White light emitting diode prototypes based on cadmium sulfide and graphene carbon quantum dots.

Prototipos de diodos emisores de luz blanca basados en puntos cuánticos de sulfuro de cadmio y de grafeno.

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Abstract: During the last years, semiconductor quantum dots (QDs) have attracted great attention due to the outstanding properties for solid-state lighting, display technology, biosensors, among others. White light emitting diodes (WLEDs) using down conversion approach is one of the new attractive alternatives in solid-state lighting. However, these devices present several shortcomings as near-UV light escape and QD-polymer incompatibility. In this work, we propose alternative WLED prototypes to overcome these problems. These prototypes have an inner and outer QD-polymer nanocomposite. A solvent exchange in the CdS QDs sample, which was embedded in the inner nanocomposite, was performed to address the QD-Polymer incompatibility. While the near-UV light escape is reduced by using Graphene Carbon QDs embedded in the outer nanocomposite

Keywords: Down conversion, Stokes's shift, Surface defects, CdS QDs.

Resumen: Durante los últimos años, puntos cuánticos (QDs) semiconductores han tenido gran atención debido a sus propiedades excepcionales para aplicaciones en iluminación de estado sólido, tecnologías de monitores, bio-sensores, entre otras. Los diodos emisores de luz blanca (WLED) que utilizan el enfoque de conversión descendente, son una de las nuevas alternativas para iluminación de estado sólido. Sin embargo, estos dispositivos presentan varias deficiencias como la fuga de luz cercana al UV y la incompatibilidad entre el QD y el polímero. En este trabajo proponemos prototipos alternativos de WLEDs para solucionar estos problemas. Estos prototipos poseen un nano compuesto (polímero-QDs) interno y externo. Para abordar la incompatibilidad entre el polímero y los QDs se realizó un intercambio de solventes en la muestra de

QDs de CdS, que estaban incrustados en el nanocompuesto interno. El escape de luz UV se reduce utilizando QDs de carbono grafeno incrustados en el nanocompuesto externo.

Palabras claves: Conversión descendente, desplazamiento de Stokes, defectos superficiales, QDs de CdS

Introduction

Colloidal semiconductor quantum dots (QDs) have attracted intense attention because they have advantages such as tunable emission, and a low temperature synthesis method, which make them well-suited for use in optoelectronic devices and biomarkers (Li et al 2018). Efficient White Light Emitting Diodes (WLEDs) have recently attracted considerable attention in solid-state illumination (Chou et al 2019).

Nowadays, the tungsten lamp, Compact Fluorescent Light (CFL) bulbs, and organic LEDs (OLEDs) are still used. These lighting systems are inefficient, generate excess heat and have environmental shortcomings (Kathirgamanathan 2015; Bansal 2016).

In 2003, Lauren Rower and co-workers were the firsts in fabricate quantum-dot-solid-WLED devices and initiated the application of QDs as light transition materials into light conversion composite (Yi et al 2016). WLEDs are generally fabricated using epitaxial growth. These devices use a UV-blue LED as an excitation source and the QD-polymer nanocomposite as the active material. However, this could be expensive. An alternative low-cost method of fabrication is the Photoactive Packaging (PAP) as reported by Chou et al. (2019). Nowadays, these devices show relevant disadvantages like near ultraviolet (UV) light escape, visible (VIS) light reabsorption and internal heating in the QD solution/polymer nanocomposite.

Here, we report the fabrication of WLEDs using the PAP method. We overcome the near-UV light escape and reabsorption problem by optimizing the amount of Graphene Carbon Quantum Dots (GCQDs) and using CdS QDs with large Stokes shift of the defect-related photoluminescent (PL) band, respectively.

