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Gas-Phase Noncovalent Functionalization of Pristine Single-Walled Carbon Nanotubes with 3D Metal(II) Phthalocyanines

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Abstract : Noncovalent nanohybrid materials combining carbon nanotubes (CNTs) with phthalocyanines (Pcs) is a subject of increasing research effort, with a particular emphasis on the design of new heterogeneous catalysts, efficient organic photovoltaic cells, lithium batteries, gas sensors, field effect transistors, among other possible applications. The possibility of using unsubstituted Pcs for CNT functionalization is very attractive due to their very moderate cost and easy commercial availability. However, unfortunately, the deposition of unsubstituted Pcs onto nanotube sidewalls through the traditional liquid-phase protocols turns to be very problematic due to extremely poor solubility of Pcs. On the other hand, unsubstituted free-base H_2Pc phthalocyanine ligand, as well as many of its transition metal complexes, exhibit very high thermal stability and considerable volatility under reduced pressure, which opens the possibility for their physical vapor deposition onto solid surfaces, including nanotube sidewalls. In the present work, we show the possibility of simple, fast and efficient noncovalent functionalization of single-walled carbon nanotubes (SWNTs) with a series of 3d metal(II) phthalocyanines Me(II)Pc, where Me= Co, Ni, Cu, and Zn. The functionalization can be performed in a temperature range of 400-500 °C under moderate vacuum and requires about 2-3 h only. The functionalized materials obtained were characterized by means of Fourier-transform infrared (FTIR), Raman, UV-visible and energy-dispersive X-ray spectroscopy (EDS), scanning and transmission electron microscopy (SEM and TEM, respectively) and thermogravimetric analysis (TGA). TGA suggested that Me(II)Pc weight content is 30%, 17% and 35% for NiPc, CuPc, and ZnPc, respectively (CoPc exhibited anomalous thermal decomposition behavior). The above values are consistent with those estimated from EDS spectra, namely, of 24-39%, 27-36% and 27-44% for CoPc, CuPc, and ZnPc, respectively. A strong increase in intensity of D band in the Raman spectra of SWNT–Me(II)Pc hybrids, as compared to that of pristine nanotubes, implies very strong interactions between Pc molecules and SWNT sidewalls. Very high absolute values of binding energies of 32.46-37.12 kcal/mol and the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO, respectively) distribution patterns, calculated with density functional theory by using Perdew-Burke-Ernzerhof general gradient approximation correlation functional in combination with the Grimme's empirical dispersion correction (PBE-D) and the double numerical basis set (DNP), also suggested that the interactions between Me(II) phthalocyanines and nanotube sidewalls are very strong. The authors thank the National Autonomous University of Mexico (grant DGAPA-IN200516) and the National Council of Science and Technology of Mexico (CONACYT, grant 250655) for financial support. The authors are also grateful to Dr. Natalia Alzate-Carvajal (CCADET of UNAM), Eréndira Martínez (IF of UNAM) and Iván Puente-Lee (Faculty of Chemistry of UNAM) for technical assistance with FTIR, TGA measurements, and TEM imaging, respectively.
Keywords : carbon nanotubes, functionalization, gas-phase, metal(II) phthalocyanines
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