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Determination of the band alignment of multi-walled carbon nanotubes decorated with cadmium sulfide

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1. Introduction

Since carbon nanotubes (CNTs) were first reported by Iijima [1], they have attracted the attention of scientists in many areas due to their extraordinary mechanical, chemical, and electronic features [2]. Their electrical transport efficiency grants them a huge potential for use in sensors [3], transistors [4], and other technological applications. Surface modification of CNTs with organic, inorganic, or biological species may dramatically alter their electronic characteristics further broadening their potential use [5]. Semiconductor NPs have also attracted the interest of many researchers in recent decades, because of their unique size-tunable properties resulting from quantum confinement [6]. The control and development of new features according to the size of the particles is of great technological value. Within the great number of possible applications for this class of material, we highlight optical sensors and other optoelectronic devices. The nanometer size of the NPs provides shorter pathways for charge carriers, which reduces the probability of charge recombination inside the crystal. On the other hand, charge transport across particles is poor, which leads to recombination at their interfaces and limits the mobility and efficiency of electronic devices based on NPs. Thus, in order to overcome this limitation, the use of a charge-collecting material attached directly to the NPs has been suggested [7].

Many authors have reported successful decoration of CNTs with semiconductor NPs. Shi *et al.* attached CdS NPs on MWCNTs [8], Ravindram *et al.* covalently coupled ZnS capped CdSe to acid-treated MWCNTs [9], and others have proposed methods to attach other semiconductors, such as TiO_2 [10] and SnO_2 [11] to CNTs, thus presenting the possibility of the CNTs functioning as a charge collector. The CdS/CNT composite is of particular interest, since it was shown that it is capable of generating photocurrent from visible light with unusually high efficiency [12]. However, despite the many reports on the synthesis of SC/CNT composites, there is little information about the electronic properties of the resulting interfaces.

Herein, we describe our recent work where we use X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS, respectively) to determine the band alignment of CdS NPs decorating metallic MWCNTs. Our approach is based on the work of Kraut *et al.* [13] and, since then, many groups have used similar approach to study the band alignment in interfaces of different materials mostly thin films [14–19].

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2. Experimental

MWCNTs decorated with CdS NPs (CdS/MWCNTs) were prepared using a solvothermal method [20]. Detailed synthesis procedures are described in supplementary material. The obtained material, after rinsing, consists of a dark green powder. Films of this dark green powder were produced by vacuum filtration [21] and transferred to gold-coated alumina plates. We also produced films of pure CdS NPs and pure MWCNTs by the same filtration method, which were also transferred to gold-coated alumina plates, to be used as reference for the PES measurements.

Transmission electron microscopy (TEM), selected area diffraction (SAD) and energy-dispersive spectroscopy (EDS) were carried out at the Microscopy Center of UFMG, using a FEI Tecnai G2-20 microscope with a LaB_6 filament operating at 200 kV. X-ray powder diffraction (XRD) was performed using a Rigaku Geigerflex diffractometer, using Cu Kα radiation in a θ–2θ geometry. A Shimadzu UV-3600 UV–Vis–NIR spectrophotometer was used to acquire diffuse reflectance spectrum of CdS/MWCNTs film in the wavelength range of 400–800 nm. XPS and UPS measurements were performed using a VG ESCALAB 220i-XL system with Al Kα radiation and base pressure of 1×10^{-10} mbar. XPS survey spectra were collected over the binding energy range from 1100 to 0 eV, with 60 eV pass energy, corresponding to a resolution of 1.0 eV. Individual S 2p, Cd 3d, Au 4f, and C 1s peaks were measured with a pass energy of 20 eV, in this case with a resolution of 0.8 eV. The Au 4f peak position at 84.0 eV was used as references for all spectra. As mentioned, the samples were grounded to the holder and no charging effects were observed. UPS spectra were taken using a homemade helium lamp at a photon energy $h\nu = 21.2$ eV (He I radiation), operating the electron analyzer at 2 eV pass energy, corresponding to a resolution of 0.05 eV. All the films were first cleaned by Ar^+ sputtering (1.5 keV at room temperature for 30 min).