Experimental section

Synthesis of quantum dots

In a synthesis of CdS QDs, a beaker with 266 mg of cadmium acetate monohydrate, 8 ml of oleic acid (OA) and 15 ml of 1-Octadecene (ODE) was heated at 120° C for 30 minutes under intense stirring. Then, it was cooling to about 30°C. When this temperature was reached, 16 mg of sulfur powder was added into the beaker. The new solution was heat up to 240°C and was keeping during 1 hour at this temperature. Then, we began to extract the CdS QD samples when the color of the reacting solution changed from clear to yellowish. A total of 12 samples of 1 mL were taken

from the hot mixture and labelled as M01-M12. After that, for the CdS samples a solvent exchange from ODE into benzene was performed using the Precipitation-Redispersion (PR) method following the procedure reported by Shen et al. (2017).
On the other hand, GCQD samples were synthesized as reported elsewhere (Cuadra et al. 2018). Then, a solvent exchange from water to ethanol was performed using PR method.

Absorption and photoluminescence measurements

To obtain the measurement of absorption spectra of all samples, we use an experimental arrangement as shown schematically in Fig. 1. A USB4000 UV-VIS Ocean Optics spectrometer with an optical resolution about 1.5 nm was used. A Deuterium lamp was used as light source.

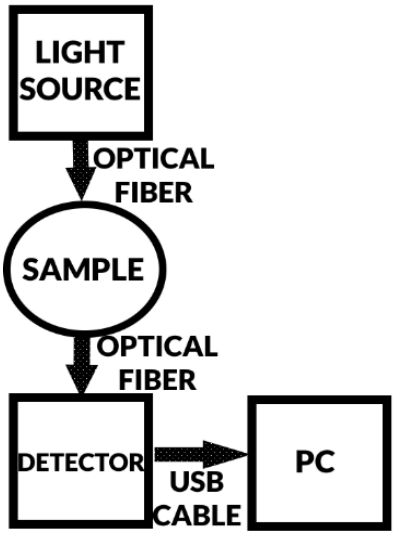

Figure. 1. Diagram of the experimental arrangement used in absorbance measurements.

For the photoluminescence (PL) measurements we used a USB4000-FL Ocean Optics spectrometer with an optical resolution around 10 nm, and a UV-365 nm LED as excitation source. The PL experimental setup is shown schematically in Fig. 2.

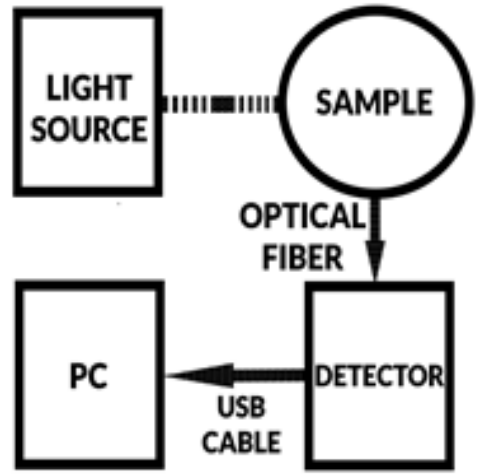

Figure. 2. Diagram of the experimental setup for the PL measurements.

Fabrication of the White LEDs

For the fabrication of WLED prototypes, we use commercial 400 nm LEDs, which were coated with two nanocomposite (crystal polyester resin-QDs) layers. The inner layer contains CdS QDs whereas the outer layer GCQDs. To mold these nanocomposites two test tube with diameters of 0.9 cm and 1.4 cm were used. We show the fabrication diagram of the devices schematically in Fig. 3.
Three WLED prototypes with volume ratio (GCQD solution/crystal polyester resin) of 0.2, 0.4, and 0.6 were fabricated and labelled as P1, P2 and P3.

