

Brilliantly Shining Semiconductor Nanocrystal Dispersed Glass for UV-LED Excitation

Norio Murase and Chunliang Li

Photonics Division, National Institute of Advanced Industrial Science & Technology, Ikeda,
Osaka 563-8577, Japan,

Phone : +81-72-751-8483, E-mail: n-murase@aist.go.jp

Abstract

We have fabricated a new-type high-brightness phosphor consisting of a sol-gel derived glass with finely dispersed semiconductor nanocrystals. It is possible to obtain visible light of any wavelength with a single UV irradiation. The glass firmly adheres to a glass substrate. Therefore it can easily be used for developing devices.

1. Introduction

In recent years, attention has focused worldwide on research of preparing semiconductor nanocrystals (with a diameter of several nanometers) which are capable of photoluminescence with high efficiency, using a solution technique to passivate surface defects. [1,2] The superior characteristics of the prepared semiconductor nanocrystals include:

(1) They have an emission lifetime a hundred thousand times shorter than rare earths. Therefore, the absorption and emission cycles repeats very quickly, which results in outstandingly high brightness.

(2) Pure full-color in visible region can be easily obtained according to their diameters due to a quantum size effect.

(3) They exhibit much less deterioration than organic pigments.

The problem, however, is that they are quite unstable in the liquid form. After a several days in

ambient, they will cease to emit light and therefore not be suitable for technical use. The purpose of the study is to stabilize the nanocrystals in glass matrix. Glass normally has some very outstanding properties against polymers, including a superior transparency, mechanical strength, heat-resistance and chemical stability. Therefore, the prepared glass phosphor is anticipated to be suitable for applications.

2. Experimental

Aqueous solution of CdTe nanocrystals were synthesized according to a reported technique that uses cadmium perchlorate and hydrogen telluride gas with an aid of a surfactant of thioglycolic acid.[2] Green- and red- emitting colloidal solutions were obtained during a reflux at 100 °C.

An incorporation of the nanocrystals into glass matrix was performed by using two types of silane coupling agents, namely 3-aminopropyltrimethoxysilane ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si(O-CH}_3)_3$, APS) and 3-mercaptopropyltrimethoxysilane ($\text{SH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si(O-CH}_3)_3$, MPS). Methanol was used as a co-solvent. After partial hydrolysis of one of the silane coupling agents, aqueous solution of CdTe nanocrystals was added.

Emission efficiencies of the solution and prepared glass were estimated relative to standard dyes

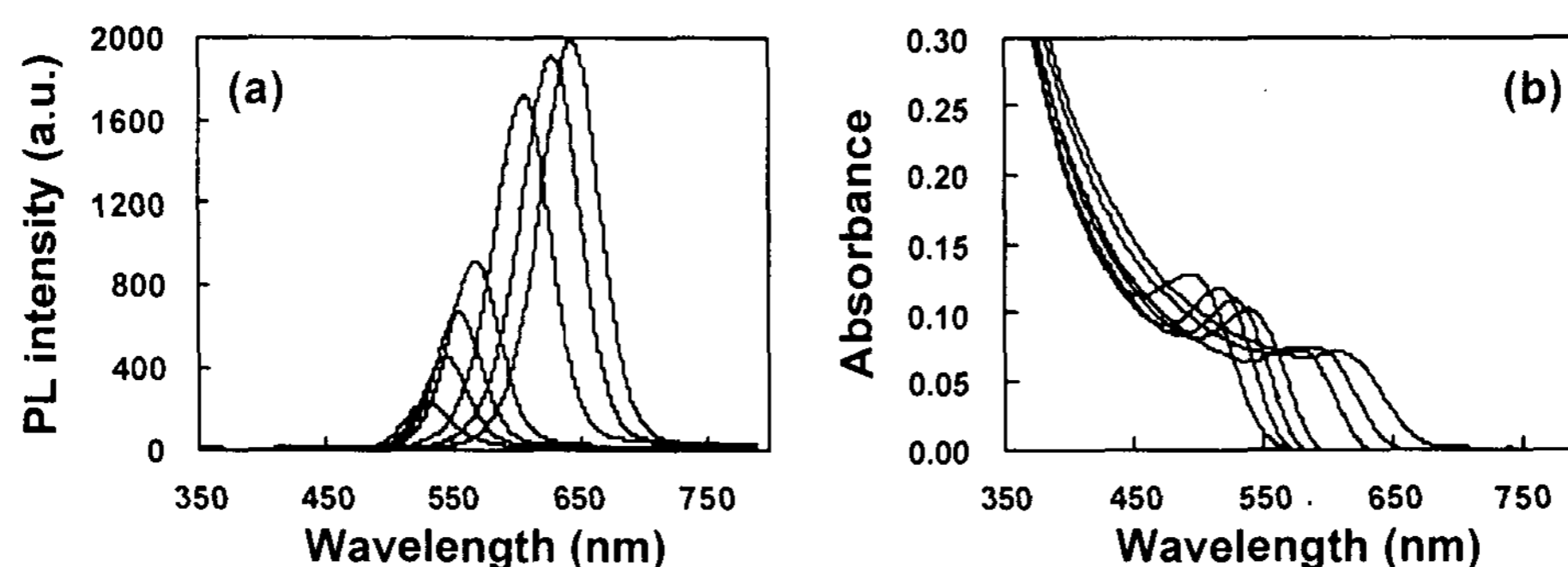


Fig. 1 Absorption and photoluminescence spectra during preparation. The spectra go to the red during reflux due to the increase of the particle size.

