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Research Article

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Studies on adsorption of whey peptides on multi-wall carbon nanotubes after treatment

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ABSTRACT

A static experiment for the absorption of whey peptides to pretreated multiwalled carbon nanotubes (t-MWCNTs) was reported. MWCNTs were prepared by catalytic chemical vapor deposition （CCVD）followed by purified and opened by oxidation method with nitric acid(HNO_3). The t-MWCNTs with whey peptides were characterized by transmission electron microscopy and fourier transform infrared spectroscopy, and integrating sphere which confirm the attachment of whey peptides to the t-MWCNTs. The results indicated that after being pretreated by HNO_3,the adsorption capacity of carbon nanotubes was increased observably. The FTIR spectra indicated that the HNO_3 treatment process introduced specifically functional groups on the surfaces of MWCNTs, such as carbonyl groups, carboxyl groups, and hydroxyl groups. Therefore, the HNO_3 pretreatment possibly improved the adsorption capacity of multiwalled carbon nanotubes for whey peptides in solution.

Keywords: Multiwalled Carbon Nanotubes, Characterize, Adsorption, Whey Peptides

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INTRODUCTION

Whey protein has a relatively low content of fat, cholesterol and lactose, and ease of digestion and absorption. After hydrolysis, the whey protein peptides are not only easier to absorbed by the body, but also contains a variety of biologically active sequences, making it a special physiological activity of the fragment, thus achieving the specific physiological functions of the human body, such as lowering cholesterol, lowering blood pressure , anti-cancer, antibacterial, sedative, etc. [1,2] Therefore, research on whey protein peptides to gradually become a hot research abroad.

Carbonaceous adsorbent, such as fullerenes, carbon nanotubes (CNTs) and graphene sheets play a huge role in environment, biological, pharmaceutical and food industry, due to their unique mechanical and electrical properties. CNTs have unique properties owing to their particular structure and are the probable constituents of future materials in many purposes. Although CNTs as a new valuable material for the storage of hydrogen gas, methane and carbon monoxide were widely investigated[3-5]. Many research focused on the dispersion of the CNTs by lysozyme protein [6-9],the adsorption of whey peptides by CNTs was not reported previously.

In this paper, A static experiment for the absorption of whey peptides to pretreated multiwalled carbon nanotubes (*t*-MWCNTs) was reported. Confirming the adsorption of multi-walled carbon nanotubes and peptides of whey protein, This will have very important significance for further study on the interaction between carbon nanotubes and biological macromolecules and will expand the application of multi-walled carbon nanotubes as novel adsorbent in food area.

Test

2.1 Test materials and equipment

Whey protein peptide were prepared by enzymatic. MWCNTs were obtained from Shenzhen Nano company (length 1–10 μm, number of walls 3–15).

FTIR-8400S infrared spectrometers and UV-2500 UV/Vis Spectrophotometers (an integrating sphere device) were purchased from Japan Shimadzu.H-7650 transmission electron microscopy was purchased from Japan Hitachi.

2.2 Test method

2.2.1preparation of MWCNTs

Acid treatment MWCNTs lets to purify carbon nanotubes from catalyst and amorphous carbon and functionalize it with OH and COOH groups, simultaneously[10]. For this purpose,desired amount of MWCNTs was firstly refluxed(at 120℃ in silicone oil bath) in concentrated nitric acid for 1 h. Then,a very precise washing with plenty of distilled water was conducted to achieve neutral pH(equal to distilled water pH).After precipitation of MWCNTs,which occurred within more than 24h,the upper water was separated and the MWCNTs were dried in an oven at 120℃ [11–13].

2.2.2The adsorption of whey peptides on MWCNTs

Whey peptides was dissolved in a series of different concentration. Carbonaceous adsorbent were added into the solution and then ultrasonic vibration for 10 min.Adsorbed for 40 min at room temperature, and then refrigerated centrifuge at 8000 r/min 4℃ for 10 min to separate the supernatant and sediment.MWCNTs were rinsed with deionized water and freeze-dried for 5h.And then dring under the infrared lamp.Supernatant was filtered by 0.22 μm aperture filter membrane to remove the MWCNTs completely. Protein concentration of protein-peptide liquid was detected by Kay-nitrogen determination method before and after adsorption, recorded as C_0, C_{e1}, C_{e2}, respectively.