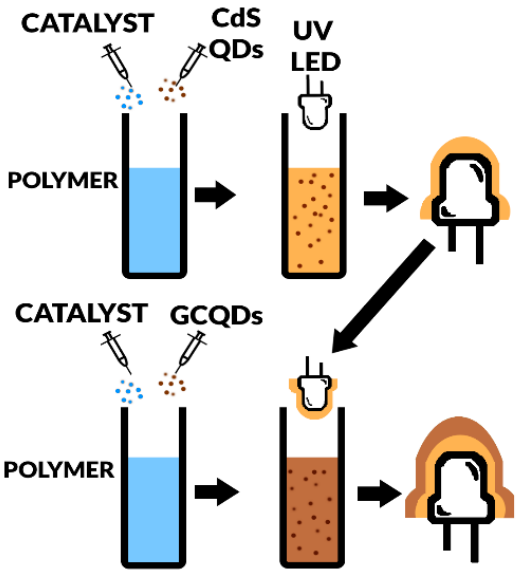

Figure. 3. WLED fabrications diagram.

Result and discussion

The absorption and PL spectra for M02, GCQDs and crystal polyester resin are shown in Fig.4.

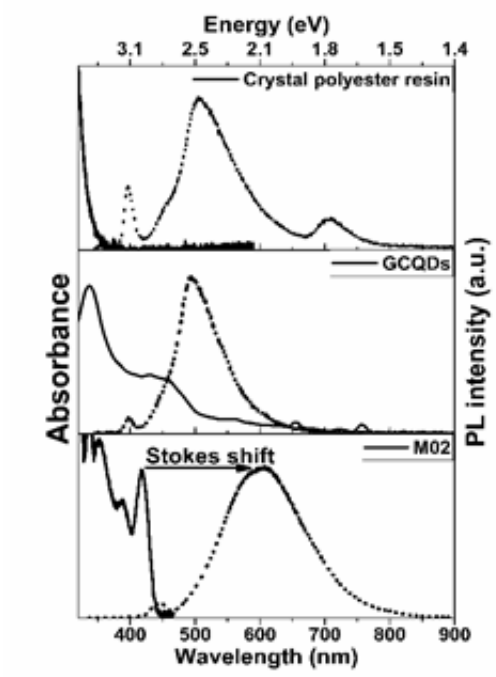

Figure. 4. Absorbance (solid line) and PL (dotted line) spectra (not to scale) of CdS QDs,

An absorption band in the UV region is clearly observed for the M02 sample. A 3.8 nm QD size was estimated, using the maximum of this absorption band, following Yu et al (2003). For this sample, two emission bands were observed in the corresponding PL spectrum. The lower intensity band is associated to the band edge emission while the higher intensity and broader band is associated to surface state emission as observed by Ponce et al. (2015) in others II-VI QDs. A large Stokes shift is observed for the latter band. Due to this property, the reabsorption in M02 was reduced. For these reasons, we choose the CdS-QDs as the active material in the WLED prototypes.

GCQDs strongly absorb in the UV region, while emitting weakly (two order of magnitude less than CdS QDs) in the VIS region. We use these carbon nanostructures to reduce the UV light scape. On the other hand, the low absorption of the crystal polyester resin in the VIS region, as observed in Fig. 4, ensure the scape of the CdS emission.

In order to observe the CdS-QD and GCQD spatial distributions in the device, we performed a light intensity map of the P1 and P3 emission. In figure 5, regions with high (yellow) and low (red) intensities are clearly observed, which could be associated to high and low concentrations of CdS QDs, respectively.

Additionally, we observed a rapid

solidification in both crystal polyester resin nanocomposites with the naked eye. The emission spectra of P1 and P3 are shown in figure 6. For P3 a clear UV reduction (around 90%) can be observe

