Report

Combinatorial Synthesis of Insoluble Oxide Library from Ultrafine/Nano Particle Suspension Using a Drop-on-Demand Inkjet Delivery System

Lei Chen, Jun Bao, Chen Gao, Sunxiang Huang, Chihui Liu, and Wenhan Liu

J. Comb. Chem., **2004**, 6 (5), 699-702• DOI: 10.1021/cc034075l • Publication Date (Web): 25 June 2004

Combinatorial Synthesis of Insoluble Oxide Library from Ultrafine/Nano Particle Suspension Using a Drop-on-Demand Inkjet Delivery System

Lei Chen, Jun Bao, and Chen Gao*

National Synchrotron Radiation Lab, University of Science & Technology of China, Hefei, Anhui 230026, China

Sunxiang Huang, Chihui Liu, and Wenhan Liu

Department of Physics, University of Science & Technology of China, Hefei, Anhui 230026, China

Received December 18, 2003

Although the combinatorial approach has been widely adapted in the search for novel functional materials,[1] the parallel synthesis and high-throughput characterization are still the major obstacles hampering the application to a diversity of materials. Among various parallel synthesis strategies, thin-film deposition combined with physical masks (or photolithography) and solution-based synthetic methods are the most commonly used techniques.[2] In solution-based parallel synthesis, droplets of precursor solutions are laid into predefined microreactors (usually microwells drilled into a ceramic substrate) from microdispensers (usually piezoelectric-driven ejectors). Then, the precursors are mixed and reacted to form a materials library. Through this method, materials libraries including phosphors, catalyst, etc., have been fabricated from solution precursors.[3,4] Inkjet delivery shows many advantages over other microdispense apparatus, such as nanoliter dispensing capability with high accuracy.[5] However, a significant limitation of the above-mentioned technique is the applicability: only soluble compounds had been used as the precursors. On the other hand, a lot of suspensions have been used with the inkjet technique in ceramic freeforming,[6] fabrication of electronic devices,[7] and functionally graded material.[8] From this point of view, suspensions can be used with inkjet technique in solution-based parallel synthesis if a universal preparation method of insoluble suspensions can be developed. Evans et al. realized this and published the point of view from philosophy analysis,[9] but to our best knowledge, no materials library was really made from suspensions. In this paper, we report a method to prepare ultrafine/nanoparticle suspensions of insoluble rare earth oxides in pure water and the synthesis of a materials library from such suspensions using a homemade drop-on-demand inkjet delivery system.

To satisfy the requirement of the inkjet delivery system for the liquid to be ejected, the suspensions should be stable (no sedimentation, no agglomeration) during the jetting and must have high surface tension, low viscosity, and fewer additives to promote the postprocessing. There are two major kinds of methods to prepare insoluble suspensions: dispersing ultrafine/nanoparticles with a small amount of dispersant, stabilizer, and binder in solvents, or agglomeration from chemical reaction in sol−gel.[10] However, suspensions made from both methods sometimes could not fully meet the critical requirements of the inkjet delivery system. From a practical point of view, it is necessary to develop a universal preparation method of insoluble suspensions suitable for combinatorial synthesis through the inkjet technique.

Procedure. A 4-g portion of rare earth oxide powder (Y_2O_3, Eu_2O_3, Tb_4O_7, La_2O_3, CeO_2, etc.; specification, 99.99%; particle size distribution, ∼0.5 to 6 μm; supplied by Shanghai YL NFM Ltd.), an equal weight of deionized water, and agate balls (Φ, 6 mm; Φ, 10 mm) with ball-to-sample weight ratio of 10:1 were loaded into an agate pot, then oxide powders were ground for 60−80 h at 250 rpm (or 40 h at 400−500 rpm) in a QM-1F planetary high-energy ball mill (Nanjing University Instrument Plant). During the ball milling, if the slurry dried, another 1−2 mL of deionized water was supplied into the agate pot to continue grinding. Finally, deionized water to bring the total amount of water to 30 mL was added into the pot, and an additional 2 h of milling was carried out to form the 11.76 wt % suspensions.

