Materials Chemistry and Physics 149-150 (2015) 405–412

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Homogeneous CdTe quantum dots-carbon nanotubes heterostructures

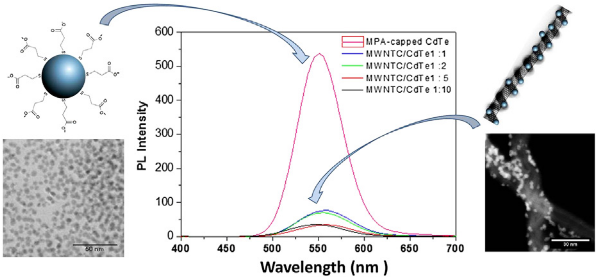
Kayo Oliveira Vieira [a], Jefferson Bettini [b], Jefferson Luis Ferrari [a],
Marco Antonio Schiavon [a, *]

[a] Grupo de Pesquisa em Química de Materiais – (GPQM), Departamento de Ciências Naturais, Universidade Federal de São João del-Rei, Campus Dom Bosco, Praça Dom Helvécio, 74, CEP 36301-160, São João del-Rei, MG, Brazil
[b] Laboratório Nacional de Nanotecnologia, Centro Nacional de Pesquisa em Energia e Materiais, CEP 13083-970, Campinas, SP, Brazil

HIGHLIGHTS

- Highly homogeneous CdTe-carbon nanotubes heterostructures were prepared.
- Simple and reproducible non-covalent functionalization route.
- CdTe nanocrystals homogeneously deposited onto multi-walled carbon nanotubes.
- Efficient energy transfer process from photoexcited CdTe to MWCNTs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 February 2014
Received in revised form
23 June 2014
Accepted 20 October 2014
Available online 29 October 2014

Keywords:
Nanostructures
Semiconductors
Heterostrucutures
Chemical techniques
Coatings

ABSTRACT

The development of homogeneous CdTe quantum dots-carbon nanotubes heterostructures based on electrostatic interactions has been investigated. We report a simple and reproducible non-covalent functionalization route that can be accomplished at room temperature, to prepare colloidal composites consisting of CdTe nanocrystals deposited onto multi-walled carbon nanotubes (MWCNTs) functionalized with a thin layer of polyelectrolytes by layer-by-layer technique. Specifically, physical adsorption of polyelectrolytes such as poly (4-styrene sulfonate) and poly (diallyldimethylammonium chloride) was used to deagglomerate and disperse MWCNTs, onto which we deposited CdTe quantum dots coated with mercaptopropionic acid (MPA), as surface ligand, via electrostatic interactions. Confirmation of the CdTe quantum dots/carbon nanotubes heterostructures was done by transmission and scanning electron microscopies (TEM and SEM), dynamic-light scattering (DLS) together with absorption, emission, Raman and infrared spectroscopies (UV–vis, PL, Raman and FT-IR). Almost complete quenching of the PL band of the CdTe quantum dots was observed after adsorption on the MWCNTs, presumably through efficient energy transfer process from photoexcited CdTe to MWCNTs.

1. Introduction

The mechanical, electrical, thermomechanical, and optical properties of carbon nanotubes (CNTs) make them undisputable materials for use in sensing devices and composites [1–10]. CNTs can be metallic with ballistic 1D charge transport, or it can be semiconducting depending on the chiral angle of the underlying grapheme lattice [11]. However, as it is well-known, CNTs are hydrophobic and poorly soluble in organic solvents, and they tend to aggregate into bundles via Van der Waals interactions, leading to inadequate CNTs dispersion in solution, preventing their application in various areas [12,13].

CNTs surface modification has become the most promising strategy to overcome such difficulties and make these nanotubes

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* Corresponding author.
E-mail address: schiavon@ufsj.edu.br (M.A. Schiavon).

http://dx.doi.org/10.1016/j.matchemphys.2014.10.036
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really applicable [14–16]. Modifying the CNTs surface with organic compounds, inorganic substances, or biological species has enabled researchers to alter the physical properties of the nanotubes, paving the way for novel applications. Binding quantum dots (QDs) to CNTs is a recent strategy that is still under development and that modifies the optical and electronic properties of the nanotubes [17–22]. Each component of the quantum dots-carbon nanotubes (QDs-CNTs) assembly has unique properties that make their combination highly desirable, and the result assembly providing for a convenient means of capturing photogenerated charges and transporting them to the electrode surface.

QDs consist of semiconducting crystals with nanometric dimensions, typically lower than 10 nm. Their reduced size gives rise to interesting optical properties, through which their emission strongly depends on particle diameter, as consequence of quantum confinement [23–25]. This size tunability is particularly powerful for multi-junction solar cells devices, allowing efficient collection of energy from the wide solar spectrum, including previously untapped infrared energy [26,27]. Additionally, some of their bulk properties such as the high extinction coefficient are preserved at the nanoscale [28].

Due to the large surface to volume ratio of both QDs and CNTs, the interfacial area in these materials should be extremely large. Therefore, interactions between them are very important for their overall behavior. Experimentally, the fluorescence emission from QDs is strongly suppressed when they are attached to CNTs, which evidences strong coupling between them [21,29]. To the best of our knowledge it is still open in the literature regarding the precise attribution of the fluorescence quenching to charge or energy transfer between the QDs and CNTs.