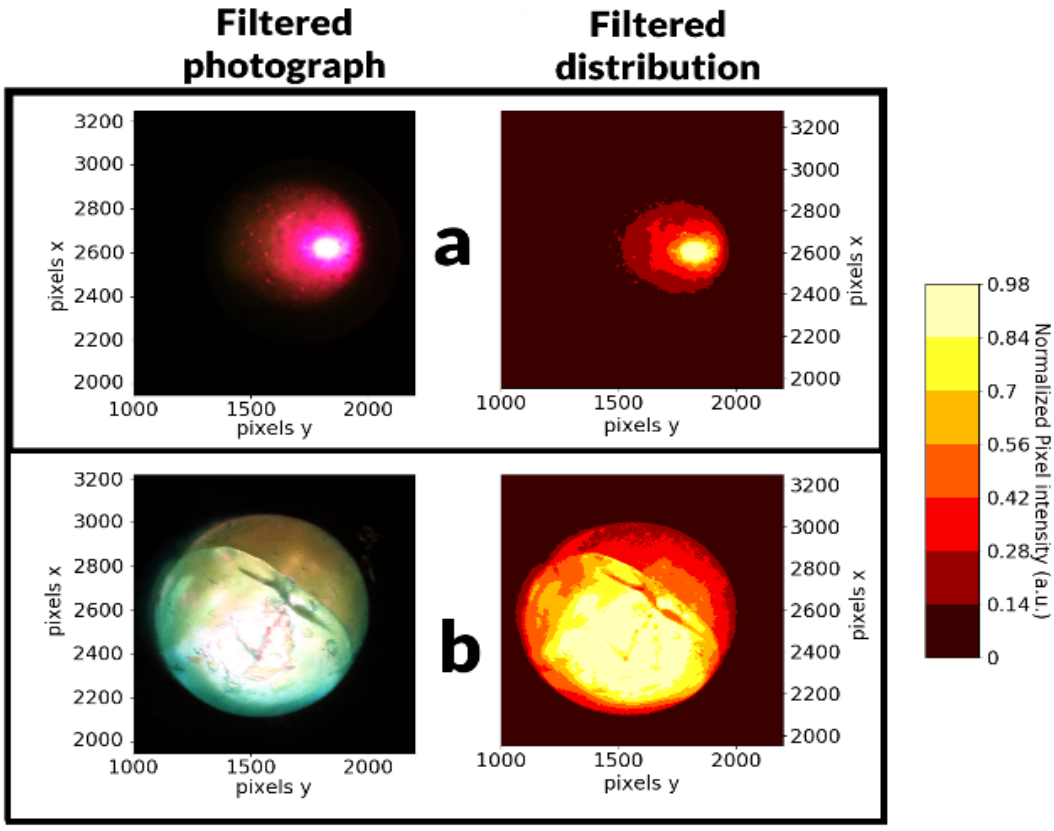

Figure 5. Light intensity maps for a) P1 and b)

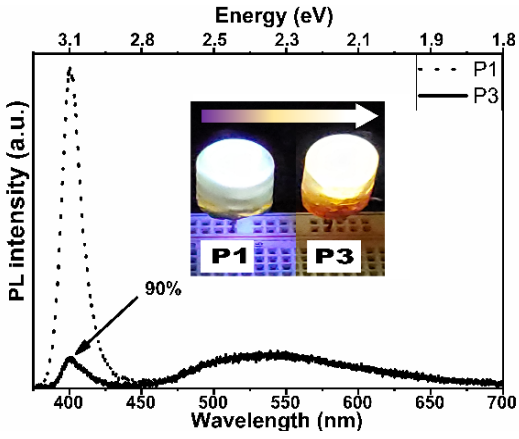

Figure 6. Emission of P1 and P3. Inset. Fabricated prototypes.

Our finding show that the UV-light escape can be reduced by increasing the GCQD solution/crystal polyester resin ratio in the devices.

Conclusion

Colloidal CdS QDs with sizes from 3.5 nm to 4.9 nm were synthesized. Strong absorption in the UV region and a high intensity and broad-band emission in the VIS region was observed for CdS QDs. The solvent exchange in the CdS QD sample allowed a rapid solidification of the nanocomposite in the device inner layer. The UV light escape was reduced by increasing the GCQD so-

lution/crystal polyester resin mixture ratio.

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