Figure 1 shows the TEM (H-800, Hitachi) micrographs of particles in La_2O_3 and CeO_2 suspensions. The typical particle size in the suspensions of La_2O_3 and CeO_2 is about 20−50 nm and 10−30 nm respectively. The stability of the suspensions of various rare earth oxides was examined, and no significant sedimentation or agglomeration was observed in several hours. For La_2O_3 and CeO_2 suspensions, the stability time exceeds 24 h. Details of the effects of milling conditions, such as ball milling time and rate on the stability of the suspensions, particles sizes, and structure, will be reported elsewhere.

The schematic diagram of the drop-on-demand inkjet delivery system developed in our group is shown in Figure 2. The eight independent piezoelectric inkjet heads and $x-y$ stage are controlled by the computer via the driving circuit and motion controller. Each inkjet head is connected to a suspension reservoir through a tube, and the substrate with a microreactor array is fixed on the stage. Software developed in our group automatically coordinates the ejection of the inkjet heads and the position of the stage to deliver an appropriate amount of solution into the microreactors according to the concentrations of the solutions, interval of the reactors, substrate size, the composition map, etc. The inkjet head consists of a sapphire nozzle, a stainless steel diaphragm, and a piezoelectric disk, as shown in Figure 3. High voltage electric pulse coming from the driving circuit is applied to the piezoelectric disk to produce a mechanical vibration. The vibration crosses the diaphragm and propagates toward the nozzle in the form of an acoustic wave. The positive pressure of the vibration accelerates the liquid around the nozzle to overcome the surface tension force to

* To whom corresponding should be addressed. E-mail: cgao@ustc.edu.cn.

10.1021/cc034075l CCC: $27.50
Published on Web 06/25/2004

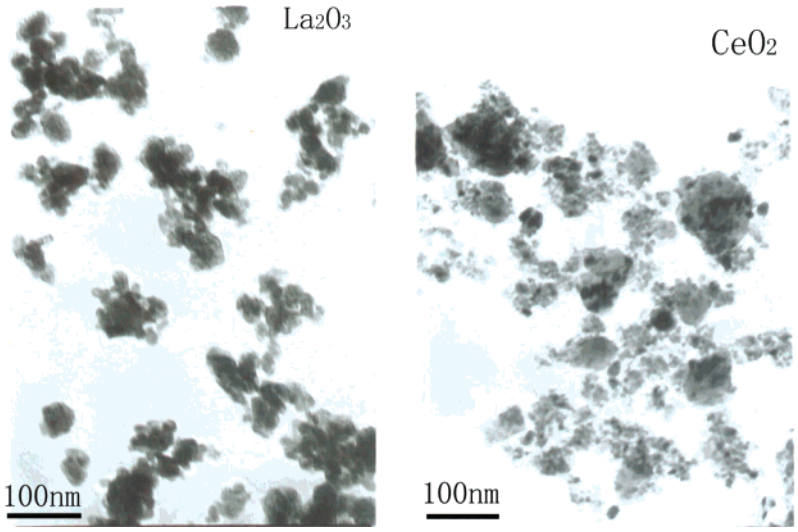

Figure 1. TEM micrographs of particles in La_2O_3 and CeO_2 suspensions.

