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Supplementary Information

Synthesis, characterization and anticancer activity in vitro of the biomolecule-based coordination complex nanotubes

*Yue Wang ,[a,b] Chi Zhang ,[a] Hongmei Li ,[b] Guoxing Zhu ,[a] Song-Song Bao ,[a] Shiqiang Wei ,[a] Li-Min Zheng ,[a] Min Ren ,[a] and Zheng Xu [a]**

a State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P.R. China.
b State Key Laboratory of Natural Medicines, School of Sciences, China Pharmaceutical University, Nanjing, 210009,P.R. China.

Corresponding Authors

E-mail: zhengxu@nju.edu.cn

XRD result

The XRD pattern of Ni-folate BMB-CCNTs indicates the non-crystalline nature of the nanotubes, and none characteristic diffraction peaks of Ni (0) was observed in the BMB-CCNTs sample (Fig. 1S).

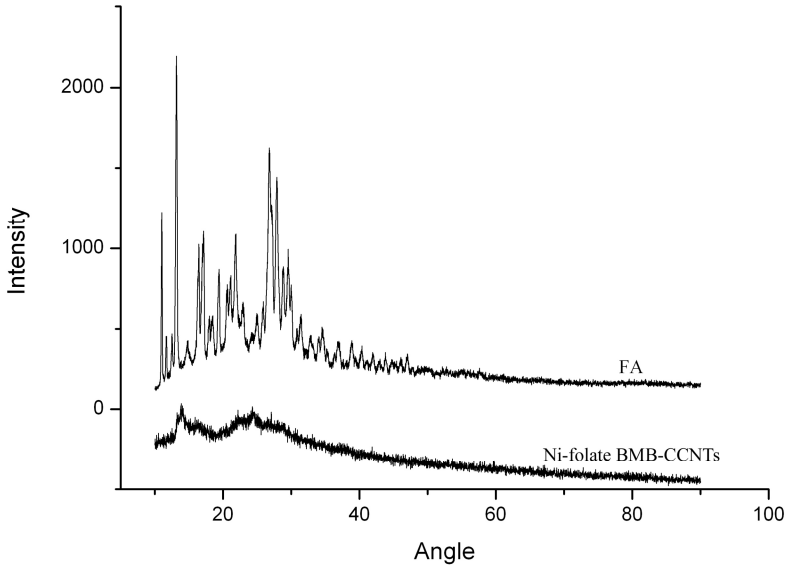

Fig. 1S XRD pattern of the Ni-folate BMB-CCNTs and FA

Absorption spectra

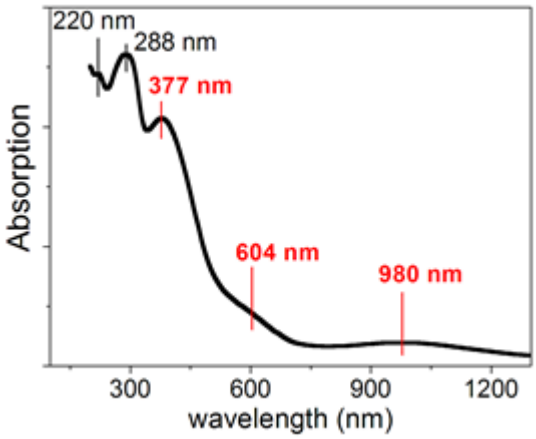

Fig. 2S UV-Vis-NIR spectra of Ni-folate BMB-CCNTs.

Infrared spectra data

The characteristic IR bands of the sample are summarized in Table 1S, and the bands of folic acid are shown for comparison. There is a very strong absorption band at 1694 cm^{-1} in the IR spectrum of folic acid; this band belongs to the stretching vibration of ν(C=O) of the carboxylic group but disappears in the nanotube sample due to the chelating coordination. The bands at 1570 cm^{-1} and 1453 cm^{-1} in folic acid can be assigned to ν_{as}(COO−) and ν_s(COO−), respectively, while they shifted to 1537 cm^{-1} and 1401 cm^{-1}, respectively, in the Ni-folate BMB-CCNTs. Both the vas(COO−) and νs(COO−) bands shift in the same direction compared with free folic acid. The absorption bands of ν_{as}(COO−) and ν_s(COO−) in the

chelating or bridging coordination mode shift in the same direction, whereas the shift in the opposite direction in the case of monodentate coordination. Thus, bidentate coordination of COO− to Ni ion was deduced for the CCNTs sample, in agreement with the XPS results.