Recently, a precise measurement of resonant energy transfer from isolated QD to individual CNT was performed, and a simple model based on dipole-dipole coupling between excitons was developed [21]. In particular, excitons were created at varying distances from the QDs at different locations along the CNT length. The authors conclude that the dominant quenching mechanism for these experiments is resonant energy transfer, in agreement with several previous studies of fluorescence quenching near nanostructures [21,30]. It was found that energy transfer efficiencies could reach values as high as 96%, regardless of CNTs chirality [21].

The most widely investigated nanomaterials for polymeric solar cells have been semiconducting nanocrystals, fullerenes, and single wall carbon nanotubes [2,3,31–34]. The particular advantages of the usage of such materials on polymeric solar cells is that they can be readily processed into thin films consisting of interconnected networks with tailored optical transparency and electrical conductivity, as well as good mechanical flexibility [3,29,32]. Therefore, the combination of both carbon nanotubes and quantum dots to form heterostrucutres with high electron affinity and high electrical conductivity would enhance the conversion efficiency of polymeric solar cells, in order to optimize the practical efficiency of generating photocurrent in these systems under visible light illumination. A hybrid architecture in which polymer, CNTs, and QDs are collectively utilized in one discrete functional configuration has drawn significant attention, recently [35].

Examples of heterostructures involving QDs and CNTs exist in the literature [4,5,36], including combination of CNTs with CdTe [17,37], CdSe [31], CdS [29] as well as core/shell structures such as CdSe/CdS [20] and CdSe/ZnS [21]. In most of these works chemical modification of the CNTs surface has enabled researchers to successfully combine QDs covalently bound to CNTs, despite the little control over CNTs surface coverage with QDs. Some procedures used to modify the CNTs surface rely on covalent functionalization, to facilitate QDs coupling via covalent binding. The covalent bonds between QDs and single wall CNTs [31], double-walled CNTs [38] and multi-walled CNTs [20] were performed by changing the surface ligands of the QDs by aminoethanethiol (AET) with subsequent coupling to carboxyl moieties from the oxidized CNTs. This approach affects the CNTs intrinsic properties [5,6,17–21], disrupting the bonding of the sp^2-hybridized orbitals and potentially resulting in undesirable alterations in conductivity as well as other electrical and mechanical properties.

The best example of the *in situ* synthesis of a QD in a carbon nanostructure was the work developed by Cao e cols. [22] who have synthesized a graphene–CdS quantum dot (G-CdS). The work was based on reduction of graphene oxide with simultaneous deposition of CdS by using dimethyl sulfoxide as sulfide source. Their results have pointed to a relative uniform QDs binding.

The most important strategy toward obtention of QDs-CNTs heterostructures is the non-covalent functionalization of CNTs. This mild functionalization method is a promising means of preserving the high conductivity of CNTs, and is based on a combination of polymer wrapping and layer-by-layer self-assembly techniques [17]. Indeed, such methods are not invasive and do not introduce defects to the structure of CNTs [20]. They were used successfully to assembly silica-coated gold nanoparticles and gold nanorods [39,40] as well as CdTe QDs [17] and CdSe/ZnS [20] onto the surface of CNTs. While polymer wrapping consists of the stabilization of well-dispersed CNTs based on thermodynamic preference for the CNT-polymer interaction over the CNTs-water interactions [17], the layer-by-layer technique is based on the alternating different monolayers of individual components attracted to each other by electrostatic and van de Waals interactions [41]. Although, the apparent simplicity of their preparation, the obtention of stable, uniformly dispersed QDs onto the CNTs is not a trivial experimental task, and stabilization of the colloidal heterostructures should be carefully performed to give rise to the desired homogeneous heterostructures.

Considering that QDs-CNTs assemblies are indeed to be pursued for various optoelectronic applications, it is clearly important to understand in more detail the energy transduction pathway as well as the experimental conditions that can give rise to stable and uniform heterostructures. In the present study, we report on a simple and reproducible non-covalent functionalization route that can be accomplished at room temperature, to prepare colloidal composites consisting of CdTe nanocrystals deposited onto multiwalled carbon nanotubes (MWCNTs) functionalized with a thin layer of polyelectrolytes by the layer-by-layer technique. Confirmation of the CdTe quantum dots/multi-walled carbon nanotubes (CdTe-MWCNTs) heterostructures was done by transmission and scanning electron microscopies (TEM and SEM), dynamic-light scattering (DLS) as well as absorption, emission, Raman, and infrared spectroscopies (UV–vis, PL, Raman and FT-IR).

2. Experimental

2.1. Starting materials

MWCNTs with external diameter ranging from 10 to 40 nm and length lying between 5 and 20 um, 95% purity, were purchased from Incheon Corea Co. Ltd. and functionalized with the anionic polyelectrolyte poly (sodium 4-styrene sulfonate) (PSS; MW ~70 000) and the cationic polyelectrolyte poly (diallyldimethylammonium chloride) (PDDA; MW 400 000 – 500 000), both of which were acquired from Sigma Aldrich. Sodium chloride was also provided by Sigma Aldrich. To synthesize the CdTe QDs, cadmium chloride monohydrate ($CdCl_2.H_2O$, 99%, Vetec), tellurium powder (200 mesh, 99.8%, Sigma–Aldrich), and 3-mercaptopropionic acid (MPA, 99%, Sigma–Aldrich) were used.