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CONFERENZA DI DIPARTIMENTO 2019

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Department of Chemical Sciences and Materials Technology

28-29-30 OTTOBRE
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Multilayers Of Carbodithioate And Sulfide-Linked CdSe Nanocrystals: Progressive Increasing Of Exciton Delocalization

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Semiconductor nanocrystals (NCs) are challenging materials to be exploited in devices like light emitting diodes, solar cells and photodetectors, because of their unique electronic, magnetic and optical properties. Typically such devices require that the NCs should be both distinct particles that exhibit quantum confinement of the charge carriers and strongly coupled to the neighbouring particles when they are assembled into a film. In fact, quantum confinement allows the electronic properties to be tuned with the size, while electronic coupling facilitates charge transport in the device.

Unfortunately, such goals are difficult to achieve because of the very poor inter-particles contacts caused by linkers between NCs¹. In fact, though much effort has been devoted in optimizing molecular core conductivity, there have been relatively few attempts at designing optimal anchoring groups to semiconducting nanocrystals. In a previous work we found that multilayered hybrid films realized by the alternation of CdSe-NCs and bi-functionalized linkers bearing dithiocarbamate moiety with ethylene or phenylene as spacers, have shown promising photoconductive properties², which were supported by photo-excited carrier dynamic experiments combined with theoretical calculations³. These latter studies show that the dithiocarbamate anchoring group causes the hybridization of the molecular HOMO state with the CdSe-NCs layers, which may favor the delocalization of the charge carriers through the layers. According to these encouraging results, other linkers bearing sulfur-based anchoring groups were taken into account.

In the present work tetrathioterephthalate (TTTP) and sulfide (S) dianions were reacted with (hexadecylamine/stearate)-capped CdSe nanocrystals (4.5 nm diameter) to form multilayers on ITO glass via layer-by-layer alternation. The study provides the determination of the electronic properties of the linkers by means of both UV-vis and electrochemical analyses. Linkers coordination to CdSe-NCs surface was investigated in bulk by FTIR analyses and in monolayers by UV-vis and electrochemical determinations. 10-multilayered film formation was monitored with UV-vis spectroscopy and it was observed a decrease of the energy of the optical band-gap (ΔE_{gn}) which depends linearly with the inverse of the number of layers (n). The change of NCs packing during multilayers build-up causes progressive increase of exciton delocalization. The effect was modeled and discussed in the light of the photoluminescence and photoconductive properties of the multilayers. Comparison with the previously investigated ethylene or phenylene bis-dithiocarbamate dianions has been performed.

References:

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Acknowledgement:

Support by the Project Accordo Quadro CNR Regione Lombardia 2016 “I-ZEB” is kindly acknowledged. We are, also, indebted with the Italian Government for the financial support.