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Photoluminescent properties of new quantum dot nanoparticles/carbon nanotubes hybrid structures

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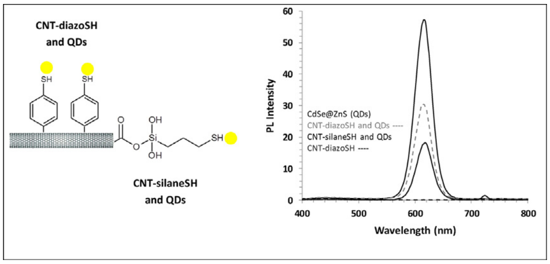
HIGHLIGHTS

- Anchoring chalcogenide QDs to carbon nanotubes using diazonium compounds.
- Charge transfer from CdSe@ZnS QDs to thiolated carbon nanotubes.
- Photoluminescence quenching in quantum dots/carbon nanotube heterostructures.

GRAPHICAL ABSTRACT



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ABSTRACT

The preparation of multi-wall carbon nanotubes (CNTs) and sulfide core–shell CdSe@ZnS quantum dot nanoparticles based hybrid materials is reported here. Photoluminescent measurements were carried out on two kinds of QD-CNT heterostructures. Indeed, strong oxidation of CNTs led to shorter nanotubes opened at their ends, allowing the grafting of mercaptotriethoxysilane whereas the generation of diazonium salts in presence of pristine nanotubes led to the functionalization of the whole lateral surface of the nanotubes and was achieved for the first time to anchor sulfide QD nanoparticles to thiol groups borne by carbon nanotubes. In both cases, we observed an important decrease in the photoluminescence peak, highlighting strong interactions between QDs and CNTs even when QDs were anchored to CNTs through a *covalent* link. Finally, we demonstrated that the morphology of the nanohybrids is governed by the surface chemistry of CNTs, leading to interesting hybrid precursors for photovoltaic applications.

1. Introduction

The photocatalytic activity of nanostructured semiconductor films has been widely explored in view of designing solar cells or producing solar hydrogen. Dye-sensitized solar cells (DSSCs) are of particular interest in the development of environmentally friendly energy resources due to their simple fabrication process, low production cost and high efficiency [1]. Titanium dioxide nanoparticles have been widely studied [2] and used as a working electrode because they provide a higher efficiency than any other metal oxide semiconductor (10% solar conversion efficiency was achieved [3]). Nevertheless, the key problem is still to achieve higher photoconversion efficiency in nanostructured electrodes [4]. Indeed, in such nanostructures, the photogenerated electrons are travelling with a random path through the network of semiconductor nanoparticles, encountering many grain boundaries and increasing the probability of their recombination with oxidized sensitizer.

Both single-wall and multi-wall carbon nanotubes (CNTs) have become increasingly popular in the last two decades [5]. CNTs have potential in several areas of interest including hydrogen

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storage, field emission devices, sensors/probes [6], and nanoelectronic devices [7]. The application of CNTs in conjunction with solar cell devices has become very popular in the photovoltaic (PV) field [8]. Recent progress in carbon nanotubes (CNTs) based nanocomposites and nanostructures development and fabrication (design of nanotube or nanowire architectures) make them attractive (a) to combine them with conducting polymers to provide more efficient organic photovoltaic devices (OPD) [9,10], (b) to be used as transparent electrodes to substitute ITO glasses [11–13] or (c) to be used in DSSC. Indeed, it should be possible to use such one-dimensional nanostructures to direct the flow of photogenerated charge carriers, the challenge being to use nanotube networks as support to anchor light-harvesting semiconductor particles and make easier the photogenerated electron transport to the collecting electrode surface.

Semiconductor (essentially chalcogenide) nanoparticles are also widely studied. The quantum confinement effect of these QDs influences both optical and electronic properties; as the size of the QD increases, the band gap decreases in energy until bulk material properties are obtained [14,15]. Tunable band gap, very large extinction coefficient and high quantum efficiency make QDs excellent candidates for donor materials. Moreover, these quantum dots are offering two main possibilities for improving the efficiency of solar cells: the modulation of the band gap of solar cells for harvesting more of the light in the solar spectrum, and the generation of more charges from a single photon. Using this strategy, composite nanostructures were prepared in the past, enhancing successfully the photoconversion efficiency of TiO_2 using CdS [16,17] or CdSe [18]. Research is currently focused on CdS quantum dots [19] even if other semi-conductor nanoparticles like CdSe and CdTe can induce charge-transfer processes under visible light irradiation when anchored to CNTs [20]. In such a context, semiconductor nanoparticles/carbon nanotubes hybrid films appear promising to develop new generation solar cells [7,21–27]. Up to now, studies have mainly focused on establishing synthetic strategies and characterization of the composite systems. These include carbon nanotubes in contact with TiO_2 [28], SnO_2 [29], CdSe [24,26] and CdS [30]. Of particular interest is the CdS–CNT composite, which is capable of generating photocurrent from visible light with unusually high efficiency [21,21]. To prepare QD-CNT heterostructures, various experimental procedures have been envisaged and are summarized in Table 1.

