Electronic Supplementary Material (ESI) for Polymer Chemistry

Preparation of Hybrid Nanomaterials by Supramolecular Interactions between Dendritic polymers and Carbon Nanotubes

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Experimental section

Materials

MWCNT with 20 nm diameter were prepared by chemical vapor deposition procedure in the presence of Co/Mo/MgO as catalyst at 900 ºC. CDDP (purity 99.9%) was purchased from Aldrich Chemical Co. Citric acid monohydrate (MW=210.14), polyethyleneglycol (MW=1000), $AgNO_3$, Sodium methoxid, Nitric acid, Sulfuric acid, Methanol, DOX, Ethylenediamine, methyl acrylate, cyanuric choloride, phenol and α- naphthol were purchased from Merck. Glycidol was purchased from Aldrich. The murine colon adenocarcinoma tumor C26 and the mouse tissue connective fibroblast adhesive L929 cancer cells were obtained from the National Cell Bank of Iran (NCBI) Pasteur institute, Tehran, Iran. MTT powder, Annexin-V FLUOS Staining Kit, was obtained from Sigma.

Characterization

Nuclear magnetic resonance (^{1}H NMR) spectra were recorded in D_2O solution on a Bruker DRX 400 (400 MHz) apparatus with the solvent proton signal for reference. Infrared spectroscopy (IR) measurements were performed using a Nicolet 320 FT-IR. Ultraviolet (UV) spectra were recorded on a shimadzu (1650 PC) scanning spectrophotometer. The samples of approximately 10 mg were heated from 25 to 500 ºC at a scan rate of 13 ºC min^{-1}, in the DSC 823-e device (Mettler Toledo, Switzerland). Ultrasonic bath (Model: 5RS, 22 KHZ, Made in Italy) was used to disperse materials in solvents. The particle size, polydispersity and zeta potential of materials were determined using Dynamic Light Scattering (DLS) (zetasizer ZS, Malvern Instruments). Morphology and size of materials were investigated using the Philips XL30 scanning electron microscope (SEM) with 12 and 15 A accelerating voltages.

Surface imaging studies were performed using atomic force microscopy (AFM) to estimate surface morphology and particle size distribution. The samples were imaged with the aid of Dualscope/Rasterscope C26, DME, Denmark, using DS 95-50-E scanner with vertical z-axis resolution of 0.1 nm. Raman spectra was obtained with an Almega Thermo Nicolet Dispersive Raman Spectrometer with second harmonic @532 nm of a Nd:YLF laser.

Thermogravimetric analysis (TGA) were carried out in a thermal analyzer (model: DSC 60, shimadzu, Japan) under dynamic atmosphere of an inert gas (i.e. N_2) at 30 ml/min (room temperature). The Transmission electron microscopic (TEM) analyses were performed by a LEO 912AB electron microscope with accelerating voltage of 200 kV. The X-ray power diffraction pattern of products were recorded on Siemens D-500 diffractometer with Cu Kα radiation (λ= 1.54056 Å) in 2θ range from 15º to 80º.

Opening of MWCNTs

MWCNTs were purified and opened according to reported procedures in literature [1]. Briefly, MWCNTs (2 g) were added to 40 mL of sulfuric and nitric acid mixture (3:1) in a reaction flask and refluxed for 24 h at 120ºC. The mixture was cooled and diluted by distillated water and then it was filtrated. The product (MWCNT-COOH) was washed by distillated water and dried at 60ºC for 3 h by vacuum oven.

Preparation of PAMAM-PEG-PAMAM

Second generation of PAMAM-PEG-PAMAM linear-dendritic copolymer was prepared according to reported procedure in literature [2].

IR: 3485 (νNH$_2$), 3271, 3066 (νN–H), 2929, 2846 (νC–H), 1458, 1325 (νC=N), 1652 (νC=O) cm^{-1} (Figure 1a). ^{1}H NMR (DMSO-d6): (3.60, PEG), (2.26–3.68, –NCH2– and – CH2O–), (8.2, N–H). ^{13}C NMR (DMSOd6): (36– 62, –NCH2–and –CH2O–), (70, PEG), (173, triazine part) (175, C=O amide).

