From ZnO colloidal nanostructures to functional nanomaterials

Fabien Grasset

The transparency and versatile chemistry of nanocolloids can be exploited to fabricate novel thin films.

Thin films are material layers ranging from fractions of a nanometer to several micrometers in thickness. They can be deposited onto metal, ceramic, glass, or semiconductor bases. Among the numerous coating techniques available, chemical or physical vapor deposition and sol-gel methods are the most commonly used in industry. Thin films are mainly used for optical coating and electronic device applications. However, the preparation of low cost functional thin films with high transparency and modulated optical properties remains a challenge for laser, photocatalytic, or display panel applications.

For example, for photocatalysis—which is increasingly used in chemical waste degradation—photostable light-harvesting nanoarchitectures are required: these are nanostructures that can be used to absorb light to facilitate chemical reactions, but are nevertheless robust to the radiation. Were they available, and provided that appropriate semiconductor catalysts were selected, charge carriers could be generated by UV or visible radiation to initiate reduction and oxidation reactions with adsorbed reactants, leading to the destruction of pollutants. However, most photocatalysts consist of metal oxides that are only functional in the UV region. The result is a lack of suitable materials with the appropriate band gap for visible absorption and the required stability for practical applications.

A second example is provided by Y2O3:Eu3+, the most widely used red phosphor for field emission display applications. Much attention has been paid to the synthesis and luminescent properties of Eu3+-doped rare-earth orthoborates (REBO3) thin films. This is due to their desirable properties as ideal vacuum UV phosphors, key materials for the development of plasma display panels. For such phosphors, both luminescence efficiency and color purity are required. Unfortunately, as a red phosphor, the intensity of the red emission of REBO3:Eu3+ is often lower than that of the orange, leading to poor chromaticity.

One of the largest application areas of sol-gel chemistry is thin-film preparation. Using this approach, we started to synthesize ZnO colloidal solutions for the preparation of functional thin films. Zinc oxide is a non-toxic semiconductor with a wide bandgap (3.37 eV) and a large exciton binding energy. In bulk or nanosized form, it can be used to absorb light to facilitate chemical reactions, but are nevertheless robust to the radiation. Were they available, and provided that appropriate semiconductor catalysts were selected, charge carriers could be generated by UV or visible radiation to initiate reduction and oxidation reactions with adsorbed reactants, leading to the destruction of pollutants. However, most photocatalysts consist of metal oxides that are only functional in the UV region. The result is a lack of suitable materials with the appropriate band gap for visible absorption and the required stability for practical applications.

A second example is provided by Y2O3:Eu3+, the most widely used red phosphor for field emission display applications. Much attention has been paid to the synthesis and luminescent properties of Eu3+-doped rare-earth orthoborates (REBO3) thin films. This is due to their desirable properties as ideal vacuum UV phosphors, key materials for the development of plasma display panels. For such phosphors, both luminescence efficiency and color purity are required. Unfortunately, as a red phosphor,


due to their desirable properties as ideal vacuum UV phosphors, key materials for the development of plasma display panels. For such phosphors, both luminescence efficiency and color purity are required. Unfortunately, as a red phosphor,
prepare highly red-luminescent RE-doped thin films: see Figure 1(b) and (e). Using a simple doping process, trivalent europium can easily be introduced in the solution and a Ti-functionalized ZnO can then be used as a nanohost. As shown in Figure 1(b), the red fluorescence of this nanomaterial at room temperature is easily observed under illumination from a compact 4W-UV lamp operating at 254nm. We showed that it was possible to activate RE fluorescence in a highly transparent Ti-functionalized ZnO thin film with simple annealing at 400°C for 15 minutes. The five characteristic emission peaks assigned to the $^5D_0 \rightarrow ^7F_J$ transition of Eu$^{3+}$ (where $J = 0, 1, 2, 3, \text{and} 4$) are observed, with the strongest emission ($J = 2$) at 613nm (Figure 2, insert).

Colored ZnTiON oxynitrides photo-active thin films

Another study was focused on tuning and controlling the transmission spectra of air-heated ZnTiO films. Above the dissociation temperature of ammonia (550°C), the spectra are progressively red-shifted with increasing nitridation temperature. This red-shift is directly related to the nitrogen content and is similar to that observed in the spectra of the corresponding nitrided oxide nanopowders. The resulting layers display a high optical transparency and coloration as illustrated in Figure 3. It can be seen that the initially colorless films first turn yellow, then orange and red before finally turning dark brown.

To conclude, we have prepared novel, highly concentrated colloidal ZnO nanostructures, using a simple, low-cost, bottom-up process. We also demonstrated that they can be used to prepare numerous functional nanomaterials, such as versatile ZnTiON or Eu,Ti-functionalized ZnO red-luminescent thin films. So far, our results have shown that new materials can also be fabricated in slabs large enough for use in macroscopic products. Our next step will be to extend our approach to new systems such as Ga or Zr-functionalized ZnO.

This work was financially supported by NIMS/ICYS, the University of Rennes 1, CNRS, Bretagne region, the Fondation Langlois, and by Nanomat and C’Nano North-Ouest Networks. The work was performed in collaboration with Prof. H. Haneda, Dr. N. Saito, Dr. S. Cordier, Dr. Y. Molard, Dr. C. Perrin, Dr. S. Pecheo, Dr. S. Ababou-Girard, Prof. Spanhel, Prof. Marchand, and Prof. M. Guilloux-Viry. The author thanks T. Sasaki, J. Le Lannic, N. Pontais, and Dr. F. Tessier for technical assistance.

Author Information

Fabien Grasset

Rennes Chemical Sciences
UMR 6226 CNRS, University of Rennes
Rennes, France
http://scienceschimiques.univ-rennes1.fr/csm/personnel/f_grasset.html

Fabien Grasset obtained his PhD in 1998 in solid state chemistry from the University of Bordeaux. He was previously a researcher at the Institute of Chemistry for Condensed Matter of Bordeaux and at the National Institute for Materials Science in Japan (1999-2001). He is currently an associate professor at the University of Rennes and his research interests are focused on the synthesis of new colloids (M-functionalized ZnO and SiO$_2$, $g - Fe_2O_3$) and functional thin films. In 2007, he received a three month fellowship from the International Center for Young Scientists program, funded by the National Institute for Materials Science (Japan).
References

© 2007 SPIE