오가노실레인 변형 산화아연 양자점에서의 고효율 백색발광 전기화학적 연구

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Highly Efficient White Light Emitting Electrochemical Cells of Organosilane-Modified Zinc Oxide Quantum dots

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Abstract

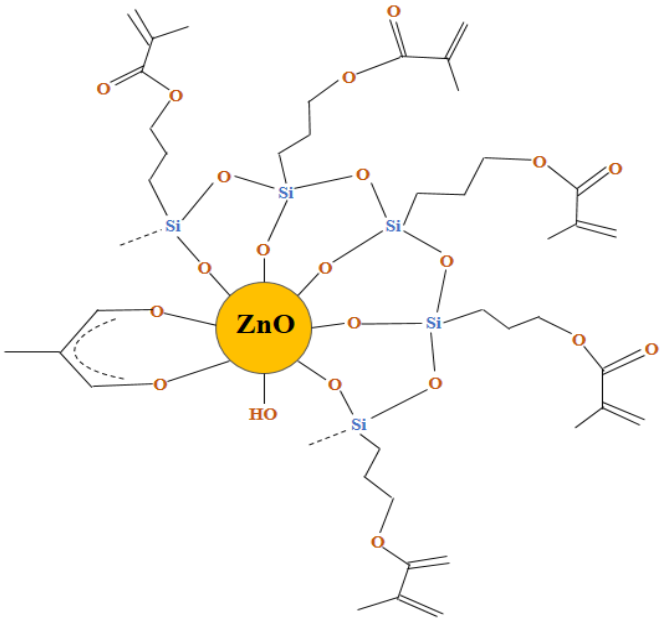
This paper reports data for WLECs generated with ZnO QDs and ZnO-MPS QDs using a spin-coating process. Due to its direct band gap of 3.3 eV at room temperature and wide exciton binding energy of 60 meV, zinc oxide nanoparticles (ZnO NPs) have been considered as a promising candidate in the production of excitonic optoelectronic devices such as QD-LECs. To avoid the agglomeration and for dispersibility improvement surface modification should be made by 3-(trimethoxysilyl) propyl methacrylate (MPS). Using a simple and low-cost updated precipitation process, the syntheses were carried out and, characterized the QDs using X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR) and solid state photoluminescence spectra (PL) were carried out respectively. Compared to the well-known effect of the reduction in nanoparticle size, an unexpected decrease in the band gap energy was obtained and provides a new insight into the relationship between the importance of the band gap energy and the existence of the organic surfactant that facilitated the reduction in the size of the nanoparticle. Finally, the material with the best light emission efficiency was used as an active layer to prepare the Quantum dot Light emitting electrochemical cells (QD-LECs).

Introduction

As we all know, after food and shelter, energy is one of the most challenging items in the world and it has evolved exponentially over the past decade and it has now become an alternative lighting solution based on solid state lighting (SSL), as SSL is now considered to be one of the most effective lighting methods. The worldwide consumption of electricity in 1990 saw a large rise in consumption and increased demand for energy. Energy saving is of great importance in this situation, and we need to find an alternative to light source materials that are more robust, eco-friendly, and also cost-effective. In recent years, Quantum dot LEDs (QD-LEDs) have attracted a great deal of attention as they have specific properties of tunable emission wavelengths by regulating the size of QDs, highly saturated emissions, narrow emissions, small Full Width Half Maximum (FWHM) emissions, solution mechanism, and versatile substrate compatibility. The quantum dot light emitting diodes (QD-LEDs) are of such kind with the advantages of wide viewing angle and color purity even though they are of the expensive side because of the multi-layer synthesize procedure. The commercialization of such QD-LED devices are now become a challenge to market them in a widespread range due to the complicated device architecture and hence due to the high cost of manufacture. The time consuming thermal vapor deposition procedures for multi-layers of active material is general disadvantage of QD-LEDs. The scientists were continuously researching on this are of SSLs and as result of that the new generation of QD-LEDs were

emerged which are called as light emitting electro chemical cells (LECs) which are capable of reducing the cost of device fabrication by reducing the cost of layer deposition which could not be attained by the multi-layer QD-LEDs so far. Quite recently, the scientific community has devoted great attention to the design of novel organic-inorganic nanostructured luminescent hybrid materials based on silica matrices, layered solids and metal oxide systems of interest for various bio sensing, bio imaging and optoelectronics applications.