3. Results and discussion

In the solvothermal method, CdS NPs grew on the outer walls of the MWCNTs forming a coaxial polycrystalline coating, as shown in the SEM image of Fig. 1a. We observed, though, that some tubes have only a few isolated NPs attached to, indicating that the coating of the MWCNTs by the CdS NPs was not completely effective. Fig. 1b depicts the results of a statistical analysis of the size distribution of the CdS NPs attached to the MWCNTs (as arrowed in Fig. 1a), indicating they have an average diameter of 60 nm. Fig. 1c and d shows the TEM images with associated SAD pattern and EDS spectrum, respectively, confirming that the NPs attached to the MWCNTs correspond to CdS. The SAD pattern also indicates that the NPs have Zinc Blende (ZB) structure, confirming the XRD results shown in Fig. 2.

From the diffractogram of Fig. 2, we have estimated that the average size of the crystallites as ~8 nm by the Scherrer method. This result indicates that each NP is composed of a few crystallites. Such finding is also confirmed by the TEM and SAD results.

The band gap, E_g, of the decorating CdS NPs was determined by the Kubelka–Munk transformation, $f(R) = (1-R^2)/2R$, where R is the diffuse reflectance spectrum of the CdS/MWCNTs sample obtained by UV–VIS spectroscopy, as shown in Fig. 3. The $f(R)$ spectrum presents a clear absorption onset that is in the expected region for CdS, however it also has a low energy contribution that may be attributed to a Drude-like contribution from the metallic MWCNTs. Due to such contribution, the common Tauc extrapolation analysis becomes difficult. Thus the value of E_g was determined as the

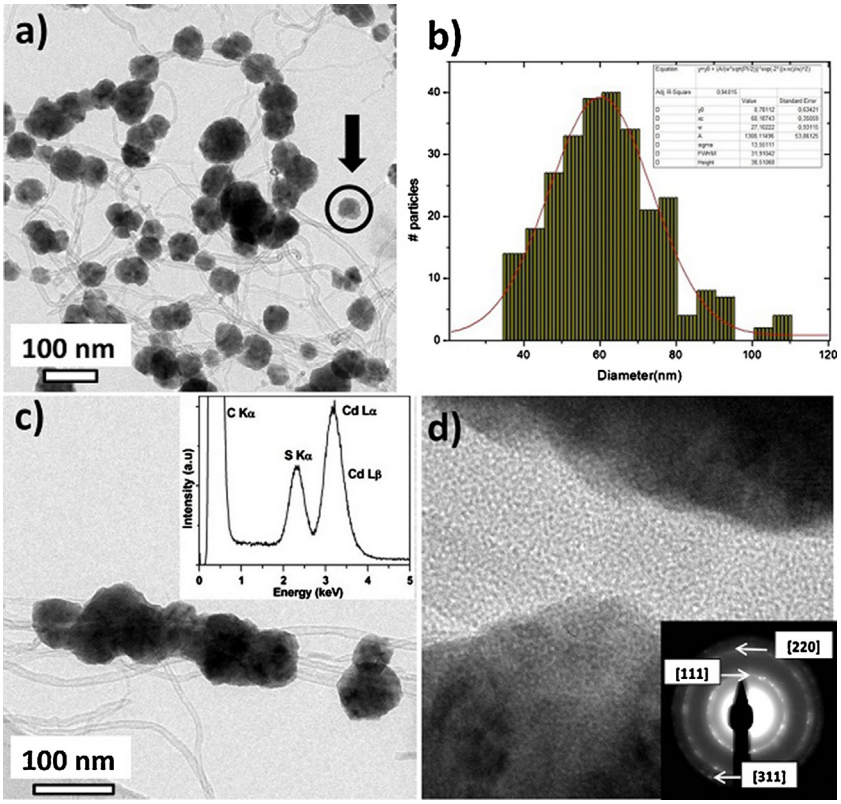

Fig. 1. (a) TEM image of the polycrystalline coating of CdS decorating the MWCNTs; (b) Size distribution of the polycrystalline coating. The average diameter is approximately 60 nm; (c) TEM image of NPs decorating MWCNTs with EDS spectrum of the decorating NPs, confirming the presence of Cd and S; (d) TEM image of NPs decorating MWCNTs; and (e) SAD pattern of the NPs. The indexed planes correspond to the cubic phase of CdS.