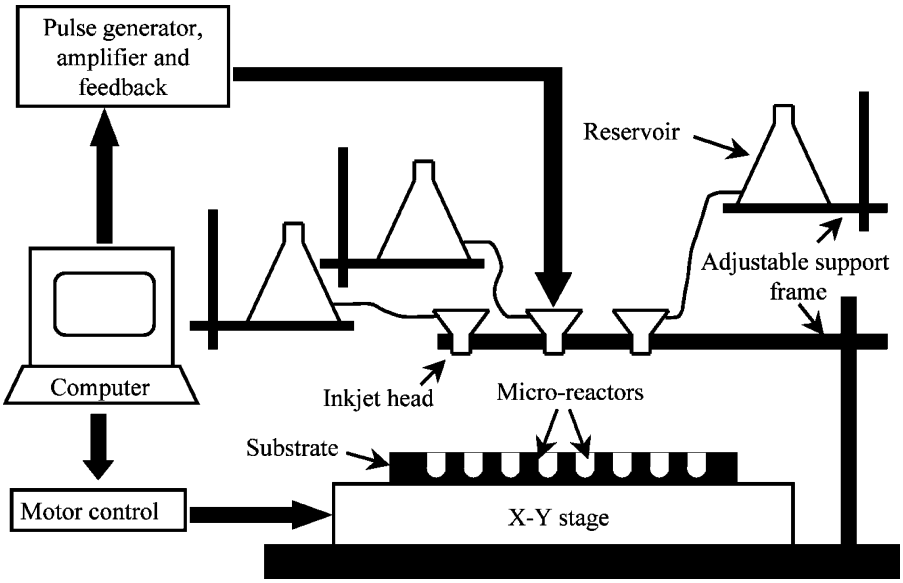

Figure 2. Schematic diagram of the homemade drop-on-demand inkjet delivery system.

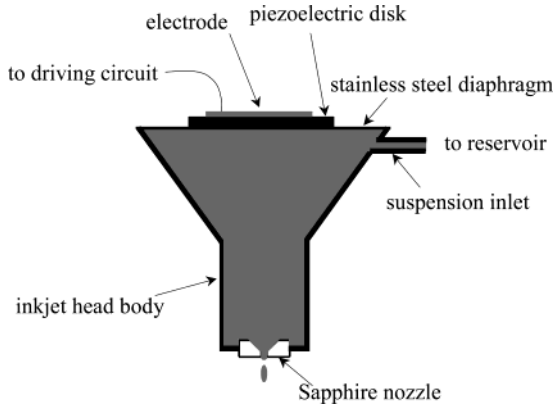

Figure 3. Schematic of the inkjet head.

form an ejected drop. A detailed description about the formation of the drops can be found in reference 11. Due to the intrinsic statistical behavior, the volume of the droplets has a distribution. By measuring the weights of some 25 000 deionized water drops ejected by the inkjet delivery system within 1 h, it was determined that the average droplet volume

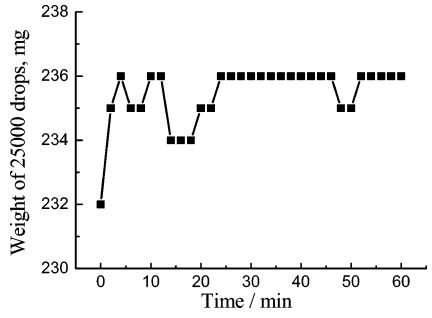

Figure 4. Stability with time of the drop-on-demand inkjet delivery system.

was ~10 nL, and the standard deviation was estimated to be ~10%, as shown in Figure 4. The ejection repeatability is ~0.5 to 2 kHz.

To verify the applicability of the method, a photoluminescent library was synthesized. Y_2O_3, Eu_2O_3, and Tb_4O_7 suspensions prepared with the above-mentioned process were ejected into the microwells drilled into an Al_2O_3 ceramic substrate according to the composition map, as shown in

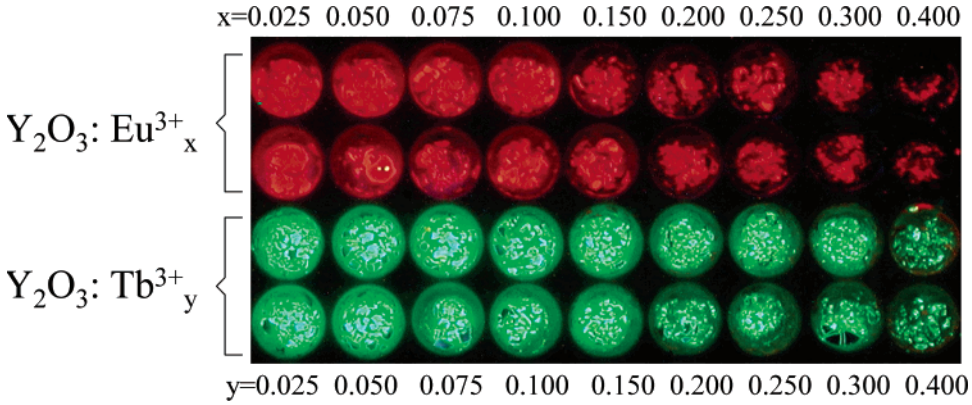

Figure 5. Composition map and photoluminescence photograph of the library excited under 254-nm UV light.

