UV-patternable nanocomposite containing CdSe and PbS quantum dots as miniaturized luminescent chemo-sensors

Pedro J. Rodríguez-Cantó, Rafael Abargues, Juan Martínez-Pastor

Intenanomat S.L., Calle Catedrático Beltrán 2, 46980 Paterna, España
pedro.j.rodriguez@uv.es

The role of nanoscience in analytical science has been greatly established for the development of (bio)chemical sensors with enhanced performance. The design of low-cost, easy-to-fabricate and portable analytical devices with a low limit of detection (LOD), good selectivity, high sensitivity and short response time are in high demand.[1,2] Part of that has been made possible by the use of nanomaterials. In particular, (bio)chemical sensors based on fluorescent quantum dots (QDs) have attracted intense interest because of their excellent optical and electronic properties compared to the routinely employed fluorescent organic dyes.[3] These properties include size-tunable light emission over a wide range of energies, high photoluminescence quantum yield (PL QY), narrow emission line width, and good solution processability.[4] In addition, the physicochemical stability of QDs, their extremely large surface area, as well as the possibility of functionalizing their surface by conjugation with appropriate molecules make them very attractive nanomaterials for ultrasensitive sensors with the possibility of multiplex (bio)chemical detection.[5]

In this work, we have developed a novel multifunctional hybrid polymer-based luminescent material particularly formulated for photolithography and tested it as a miniaturized chemosensor. This nanocomposite was formulated with either luminescent CdSe (for the visible) or PbS (for the near-IR) colloidal QDs embedded in a polyisoprene-based photoresist (PIP). The resulting nanocomposite combined the extraordinary optical properties of the QDs with the lithographic characteristics of the resist matrix. Both the optical properties of QDs and the lithographic performance of the photoresist were preserved after the incorporation of QDs into the photoresist (Fig. 1). We checked the sensing capability of this QD–PIP nanocomposite using 1 cm^2 square patterns as a disposable gas sensor by monitoring the PL intensity upon exposure to 2-mercaptoethanol (MET) and ethylenediamine (EDA) using two types of QDs: CdSe and PbS. The transduction mechanism of the sensor is based on the changes of the QD photoluminescence (PL) when molecules are adsorbed onto the QD surface. The CdSe–PIP pattern sensor showed a decay of PL when exposed to different amounts of MET and EDA in vapour and found LOD values around 10^{-3} ng L^{-1} and 125 ng L^{-1}, respectively (Fig. 2). From the calibration curve, we determined that the binding affinity of MET to CdSe–PIP is around four orders of magnitude higher than that of EDA. We also observed a linear sensing behavior within a broad concentration range, which allows us to use CdSe–PIP as quantitative sensor for MET and EDA. Furthermore, the PbS–PIP nanocomposite showed different sensor responses depending on the target analyte, whereas the exposure of PbS–PIP sensor to EDA led to the quenching of the QD PL, and exposure to MET molecules resulted in a 6.5-fold enhancement of the PL intensity. The different responses of CdSe and PbS QDs to MET can be explained by the difference in the energy of these QDs valence band top with respect to the redox level of the thiol molecule. In conclusion, these results demonstrate that a completely disposable sensing platform technology can be developed using this novel QD–PIP luminescent nanocomposite, which may also form the basis for the development of miniaturized chemosensors, which may be of interest for several fields such as the food industry, environmental monitoring, and health.

References

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Figures

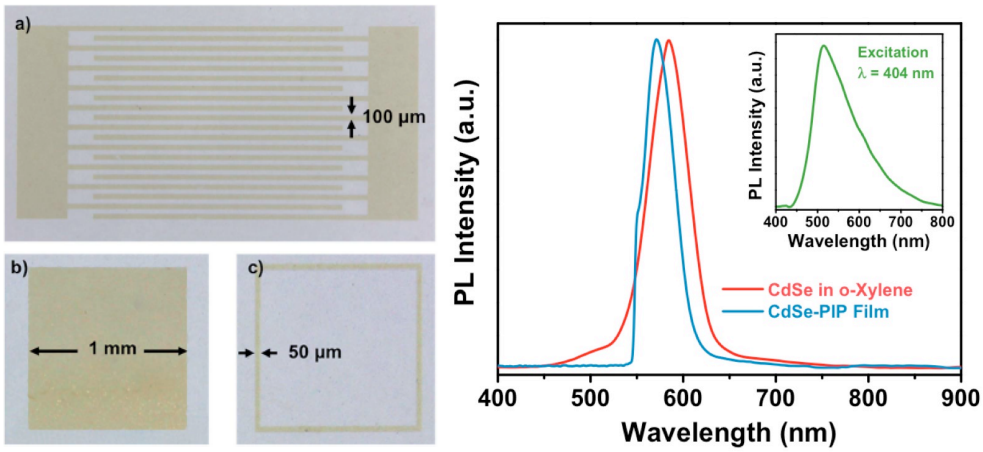

Fig. 1: (left) Optical microscope pictures of different CdSe–PIP nanocomposite structures on glass patterned by UV lithography: (a) interdigitates,(b) solid square, and (c) framework. (right) Emission spectra of CdSe QDs in o-xylene and in the nanocomposite film upon excitation at 532 nm. Inset: Emission of the bisazide molecule contained in the photoresist film upon excitation at 404 nm.

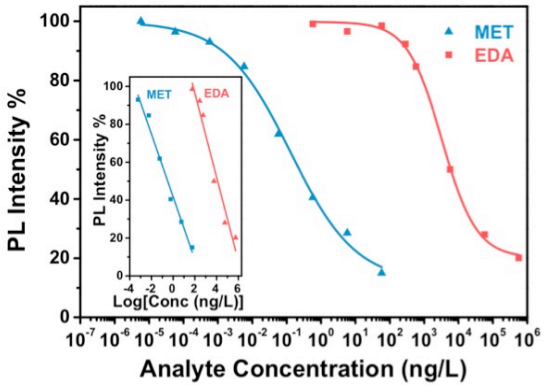

Fig. 2. PL decay response of CdSe-nanocomposite miniaturized sensor as a function of the mass concentration of EDA and MET in the vapour phase for an exposure time of 15 min. Inset: linear dependence and corresponding regression line of the sensor response.