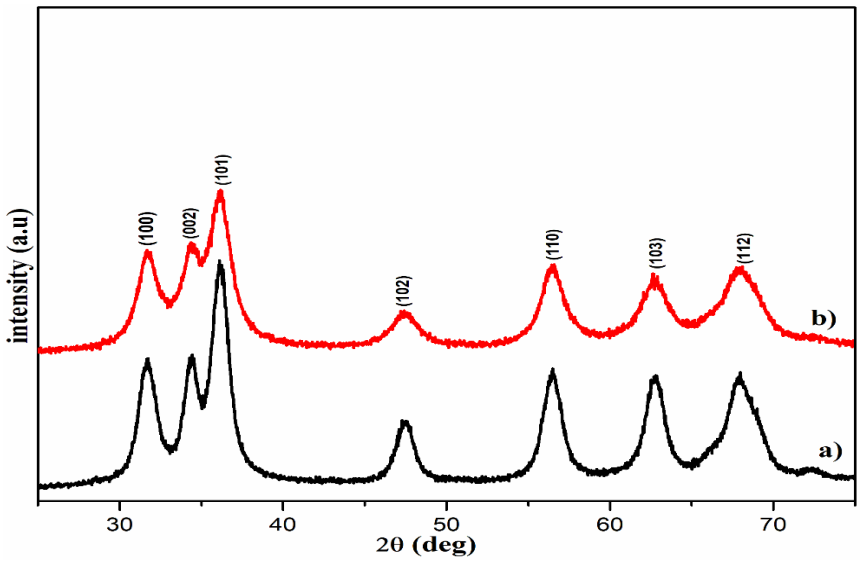
Experimental section



Proposed structural model of surface modified ZnO QDs after synthesis.

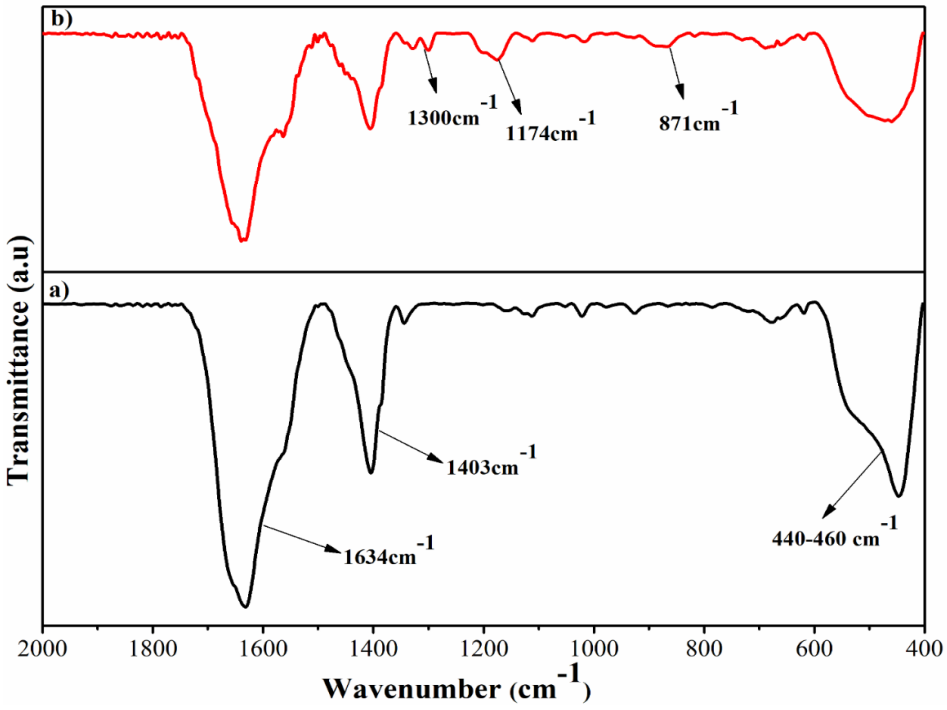
Results and Discussion

Structural properties



The structural properties of both the samples ZnO QDs and ZnO-MPS QDs were analyzed using X-ray diffraction (XRD). The XRD patterns of all the samples (Fig.1) show the major diffraction peaks at 31.6°, 34.4°, 36.3°, 46.6°, 56.4°, 62.2°, 67.1° 2θ, assignable to the ZnO (100),(002),(101),(102),(110),(103) and(112) planes. Using the Debye-Scherrer equation, the mean crystallite size (L) of the synthesized ZnO QDs was calculated. A decrease was seen in the estimated crystallite size after surface modification for ZnO QDs from 8.01 nm to 4.4. Although the XRD pattern of unmodified ZnO NPs displayed well-resolved reflections, when GPTMS was used in various concentrations to adjust the ZnO NPs, a progressive slight expansion of the diffraction peaks could be observed. The surface is a symbol of declining crystallinity.