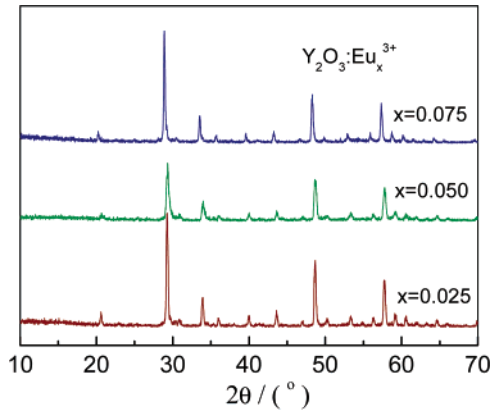

Figure 6. XRD patterns of Y_2O_3:Eu_x^{3+} samples after sintering.

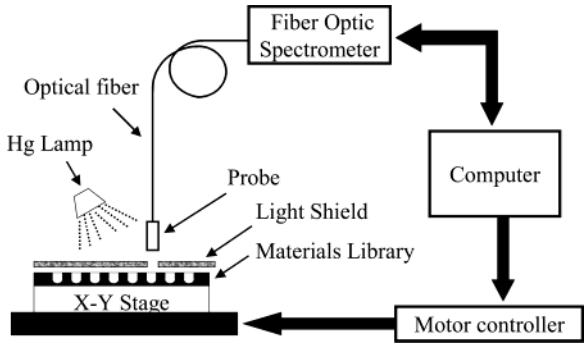

Figure 7. Schematic diagram of the setup for emission spectra measurements from the materials in library.

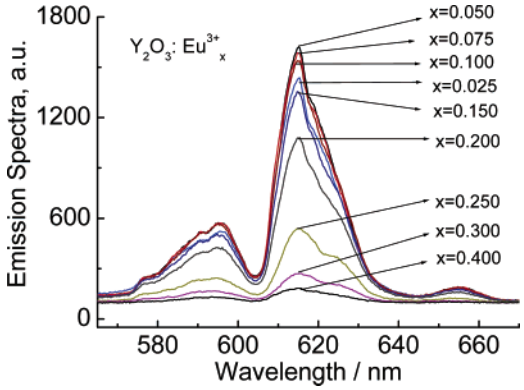

Figure 8. Emission spectrum of the samples with different Eu^{3+} contents in the library.

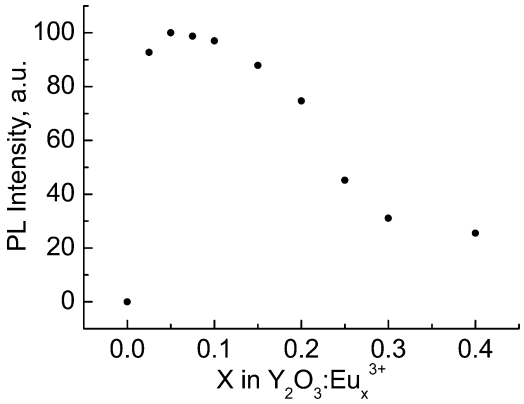

Figure 9. The red PL intensity as a function of the Eu^{3+} content.