(Rhodamine 6G and quinine, which have emission efficiencies of 95% and 55%, respectively).[3] Standard dye solutions having several concentrations were filled in various cells with different optical lengths. The relationships among PL intensity, sample thickness, and absorbance were obtained for a purpose to calculate quantum efficiencies of emission.

3. Results and discussion

When MPS was used, it dispersed the nanocrystals finely because of the affinity of the mercapto-group to the surface of the CdTe. However, it took a month to obtain a gelatinous matrix. In contrast, APS gave a hard and transparent glass matrix within a couple of days.

Whole of the procedure of the preparation using APS consists of the following three steps:

(1) Synthesis of the semiconductor nanocrystals, CdTe, in an aqueous solution. The evolutions of the absorption and photoluminescence spectra during preparation are shown in Fig.1.

(2) Complete intermingling of alkoxides with a favorable affinity with the nano-crystal surface. This becomes possible because APS has an affinity to the carboxylic group in the surfactant attached to the surface of the nanocrystals.

(3) Preparation of a glass with nanocrystals by a sol-gel method while preserving the surface condition of the nano-particles to prevent coagulation. Another advantage of APS is the fact that an amino group in APS accelerates the sol-gel reaction. [4]

The obtained glass has an emission efficiency of ca. 10% relative to the standard dyes. The concentration

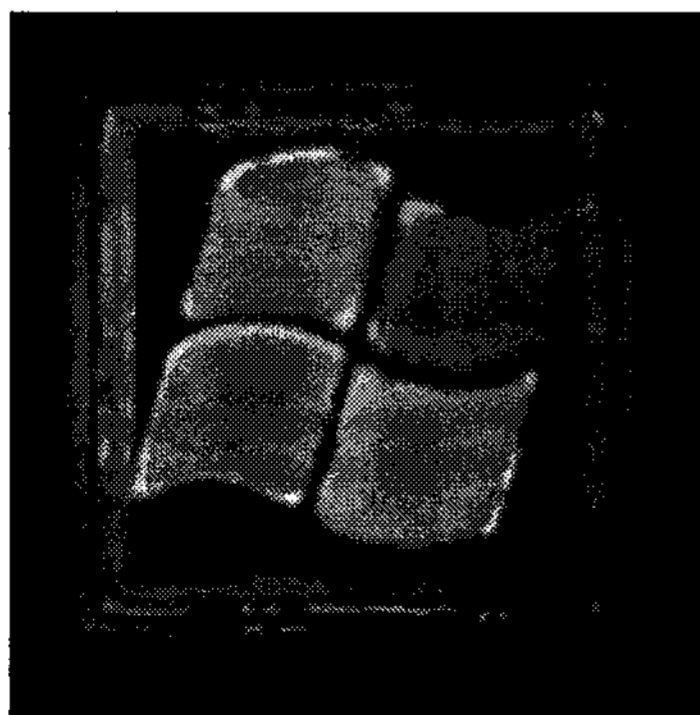


Fig. 2 The glass phosphor prepared on a glass plate under irradiation of UV light.

of the CdTe nanocrystals is ca. 3×10^{-5} mol/L. Figure 2 shows a picture of the glass when it is poured into grooves on a glass substrate. The phosphor glass has a high stability and firmly adheres to the glass substrate. Therefore, we proposed a way to fabricate a patterning of glass phosphor by using plural nozzles normally used for printing as shown in Fig. 3. The phosphor can be excited by compact UV-LED because the emission efficiency does not substantially depend on the excitation wavelength.

4. Conclusion

We used a sol-gel method to incorporate semiconductor nanocrystals in glass. The nanocrystals used were water dispersible CdTe stabilized by thioglycolic acid. A silane coupling agent having an amino group is superior because it has an affinity to a carboxylic group in thioglycolic acid.

5. Acknowledgement

This study was supported by Nanotechnology Glass Project as part of Nanotechnology Materials Program, by New Energy and Industrial Technology Development Organization (NEDO), Japan. We thank Dr. M. Ando for his help with aqueous synthesis of CdTe nanocrystals.

