Indium Phosphide Quantum Dots with Polymer Linker for Space Control between QDs and Dispersion in Siloxane Matrix

Boram Kim[1], Yonghyeok Choi[1], Kangwoo Lee[1], and Heeyeop Chae[1,2*]

hchae@skku.edu

[1]School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea

[2]Sungkyunkwan Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea

Keywords: quantum dots, ligand exchange, color conversion films

ABSTRACT

High concentration InP quantum dots (QDs) in siloxane composite were prepared by exchanging ligands of InP QDs using siloxane-based epoxy groups having functionalized with a poly (dimethylsiloxane) diglycidyl ether terminated (PDMS-DGE). The siloxane capped QDs show improved stability in the siloxane matrix due to the compatibility between QDs and matrix.

1 Introduction

Colloidal quantum dots (QDs) offer nanometer scale size, and meet high efficiency, wide color gamut, narrow emissivity of QDs.[1, 2] QD luminescence is divided into photoluminescence (PL) and electroluminescence (EL).[3] Photoluminescence is applied in the form of a QD color conversion films or pixels in the display panel.[4, 5] QD color conversion films are excited by a blue light source with excellent luminance efficiency. The homogeneously dispersed QDs in a polymer matrix are essential in enhancing the optical properties of color conversion layers.[6, 7] Previous research reported various methods to solve the aggregation problem, such as silica growth of QD surface, and introduction of covalent bonds between the QD surface and polymer.[8-10]

In this study, poly (dimetylsiloxane) diglycidyl ether terminated (PDMS-DGE) ligand similar to that of a siloxane matrix was used as the ligand. The hydroxyl (-OH) groups on the QD were first exchanged, and a siloxane-based polymer ligand was introduced through an epoxy ring-opening reaction to control the QD distance and to improve the affinity with the siloxane polymer.

2 Experiments

The novel InP-PDMS-DGE was prepared via two synthetic steps. Ligand exchange was modified to introduce the terminal hydroxy groups.[11] The terminal hydroxy groups were reacted with the epoxy group PDMS-DGE at 40 °C with triethylamine as a basic catalyst. The solution was diluted with chloroform, and then excess hexane was added to precipitate the QDs for collection by centrifugation three times. The QD film was prepared by a dropping method by mixing QDs and acrylate-based siloxane polymer.

3 Results

The strategy of the QD ligand exchange process is shown in Fig 1. The photophysical properties of InP-OA and ligand exchanged InP-PDMS-DGE were compared, and no peak shift was observed after ligand exchange and after the epoxy ring open reaction.

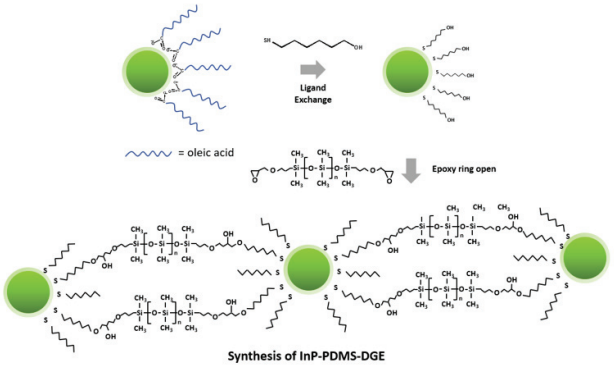

Fig. 1 Schematic of ligand exchange in InP-PDMS-DGE

The PL peaks of InP-OA and InP-PDMS-DGE were confirmed at 513 nm and 514 nm, and there was no significant change in the shift of the emission peak. This indicates that the QD surface damage was negligible during the ligand exchange in InP-PDMS-DGE. The affinity of QD and siloxane matrix was investigated by preparing a polymer mixed QD composite solution. It was confirmed that aggregation between the QDs occurred due to poor affinity between the InP-OA and acrylate siloxane matrix, and InP-PDMS-DGE did not cause aggregation in the acrylate siloxane matrix as shown in Fig. 2.