Figure 5. Before ejection, suspensions were infused with argon gas for 2−3 h to expel any air dissolved in the suspension, which tends to agglomerate and block the nozzle. After drying, the library was sintered at 1450 °C for 3 h. Figure 6 presents the XRD patterns of three selected samples (Y_2O_3:Eu_x^{3+}, $x = 0.025$, 0.05, and 0.075) in the library. The three samples exhibit the same diffraction peaks, which can be indexed to the cubic phase of Y_2O_3 (JCPDS card 86-1326), and no Eu species is detected. This indicates that the Eu^{3+} is doped into the Y_2O_3 lattice. The photoluminescent photograph of the library under 254-nm UV excitation is also shown in Figure 5. The emission spectra of the samples on the library were measured using an automatic system, as shown in Figure 7. The main parts of the system consist of an Hg lamp, a portable optical fiber spectrometer (Ocean Optics, Inc., model SD2000), and an $x-y$ stage. The spectrometer was equipped with a 25/200-μm slit, a 600 grooves/mm grating blazed at 400 nm and covering the spectral range from 200 to 850 nm with efficiency >30%, and a 2048-element linear silicon CCD-array detector. The materials library was fixed on the moving table of the $x-y$ stage. Emission spectra from the materials in each microreactor were measured when the fiber-optic probe was focused on the bottom of the reactor. To avoid the interference from other samples, a light shield was used. Figure 8 presents the emission spectra of Y_2O_3:Eu_x^{3+}, which varies with the content of Eu^{3+} in the materials library. The photoluminescent intensities of red integrated from $\lambda = 570.44-664.80$ nm according to Figure 8 are plotted in Figure 9. From Figure 9, the concentration quench effect is clearly exhibited, and the Eu^{3+} concentration of maximum PL intensity is ~5%, which is in fair agreement with reports in the literature.[12] This result indicates that an appropriate amount of Eu_2O_3

was properly doped into the Y_2O_3 matrix and formed homogeneous materials in the library. In fact, due to the nanometric particle size of the suspension, the mixing of different precursors and the interdiffusion between the particles are easier than that in the homogeneous solutions, where one precursor could be precipitated prior to others, and the particle size is usually at the micrometer level.

In conclusion, combinatorial material libraries were synthesized from suspensions prepared from insoluble oxides using a drop-on-demand inkjet delivery system. Meanwhile, a method to prepare inkjet-compatible insoluble oxide suspension with an ultrafine/nano particle size, high surface tension, low viscosity, and high concentration was also developed.

Acknowledgment. This work was financed by NSFC (Programs 20131010 and 50125207), CAS (Program KGCX2-201-2), NSRL Knowledge Innovation Program, and Educational Bureau of Anhui Province (2001kj266zd). The authors thank Jianjun Ding, Jiajing Han, and Lei Shen for their help in experiments.

References and Notes

(1) Jandeleit, B.; Schaefer, D. J.; Powers, T. S.; Turner, H. W.; Weinberg, W. H. *Angew. Chem. Int. Ed.* **1999**, *38*, 2494.
(2) Xiang, X. D.; Schultz, P. G. *Physica C* **1997**, *428*, 282.
(3) Sun, X. D.; Wang, K. A.; Yoo, Y.; Wallace-Freedman, W. G.; Gao, C.; Xiang, X. D.; Schultz, P. G. *Adv. Mater.* **1997**, *9*, 1046.
(4) (a) Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangapani, S.; Smotkin, E. S.; Mallouk, T. E. *Science* **1998**, *280*, 1735. (b) Reichenbach, H. M.; McGinn, P. J. *Appl. Catal., A* **2003**, *244*, 101.
(5) Lemmo, A. V.; Rose, D. J.; Tisone, T. C. *Curr. Opin. Biotechnol*. **1998**, *9*, 615.
(6) Slade, C. E.; Evans, J. R. G. *J. Mater. Lett.* **1998**, *17*, 1669.
(7) Ridley, B. A.; Nivi, B.; Jacobson, J. M. *Science* **1999**, *286*, 746.
(8) Mott, M.; Evans, J. R. G. *Mater. Sci. Eng., A* **1999**, *271*, 344.
(9) (a) Evans, J. R. G.; Edirisinghe, M. J.; Coveney, P. V.; Eames, J. *J. Eur. Ceram. Soc*. **2001**, *21*, 2291. (b) Mohebi, M. M.; Evans, J. R. G. *J. Comb. Chem.* **2002**, *4*, 267. (c) Evans, J. R. G *Brit. Ceram. Trans.* **2001**, *100*, 124.
(10) (a) Timms, L. A.; Ponton, C. B. *J. Eur. Ceram. Soc*. **2002**, *22*, 1553. (b) Chen, Z. Q.; Dai, M. G. *Colloid Chemistry*; Higher Education Press: Beijing, March 1984, p 184.
(11) Le, H. P. *J. Imaging Sci. Technol*. **1998**, *42* (1), 49.
(12) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer-Verlag: Berlin, Heidelberg, 1994; p 96.

CC034075L