Preparation of PAMAM-PEG-PAMAM/CNT LLNs

Typically, MWCNTs (2 mg) and PAMAM-PEG-PAMAM linear-dendritic copolymers (0.2 mg) were mixed in distilled water (5 ml) and mixture was sonicated for 30 min at room temperature. Mixture was filtrated to obtain a clear black solution.

Result and discussion

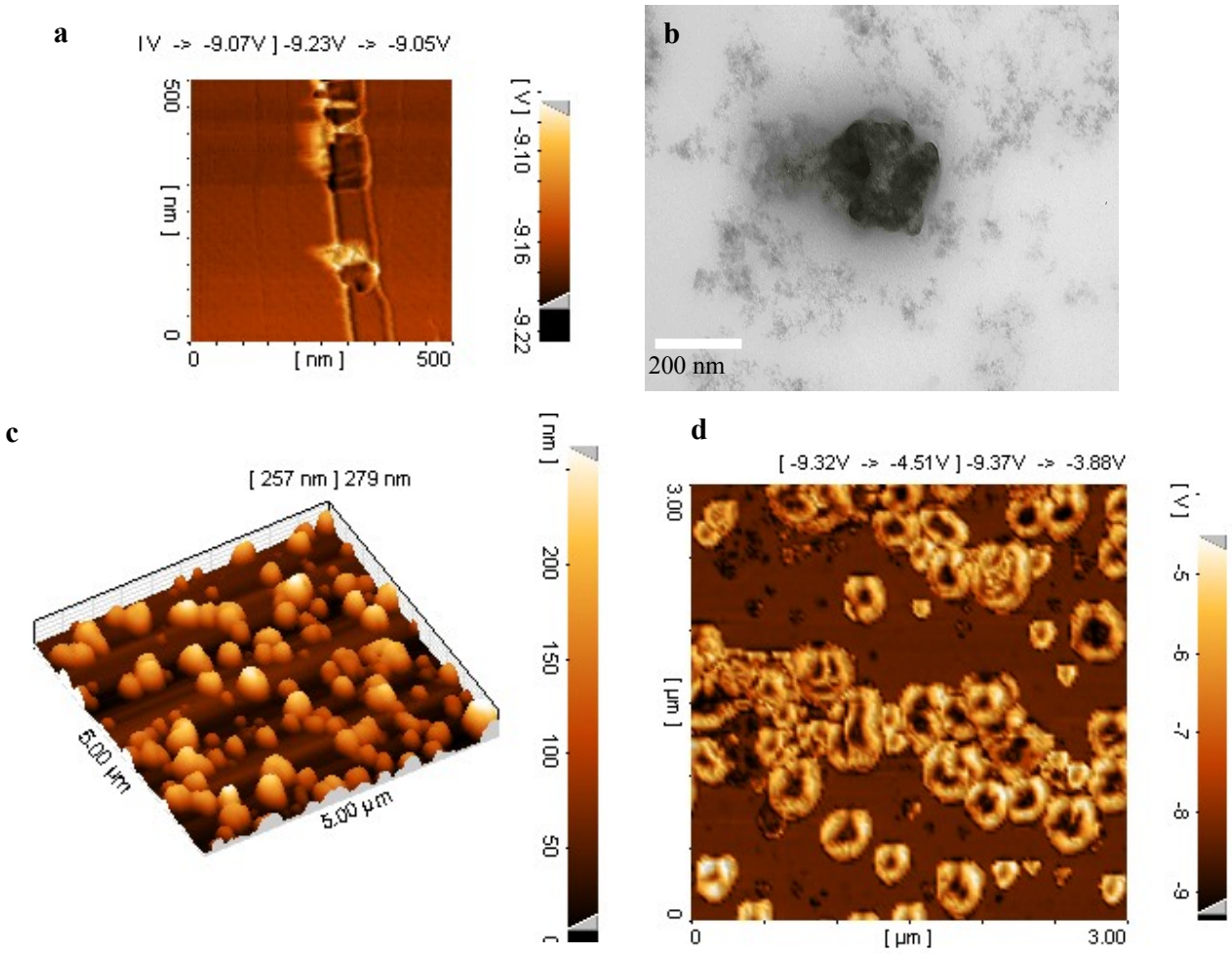

Figure 1. (a) Topographic AFM image of an acid treatment MWCNT: the created defects on the surface of carbon nanotubes during refluxing in HNO3/H2SO4 mixture can be clearly seen. (b) TEM image of a LLN consisting of MWCNT, polycitric acid grafted onto its surface and paclitaxel molecules conjugated to the carboxyl functional groups of polycitric acid.

