Quantum Confinement and Carrier Transport in π-SnS Colloidal Quantum Dot Solids

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Solution-processable material technology is beneficial because of low-cost and large-scale production. Colloidal quantum dot (QD) solids are materials that also exploit the quantum confinement properties of the constituent nanocrystals. Among the manifestation of the quantum confinement effect is the energy bandgap value variations by size that make them suitable for spectral matching in optoelectronic applications, such as photodetectors and photovoltaics. Significant progress in QD optoelectronic devices has been made mainly by Pb-based, Hg-based, and Cd-based binary compounds. Nevertheless, their high degree of toxicity is among the main concerns for practical applications. Sn-chalcogenides are among the possible environmentally benign alternatives which their bulks have demonstrated intriguing properties for energy devices. Nanostructuring these Sn-chalcogenides into QD form may create variations of their crystal structures and properties. While SnS commonly comes as an orthorhombic herzenbergite structure, its natural occurrence, recently another thermodynamically stable low-symmetry cubic SnS bulk crystal has been identified,[1] which is predicted to have distinctive properties.

Here we demonstrate robust quantum confinement effects in small diameter π-type cubic SnS colloidal NCs and its exploitation for high-performing photodetector devices. Well-controlled production of π-cubic SnS colloidal NCs with a 4-10 nm diameter is established by developing a one-pot synthesis procedure inside an inert glove box. The inert synthesis condition allows Sn complexation with only a single type of ligand molecule to form the Sn precursor. This complexation enables the synthesis of the nanocrystals to form π-type cubic SnS ($P2_13$). The synthesized NCs exhibited a quantum confinement effect with strong variations of energy bandgap by size. The bandgap value at the larger size limit was around 1.53 eV, while the smallest obtainable QD gives 1.7 eV. The cubic structure of the QDs eases the device fabrication, analogous to the established approaches in rocksalt QDs (e.g., PbS).[2] Simple photodetector devices are fabricated using either a layer-by-layer ligand-exchanged spin-coating or assembly at a liquid/air interface to form a QD monolayer. Although their channels are made from only a single or few monolayer(s) of the π-SnS QD, the photodetectors demonstrate high responsivity comparable to the established QD photodetectors.[3] This new compound will open new pathways for establishing safe and high-performing QD optoelectronic devices.

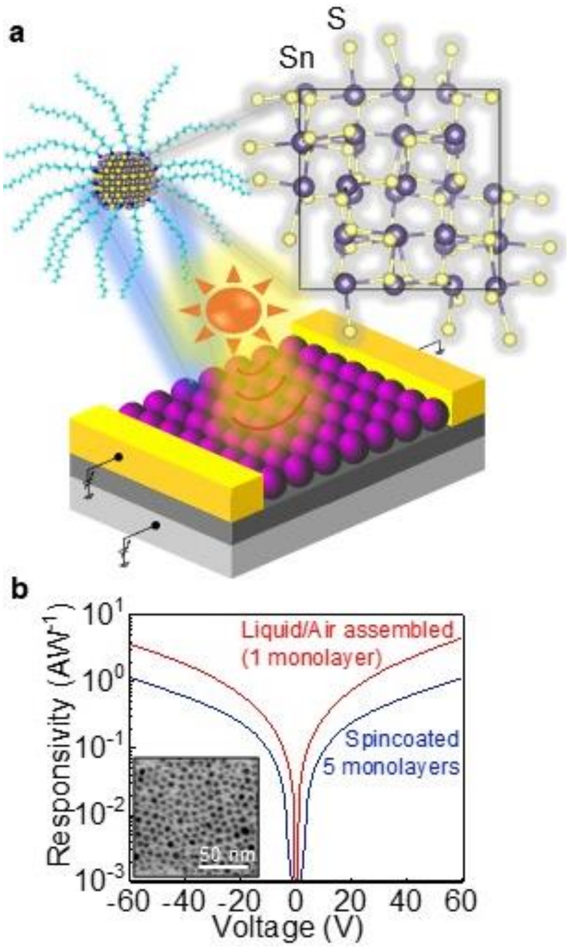

Fig. 1. (a) A schematic of a planar photodetector device based on π-SnS colloidal quantum dots (QD). The π-SnS has a low-symmetry cubic structure. **(b)** The comparison of responsivity values of photodetectors made by π-SnS QDs which were fabricated using two different methods. (inset) the eleTEM image of the QD before ligand exchange.

Ref.; [1] R.E. Abutbul, Adv. Mater. 30, 1706285 (2018); [2] R.D. Septianto, et al. *NPG Asia Materials* 12, 33 (2020); [3] S.Z. Bisri, et al. JP Patent filed (2021).