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Enhancement of charge transport in quantum dots solar cells by *N*-butylamine-assisted sulfur-crosslinking of PbS quantum dots

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ABSTRACT

A novel and facile strategy to realize selective inorganic ligand (S^{2-}) exchange on Pb-rich surface of PbS colloidal quantum dots (QDs) has been demonstrated. This was achieved via xanthate ligand decomposition at room temperature without damaging the QDs surface. This proposed method offers an amicable solution for the limitation that inorganic-terminated colloidal QDs are restricted by the specific requirement to solvents with high dielectric constant. Furthermore, Introduction of S^{2-} to form sulfur-crosslinking PbS QDs enables reaction force-induced QDs arrays and smooth surface morphology of the spin-coated QDs film as evidenced by atomic force microscopy. Passivation of QDs by bromide combined with sulfur led to stronger electronic coupling between adjacent QDs as compared to bromide-only passivated QDs counterparts. Bromide and sulfur hybrid-capped QDs exhibited remarkably enhanced carrier mobility from 1.66×10^{-4} cm^2/V s to 5.0×10^{-1} cm^2/V s as evidenced by the Hall- Effect measurement. The smooth QDs film morphology and higher charge transport contributed to the boost in the power conversion efficiency of QDs solar cells up 4.96% compared that using only CTAB passivated PbS QDs solar cells (3.04%). This controlled sulfurization approach paves a potential way for improved optoelectronic properties and devices based on QDs.

1. Introduction

Semiconductor nanocrystals (NCs), specifically colloidal quantum dots (QDs) are promising materials for photovoltaics and light emitting diodes due to their band gap tunability, high photo-stability, excellent charge transport properties and low cost fabrication process (An et al., 2017; Chuang et al., 2014; Kramer and Sargent, 2013; Protesescu et al., 2015; Tang et al., 2018). The exploitation of these superior properties requires the knowledge of nanocrystal surface chemistry as this determines the size and morphology of the resultant NCs and hence the overall optoelectronic properties. Mass production of colloidal QDs is another advantage of this material, being made possible through the use of colloidal aqueous synthesis in which various capping ligands could be used to functionalize the surface of QDs without the need of inert atmosphere and using conventional solvents (Aruda et al., 2015; Liu et al., 2017). Introducing inorganic/organic capping ligands passivates the dangling bonds on the surface of QDs and reduces the presence of charge trapping sites (Ip et al., 2012). On the negative side, Incorporation of long insulating organic molecules on the surface of QDs for dispersion in organic solvents results in to weak inter-particle interaction leading to the hampered charge separation and charge transfer (Kodaimati et al., 2017). Therefore, logical efforts must be directed towards the reduction of inter-QD distance and lowering of energetic barrier along with effective surface states passivation to improve the optoelectronic properties and devices performance.

Reducing the alkyl chain length of organic ligands by their short alkyl-chain counterparts or inorganic species has been reported to improve the surface passivation and optoelectronic properties (Ananthakumar et al., 2014; Fafarman et al., 2011; Ko et al., 2016; Mustakim et al., 2018; Nag et al., 2011; Zhang et al., 2014). However, there is tradeoff between electronic defects and the charge transport properties when shorter ligands are used. To address this issue, researchers have explored inorganic materials as one of the potential candidates for surface modification due to their versatility and high

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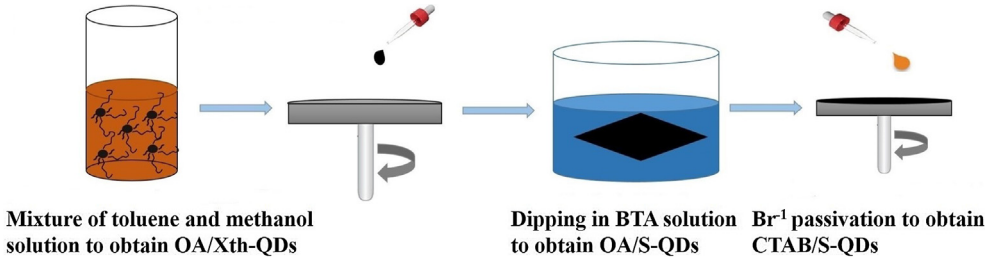

Scheme 1. Schematic representation for the fabrication of sulfur-connected thin films of PbS QDs.