RESULTS AND DISCUSSION

3.1 Calculation of adsorption

the absorption efficiency of carbon nanotubes was calculated as the formula (1). Using Langmuir and Freundlich adsorption isotherm equation fitting the adsorption content of peptides on two kinds of MWCNTs.

Adsorption efficiency formula was

$$q = V(c_o\text{-}c_e)/m \quad (1)$$

where q----absorption efficiency (g/g), v ---- solution volume (mL), c_o---- solution concentration before adsorption (g/L), C_e---- the equilibrium concentration (g/L), m---- the amount of carbon nanotubes (g).

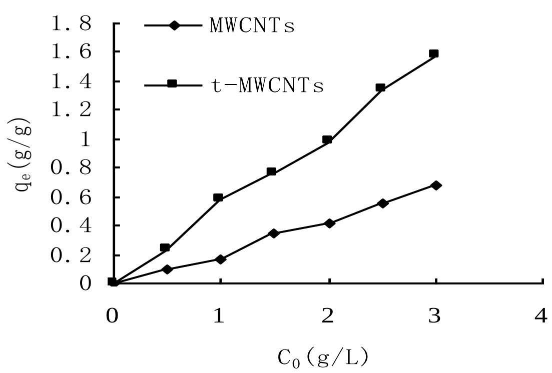

Fig 1 The adsorption isotherms of the two adsorbents at 25℃

The adsorption isotherms of peptides on two types of MWCNTs were shown in Figure 1.The absorption efficiency of MWCNTs oxidated by nitric acid was improved greatly. The reason may be attributed to the treatment in nitric acid. More functional groups, such as hydroxy, carboxy, were introduced on the surface of multi-walled carbon nanotubes. These groups may be coordination reaction with whey peptides peptide by terminal amino acid residues, thereby enhancing the absorption efficiency. In addition, after handlling with concentrated nitric acid, the length of carbon nanotubes became shorter and the port was opened, so that the surface area was increased and the adsorption efficiency was improved.

3.2 Surface modification of multi-walled carbon nanotubes by nitric acid oxidation method

It was effective to increase the rate of adsorption of multi-walled carbon nanotubes by decoratting multi-walled carbon nanotubes with nitric acid oxidation method. The changes of microstructure and functional groups of MWCNTs was characted, respectively. The results were shown in Figure 2 and Figure 3.

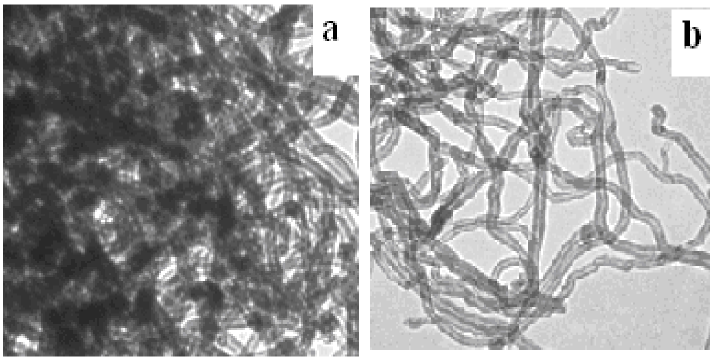

Fig 2 The TEM images of the two adsorbents with before(a) and after(b) treatment by oxidation method with nitric acid(HNO_3)

Fig.2a shows that unhandled MWCNTs stack on each other, distributed ruleless, line spacing is small, and there are plenty of "black spot". This was mainly because the ratio of length and diameter of MWCNTs was too large, as well as the gathered of MWCNTs by intermolecular forces. Combined with impurities and residues of metal catalysts and so on, exists in a large number of multi-walled carbon nanotubes. So most MWCNTs were able to observe, within the limited field of vision was existed in the form of fold, crimp stacked together. Without the prior treatment of concentrated nitric acid, it is hardly to see the port of MWCNTs in the TEM image, and a large number of "black spot" appears.

In figure 2b, it could be clearly found that the number of MWCNTs in units area, and significantly reduced compared to original MWCNTs, the length was shorter, port was more, and MWCNTs were purer then before. It means that after treatment with concentrated nitric acid, the ports of MWCNTs were opened which means the solubility, dispersion and surface area of part of MWCNTs were increased, at the same time, metal catalyst particles and other impurities were removed, further improves dispersion of multi-walled carbon nanotubes in solution, thus increasing the absorption of whey peptides.