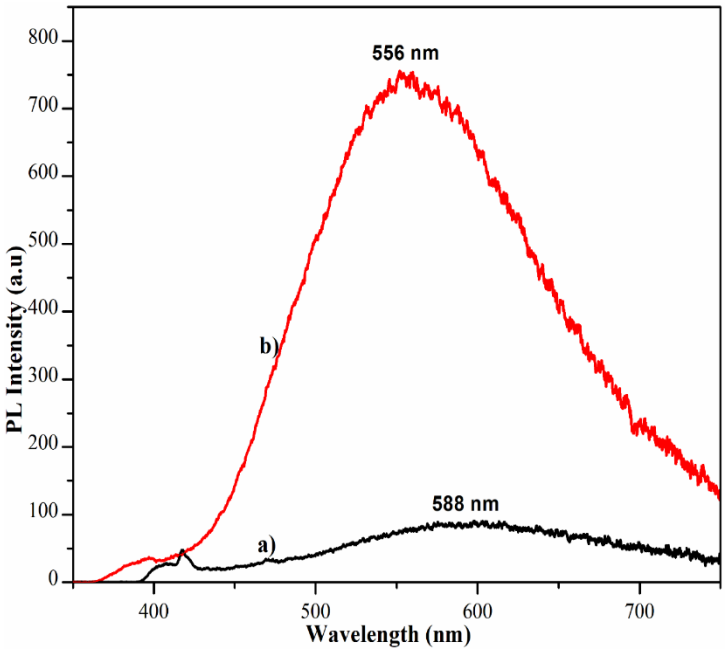
The binding of the MPS molecules to the surface of the ZnO QDs was investigated using FTIR spectrometry. The stretching vibration of OH groups in the residual water physically adsorbed on the surface of the particles can be assigned to a wide band in the 1500-1700 cm^{-1} range. The asymmetric and symmetrical stretching modes of the carboxylate groups (COO) of residual acetate anions chemically bound to the ZnO surface during the synthesis process are allocated to large bands at 1403 cm^{-1}; these are difficult to fully detach, even with vigorous washing of the samples. The formation of both Zn-O-Si bonds during the functionalization process and Si-O-Si bridges by self-condensation of the organosilanes used to change the ZnO surface may be indicated by a new split and very strong band located at 871 cm^{-1} that appears in the MPS-grated ZnO samples.



Photoluminescence properties

Photoluminescence spectra of both Organosilane modified and ZnO QDs were qualitatively compare the emission properties. Both samples were irradiated at 365 nm. The unmodified ZnO QDs shows a wide emission centered at 588 nm, which is associated with electronic transitions of surface defects. As the Organosilane modified ZnO QDs shows increase in the emission intensity and shows blue shift. Intense emission band with maximum centered at 556 nm. Due to quantum size effects, as the size of the ZnO nanoparticles becomes

smaller during functionalization with organic surfactants, the band gap energy increases. A tuning of the photoluminescence efficiency and emission wavelength was obtained on the basis of these findings by adjusting the organic load of the ZnO nanoparticles.



Conclusion

Therefore, we confirmed that by altering the silane load anchored on the ZnO surface, a tuning of the photoluminescence efficiency and emission wavelength is possible. In addition, it is important to note that the silane selected to decorate the surface of ZnO (3-(trimethoxysilyl) propyl methacrylate (MPS) could be used to bind various entities (such as quantum dot, organic dyes, etc.) of interest in various fields of nanotechnology, ranging from optoelectronic to sensoristic and light harvesting applications, using covalent and/or ionic bonds. Finally, we found that hybrid ZnO QDs with the best emission properties can also be successfully used in modern QD-LECs devices for the processing of active layers and it pave the way for the development for the development of novel optimized devices.

Acknowledgements

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References

[1] Q. Pei, G. Yu, C. Zhang, Y. Yang, A.J. Heeger, Science (80-.). 269 (1995) 1086.

[2] S. Tang, W. Tan, X. Zhu, L. Edman, Chem. Commun., 49 (2013) 4926-4928.