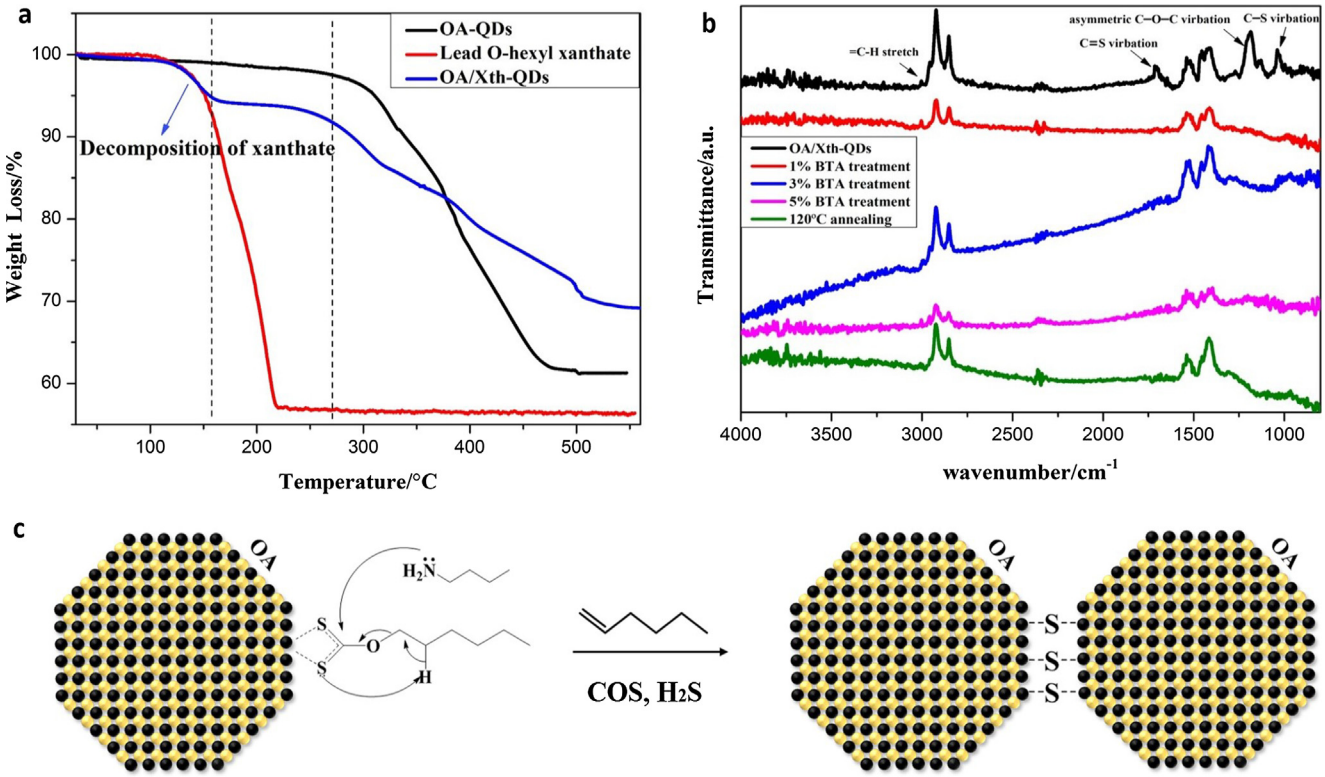

Fig. 1. (a) Thermogravimetric analysis (TGA) to document weight loss of OA/Xth-capped QDs compared with lead *O*-hexyl xanthate and OA-QDs. (b) Scheme of OA/S-QDs obtained from OA/Xth-QDs after BTA treatment. (c) Attenuated total reflectance FTIR spectra of OA/Xth-QDs through 1%, 3%, 5% BTA and 120 °C annealing treatment.

Table 1
Summary of PbS QDs chemical composition obtained from as-deposited films, including traditional CTAB-QDs, native OA-QDs, OA/Xth-QDs, OA/S-QDs and CTAB/S-QDs.[a]

	Pb	S-total	S-interior	S-Xanthate (Xth)	Br	Ratio of $(S^{2-} + 0.5 * Br^{-})/Pb^{2+}$
CTAB-QDs	1	0.75	0.75		0.67	1.08
OA-QDs	1	0.64	0.64			0.64
OA/Xth-QDs	1	0.91	0.63	0.28		
OA/S-QDs (1%BTA treatment)	1	0.71	0.71	0		
OA/S-QDs (3%BTA treatment)	1	0.72	0.72	0		
OA/S-QDs (5%BTA treatment)	1	0.72	0.72	0		
CTAB/S-QDs	1	0.78	0.78	0	0.32	0.94

[a] All chemical compositions are normalized to Pb, S-total represents the total Sulfur amount in film, S-interior refers to sulfur content inside PbS QDs or sulfur content binding to Pb only, S-xanthate refers to sulfur content in xanthate.

binding affinity to QDs surface. Implementation of this approach led to efficient passivation, increased conductance and reduced defect density while maintaining high charge carrier mobility (Lan et al., 2016; Liu et al., 2017; Ning et al., 2014). Lan et al has reported about the fabrication of high efficiency QDs solar cells utilizing halide ions for the surface functionalization leading to improved packing density of QDs allowing better exciton dissociation and charge transfer (Lan et al., 2016). However, application and electrostatic stabilization of inorganic-terminated QDs in wide concentration range have been found to be difficult owing to need for high dielectric constant of solvent and well-balanced Lewis acidity and basicity (Sayevich et al., 2016). Additionally, small ordering of QDs due to the long-range electrostatic repulsion in inorganic-terminated QDs (Kovalenko et al., 2009) negatively affects the charge carrier transport (Talapin, 2012). Utilization of