The easiest preparation of CNT-QD heterostructures is based on the simple addition of QDs to carbon nanotubes, leading to van der Waals interactions between QDs and the surface of the CNTs. Nevertheless, one cannot control the morphology developed by the resulting materials. Kamat et al. proposed an interesting chemical precipitation approach, allowing the in situ synthesis of semiconductor nanoparticles directly on the surface of CNTs [34]. However, this route is also known to usually lead to the formation of inhomogeneous crystalline structures with large polydispersity in shape and size. Haremza et al. reported that sidewall functionalization of CNTs is acceptable for some applications such as chemical and bio-sensing [26] or for the preparation of composite materials, but for electronic devices, this particular functionalization can compromise their unique electronic properties. For successful device applications, the CNT electronic structure should remain unaffected, and this can be achieved only by preferential oxidation of the CNT tips [26], allowing coupling reactions (e.g. [27]). Whereas the use of oxidized CNTs led to non-uniform coverage of the surface as particles tend to be attached at the ends of carbon nanotubes and defect sides, where the concentration of carboxylic groups is the largest [26,27,28,40], other groups reported covalently conjugated QDs to CNTs, involving complex reactions and functionalizations, making these strategies more complicated and time-consuming [26,41,28].

The use of polyelectrolytes can be of interest for straight coupling of QDs to CNTs from aqueous or organic dispersions of nanocrystals. The step-by-step process described by Giersig et al. gave the flexibility to tailor the QDs prior to conjugation [20] as well as the use of a thiol derivative perylene compound (ETPTCDI) able to bond to the sidewalls of CNTs by π-stacking significantly increases the adhesion between QDs and CNTs through bonding between QDs and thiol groups on ETPTCDI and π–π interactions between ETPTCDI and CNTs [39].

The main goal of such functionalizations is to maximize the coverage of CNT surface by semiconductor nanoparticles (QDs). To the best of our knowledge, diazonium salts have been used only once to anchor chalcogenide based QDs to CNT surface, through a cyclodextrine derivative obtained by a diazotization reaction [42]. Though, aryl diazonium compounds arose as a new class of coupling agents for grafting polymer thin layers onto various substrates such as carbon, metals, metal oxides, semi-conductors, ceramics, polymers... [43–45]. First, carbon nanotubes derivatized by aryl diazonium salts via electrochemical reduction were found to possess significantly improved solubility in organic solvents [46]. Then, the use of aryl diazonium coupling agents was extended to the attachment and immobilization of metal nanoparticles at the surface

Table 1
Examples of experimental procedures to prepare QD-CNT heterostructures.

Synthesis	Description	Reagents	Ref.
Simple addition of QDs to CNTs	Van der Waals interactions		[31–33]
Chemical precipitation approach	CdS QDs directly grown on the SWCNT surface by adsorption of Cd^{2+} ions on the CNT surface and reaction with S^{2-}	Surfactant: tetraoctylammonium bromide	[34,35,23,29,23,29]
Coupling reaction	Conjugation of thiol-stabilized ZnS-capped CdSe QDs containing amine terminal groups ($QD{-}NH_2$) with acid-treated MWCNTs	Coupling agent: ethylene carbodiimide	[27]
Coupling reaction	Coupling at the surface of oxidized MWCNTs	Aminoethanethiol/dicyclohexylcarbodiimide	[36,37]
Adsorption using a cationic polymer	Stable dispersions of MWCNT-PAH in both polar and nonpolar solvents allowing the direct adsorption of QDs (CdS or CdSe)	Polyelectrolyte: poly(allylamine hydrochloride) (PAH)	[20]
	Chitosan used to link CNTs and thioglycolic acid for anchoring CdTe QDs	Natural polysaccharide: chitosan	[38]
Adsorption using a molecular linker	Preparation of CdSe/MWCNTs using a thiol derivative perylene compound (ETPTCDI) able to bond to the sidewalls of CNTs by π-stacking	Thiol derivative perylene compound (ETPTCDI)	[39]