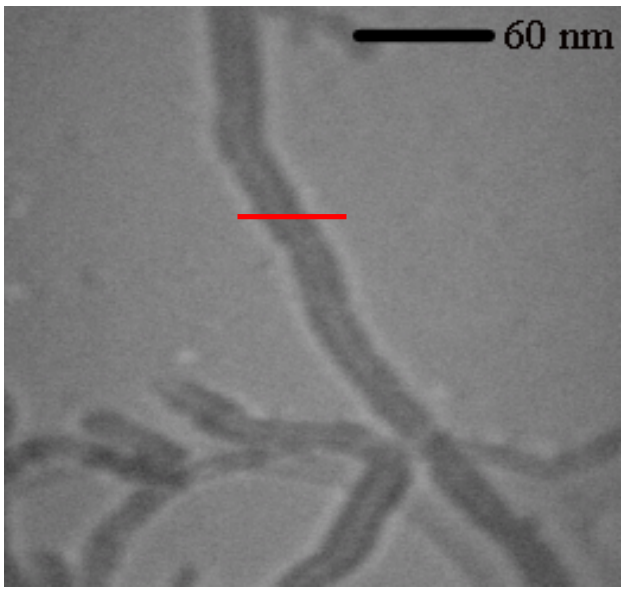

Figure 2. TEM image of G2-PT/CNTs hybrid nanomaterials.

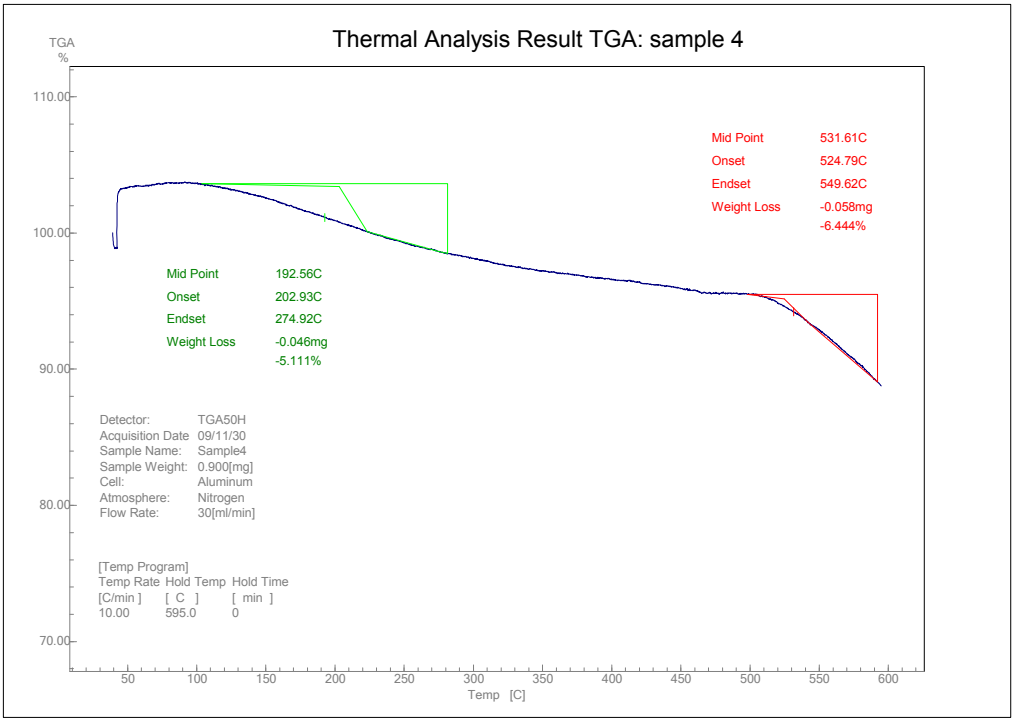

Figure 3. TGA analysis of acid-treated MWCNTs.

References

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