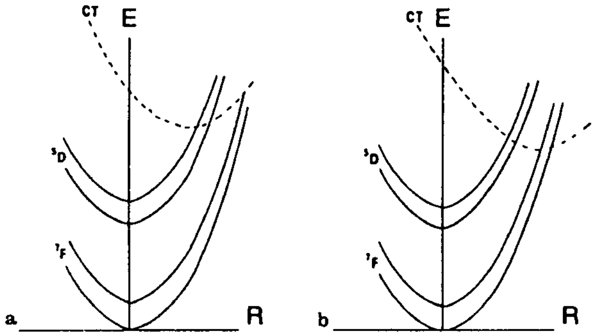

Figure 7. Role of the charge-transfer state (CT) in the quenching of the luminescence of the Eu^{3+}: (a) the CT state feeds the emitting ^{5}D levels; (b) the CT state has a large offset.

If this were true, these defects should be one of the main factors to diminish the luminescence intensity of nanoscale Y_2O_3:Eu^{3+} powders.

In an isolated luminescent center, such as Eu^{3+}, the luminescence process competes with the nonradiative transition. The charge-transfer state(CT) is important in the quenching of the luminescence of the Eu^{3+}. Let us consider the configurational coordinate diagrams of Figure 7 in order to understand the relevant physical processes.[9] In Figure 7a, the normal situation for Y_2O_3:Eu^{3+} is depicted: the CT state feeds the emitting ^{5}D, Eu^{3+} emits efficiently from ^{5}D. However, in Figure 7b, the CT state has a large offset. As a consequence the CT state populates the ground state levels, so that the luminescence is strongly reduced. The CT state is very sensitive to coordination. The results of FT-IR imply that the coordination of the Eu^{3+} on the surface is imperfect. As a result the Eu−O group has a high vibrational level and a large offset, which causes the nonradiative transition.

However, this shoulder peak disappeared in the FT-IR spectra of coated nanoscale powders. This means that these kinds of defects were mostly now gone. Of course, the luminescence intensity should be increased. Due to the importance of surface sites, the coating process may be an important procedure in the preparation of other nanoscale materials.

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