Table 1S. Characteristic IR frequencies (cm^{-1}) of folic acid and the Ni-folate CCNTs

Assignments	Folic acid	Ni-folate BMB-sample
ν(COOH)	1694	-------
ν_{as}(COO−)	1565	1537
ν_{s}(COO−)	1453	1401
ν_{s}(N-N)	-------	983, 940

EXAFS measurements

The EXAFS measurements at the Ni-K edge (8333 eV) were carried out in transmission mode at the beamline U7C in the National Synchrotron Radiation Laboratory (NSRL) in China. In a typical experiment, about 41 mg of sample was ground into fine powder and mixed with ca. 116 mg of BN and then pressed into a 13.0 mm diameter circular sample holder. The spectrum of nickel foil was recorded periodically to check the energy calibration, and the first derivative of the nickel foil K-edge spectrum at 8333 eV was used to define the zero-energy reference point. The XANES spectra were background subtracted and were normalized to the edge step at the beginning of the EXAFS oscillations in order to make a meaningful comparison of the intensity of the pre-edge features. The EXAFS signals, χ (k), were extracted from the absorption raw data, μ (E), with ATHENA 0.8.056 program choosing the energy edge value (E_0) at the maximum derivative. The quantitative analysis was carried out with the IFEFFIT 1.2.11-ARTEMIS 0.8.012 program with the coordination sphere N_2O_4. Theoretical EXAFS signals were computed with the FEFF7.0 code using muffin-tin potentials and the Hedin-Lunqvist approximation for the energy-dependent part. The employed fitting ranges are summarized in Table 2S. The intrinsic reduction factor S_0^2, the edge-energy shift ΔE_0, the coordination number N, the inter-atomic distance R and the mean-square relative displacement σ^2 were fitted. The XANES spectra of two samples are given in Figure 4S. The Ni K-edge k3-weight (k) data and their Fourier-transformed (FT) data are shown in Figures 5S and 6S. The X-ray absorption near-edge structure (XANES) spectra further evidence above conjecture.

Table 2S. Forward Fourier Transform and backward Fourier Transform selected parameters of the Ni-N/O first shell at Ni-K edge.

Sample	Shell	K-range	Window type	R-range	Window type
Ni-FA	Ni-O	2.399~12.161	kaiser-bessel	1.044~1.993	kaiser-bessel
CCNTs	Ni-N/O	2.483~12.161	kaiser-bessel	1.040~1.993	kaiser-bessel
$Ni(acac)_2{\cdot}2H_2O$	Ni-O	2.549~12.161	kaiser-bessel	1.044~1.941	kaiser-bessel

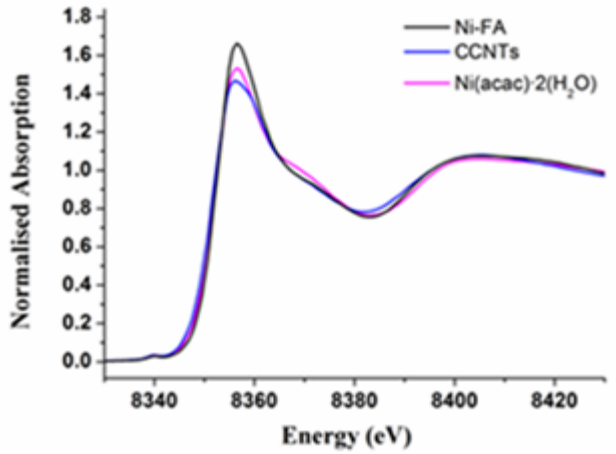

Fig. 3S Ni K-edge XANES spectra of Ni-FA, CCNTs and $Ni(acac)_2 \cdot 2H_2O$ (acac: acetylacetonate).

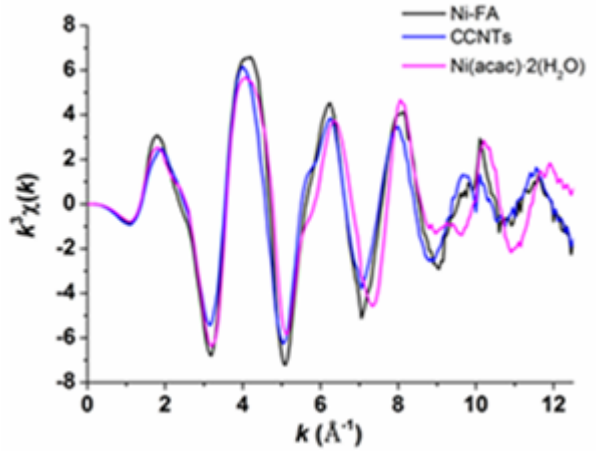

Fig. 4S Ni K-edge k3-weight EXAFS signals of Ni-FA, CCNTs and $Ni(acac)_2 \cdot 2H_2O$.

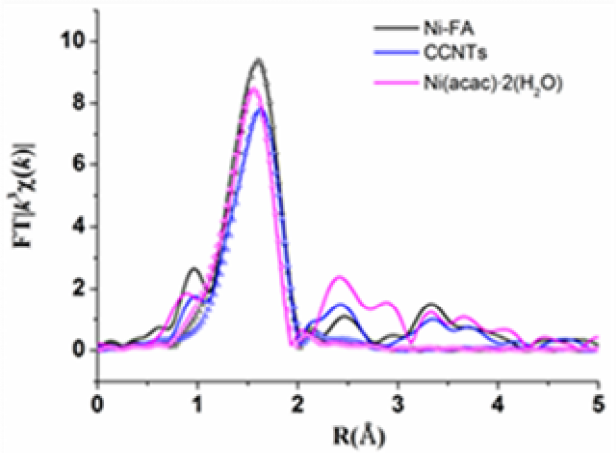

Fig. 5S Fourier transformed space (R space) and their fitting curves (dotted lines) at Ni K-edge.