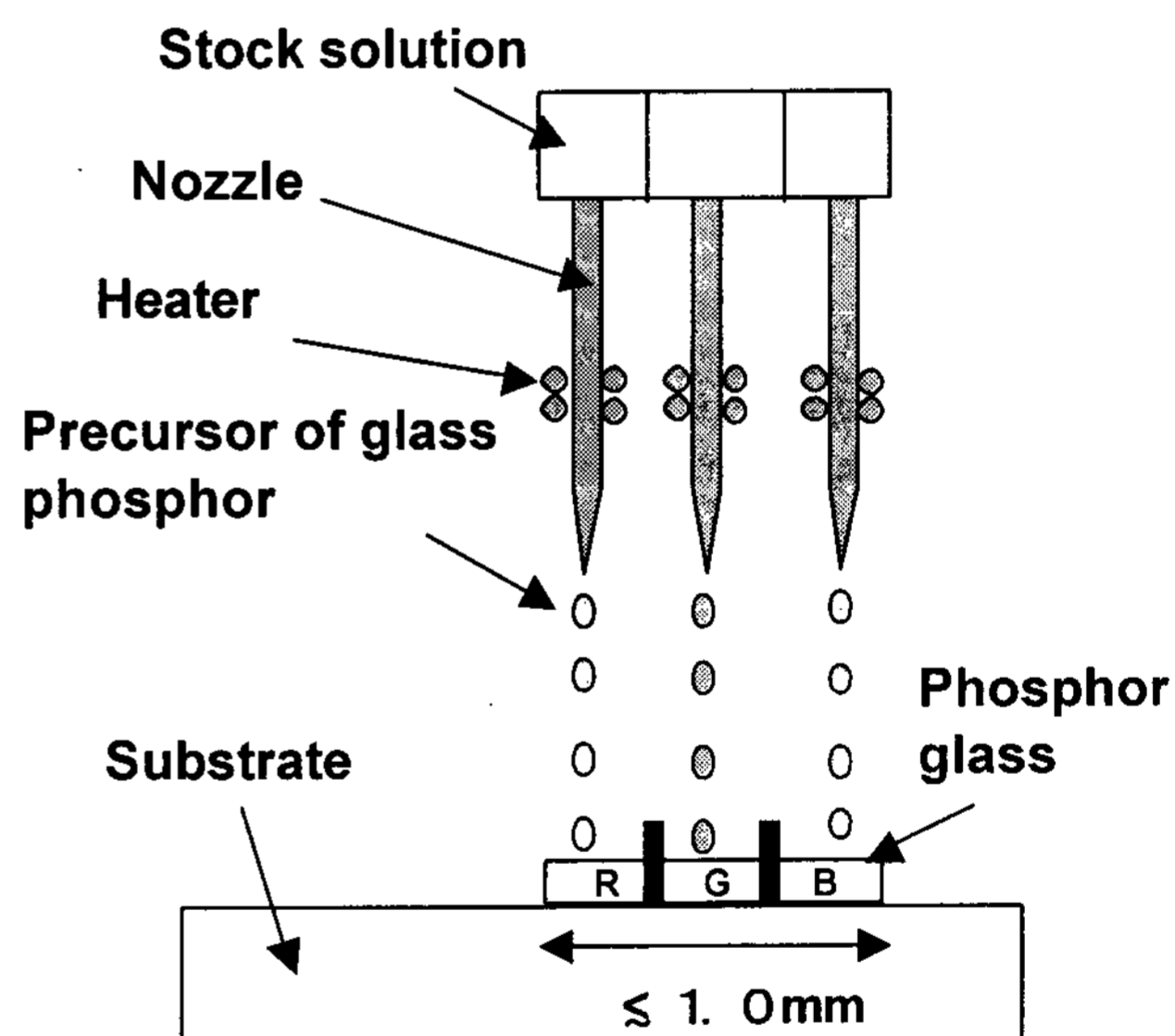


Fig. 3 Schematic diagram for fabrication of patterning of the glass phosphor by an ink jet printing method.[3]

6. References

- [1] B.O. Dabbousi, J. Rodriguez-Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, and M.G. Bawendi, *J. Phys. Chem. B*, 101, 9463(1997).
- [2] A.L. Rogach, L. Katsikas, A. Kornowski, D.S. Su, A. Eychm? ler, and H. Weller, *Ber. Bunsen-Ges. Phys. Chem.*, 100, 1772(1996).
- [3] Norio Murase and Tetsuo Yazawa, Japan Patent 2001-7183.
- [4] a) R.F. Kubin, A.N. Fletcher, *J. Lumin.* 1982, 27, 455. b) W.R. Dawon, M.W. Windsor, *J. Phys. Chem.* 1968, 72, 3251.
- [5] a) C.J. Brinker, G.W. Scherer, *Sol-Gel Science*, Academic Press, San Diego, 1990. b) E.P. Plueddemann, *Silane Coupling Agents*, Plenum press, New York, 1991.