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ENZYME-LESS SENSING OF KIDNEY DYSFUNCTION BIOMARKER -CREATININE USING INULIN BASED BIO-NANOCOMPOSITE

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1. FT-IR spectral characterization

The FT-IR spectra of Inu, Inu-TiO_2, MWCNT, MWCNT-Inu and MWCNT-Inu-TiO_2 were shown in Fig.S1(a). In the FT-IR spectrum of Inu a peak at 3426 cm^{-1} ascribed to –OH stretching vibration, a broad peak at 1022 cm^{-1} having two shoulders at 1130 and 940 cm^{-1} owing to the stretching vibrations of C-O-C groups and cyclic ring vibrational modes, respectively, were observed. Another broad peak appeared at 1649 cm^{-1} corresponding to the coexistence of the open-chain form and the closed ring form of a monosaccharide.[1] The –CH stretching and bending vibrations peaks were observed at 2924 cm^{-1} and 2360 cm^{-1}, respectively. FT-IR spectrum of TiO_2 consisted of –OH stretching frequency observed at 3447 cm^{-1} owing to the presence of water molecules adsorbed over TiO_2 surface. Ti-O stretching modes were observed in the low frequency regions 640 cm^{-1} and 534 cm^{-1}. [2, 3] The interaction of TiO_2 with Inu was indicated by the slight shift in the Ti-O and –OH stretching frequencies. The peak at 440 cm^{-1} corresponding to Ti-O bending mode which was also observed in the FT-IR spectrum of Inu-TiO_2 bio-nanocomposite without any major shift suggested the retention of the rutile phase of TiO_2. The incorporation of TiO_2 into Inu matrix have been confirmed through such observations.[2]

In the FT-IR spectrum of MWCNT, the peak at 2360 cm^{-1} corresponding to the CHx groups and the peak at 1571 cm^{-1} that may due to the IR-active graphite-like E_{1u} mode (G band) originating from the sp^2- hybridized carbon[4] were observed. A shift in the peak from 3426 cm^{-1} (for Inu) to 3436 cm^{-1} in the presence of MWCNT suggested the interaction of MWCNT with –OH groups of Inu. In the FT-IR spectrum of the MWCNT-Inu-TiO_2, a slight shift in the characteristic peaks of MWCNT, Inu-TiO_2 was observed suggesting the interaction of MWCNT with Inu-TiO_2 thereby forming MWCNT-Inu-TiO_2 bio-nanocomposite.

2. Raman spectral characterization

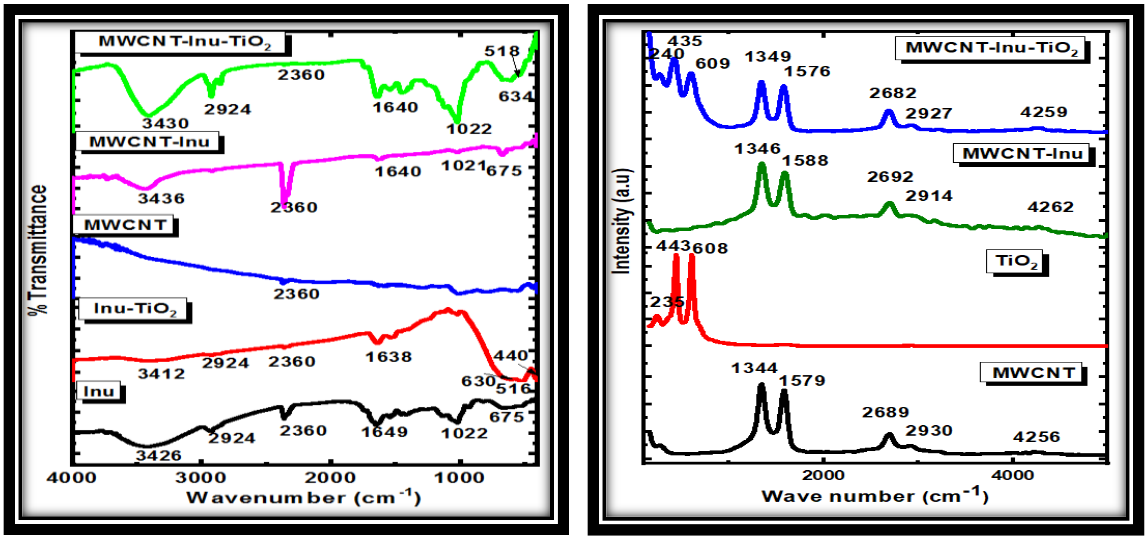
The Raman spectra of MWCNT, TiO_2, MWCNT-Inu and MWCNT-Inu-TiO_2 were shown in Fig. S1 (b). In the Raman spectra of rutile TiO_2, the bands at 235 cm^{-1} & 443 cm^{-1} corresponding to E_g modes and the band at 608 cm^{-1} corresponding to A_{1g} mode were observed. These peaks were attributed to the vibrational modes of rutile TiO_2. In case of MWCNT, a band around 1579 cm^{-1} due to the defect- induced dispersive G band and a band at 1344 cm^{-1} due to the D band originating from the vibrational mode associated with graphite structure were observed. This suggested the presence of some disorder in the structure. RBM (Radial Breathing Mode) was absent in the Raman spectra of MWCNT due to prevention of expansion and contraction of the tubes by the outer tubes. The second order harmonic band (2D band) was seen at 2689 cm^{-1}. The additional bands at 2930 cm^{-1} and 4256 cm^{-1} due to combination frequencies corresponded to (G+D) and (2D+E_{2g}), respectively.[5]

A very slight shift in peak positions and peak intensities was observed for MWCNTs modified with Inu-TiO_2 in comparison with pristine MWCNTs which suggested the interaction between Inu-TiO_2 and MWCNTs. Intensity redistribution occurred as indicated by the shift in the ratio of the intensity of the two characteristic peaks at constant half width from 1(pure TiO_2) to ~ 1.3 suggesting heterogeneity upon the formation of MWCNT-Inu-TiO_2 composite.[6]

The ratio of the intensities of the D and G bands (I_D/I_G) for pristine MWCNT, MWCNT-Inu, and MWCNT-Inu-TiO_2 were calculated to be 1.09, 1.14 and 1.16, respectively. The slight variation in the I_D/I_G value suggested a slight increase in the defect states of MWCNT upon modification. The quantification of edge-defects in MWCNT can be done by determining the in-plane crystallite dimensions (dimension of the basic sp^2 structural unit of the carbon) (L_a). This can be obtained by measuring the intensity ratio of D to G bands and by including the dependence of I_D/I_G with the excitation wavelength (λ=541.5nm)[7] as given by equation (1).

$$L_a(nm) = (2.4 \times 10^{-10})\lambda^4 \left(\frac{I_D}{I_G}\right)^{-1} \qquad (1)$$

The L_a values for pristine MWCNT, MWCNT-Inu, and MWCNT-Inu-TiO_2 were calculated to be 15.4, 14.8 and 14.5 nm, respectively. The decrease in L_a value upon modification suggested an increase in the edge defects thereby creating more number of active sites.



(a) (b)

Fig. S1. (a) FT-IR Spectra of Inu, Inu-TiO_2, MWCNT, MWCNT-Inu, MWCNT-Inu-TiO_2 (b) Raman spectra of MWCNT, TiO_2 , MWCNT-Inu and MWCNT-Inu-TiO_2

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