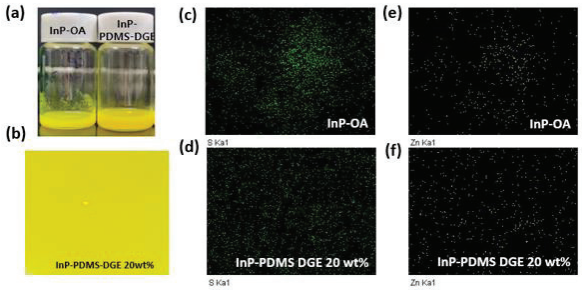

Fig. 2 Photograph of green InP-OA and InP-PDMS-DGE composite solution and films, SEM-EDS mapping images of Zn and S InP-OA in siloxane, InP-PDMS-DGE in siloxane

The PL intensity of InP-PDMS-DGE was 1.5 times higher than that of InP-OA, and this difference is also due to the film stability. Stability tests were performed by exposing both films to 85 °C / 85 relative humidity (RH) for 24 hours. After 24 hours, the brightness of the InP-OA film decreased more than that of the InP-PDMS-DGE film. The color conversion efficiency of InP-PMDS-DGE was 30 % and for InP-OA was 19 %.

4 Conclusions

The surface of the pristine QDs was modified to hydroxyl terminated ligands. The functionalized hydroxyl groups undergo an epoxy ring-opening reaction with an epoxy group under a catalyst. Ligand on the QDs verified and characterized using FT-IR spectroscopy. The QD optical properties were maintained during the ligand exchange process. The InP-PDMS-DGE film showed improved dispersibility, film stability and high dispersibility despite the simple mixing method. This work provides a potential solution for the mixing of QDs and polymer.

Refernece

[1] Z. Yang *et al.*, "Recent advances in quantum dot-based light-emitting devices: Challenges and possible solutions," *Materials Today,* vol. 24, pp. 69-93, 2019.

[2] D. A. Hines and P. V. Kamat, "Recent advances in quantum dot surface chemistry," *ACS applied materials & interfaces,* vol. 6, no. 5, pp. 3041-3057, 2014.

[3] C.-Y. Han and H. Yang, "Development of colloidal quantum dots for electrically driven light-emitting devices," *Journal of the Korean Ceramic Society,* vol. 54, no. 6, pp. 449-469, 2017.

[4] B. Xie *et al.*, "Targeting cooling for quantum dots in white QDs‐LEDs by hexagonal boron nitride platelets with electrostatic bonding," *Advanced Functional Materials,* vol. 28, no. 30, p. 1801407, 2018.

[5] H. Zheng, X. Lei, T. Cheng, S. Liu, X. Zeng, and R. Sun, "Enhancing the thermal dissipation of a light-converting composite for quantum dot-based white light-emitting diodes through electrospinning nanofibers," *Nanotechnology,* vol. 28, no. 26, p. 265204, 2017.

[6] H. Skaff, K. Sill, and T. Emrick, "Quantum Dots Tailored with Poly (p ara-phenylene vinylene)," *Journal of the American Chemical Society,* vol. 126, no. 36, pp. 11322-11325, 2004.

[7] Y. Hao, Z. Gan, J. Xu, X. Wu, and P. K. Chu, "Poly (ethylene glycol)/carbon quantum dot composite solid films exhibiting intense and tunable blue–red emission," *Applied surface science,* vol. 311, pp. 490-497, 2014.

[8] C. Lee, E. Nam, W. Lee, and H. Chae, "Hydrosilylation of Reactive Quantum Dots and Siloxanes for Stable Quantum Dot Films," *Polymers,* vol. 11, no. 5, p. 905, 2019.

[9] Y. H. Kim, S. Koh, H. Lee, S.-M. Kang, D. C. Lee, and B.-S. Bae, "Photo-patternable quantum dots/siloxane composite with long-term stability for quantum dot color filters," *ACS applied materials & interfaces,* vol. 12, no. 3, pp. 3961-3968, 2019.

[10] S. Jun, J. Lee, and E. Jang, "Highly luminescent and photostable quantum dot–silica monolith and its application to light-emitting diodes," *Acs Nano,* vol. 7, no. 2, pp. 1472-1477, 2013.

[11] E. Nam, C. Lee, S. J. Kim, H. K. Chung, and H. Chae, "Stability and dispersion improvement of quantum-dot films by hydrosilylation between quantum-dot ligands and a siloxane matrix," *Optics Express,* vol. 27, no. 14, pp. 20037-20046, 2019.