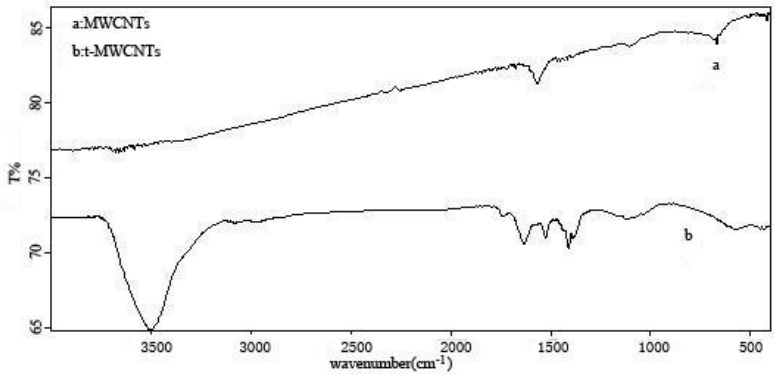

Fig 3 The FTIR of the two adsorbents with before (a) and after(b) treatment by oxidation method with nitric acid(HNO_3)

Figure 3 showed that after nitric acid oxidation process, some new characteristic absorption peak could be observed. Absorption peak in 1558cm^{-1} is the characteristic diaphragm of graphite structure of carbon nanotubes under infrared light, absorption peak in 1400cm^{-1} is characteristic absorption peak of Carbonyl, and absorption peak in 1650cm^{-1} is characteristic absorption peak of carboxylated, the broad peak occurrence in 3500cm^{-1} shows that the -OH was add to surface of carbon nanotubes during processing of oxidation by nitric acid, large numbers of these functional groups exist in the external and internal surfaces of multi-walled carbon nanotubes, introduction of these functional groups not only increases the polarity of the surface of carbon, and further changed the number of its surface charge.

3.3 t-MWCNTs adsorb the peptides of whey protein

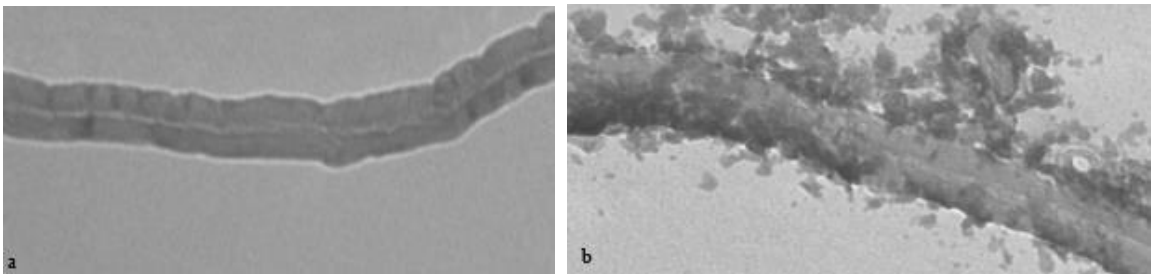

Fig 4 The TEM images of the *t*-MWCNTs with before(a) and after(b) adsorption of whey peptides

Figure 4 showed The TEM images of the *t*-MWCNTs with before and after adsorption of whey peptides.Whey polypeptide were mainly adsorbed on the outer wall of t-MWCNTs, and the surface utilization of t-MWCNTs was very high and the adsorption effect was visible.

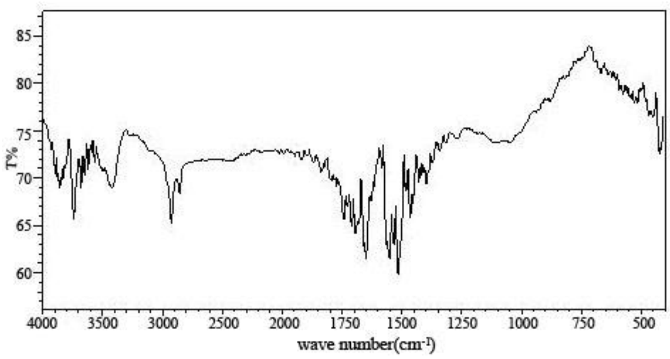

Fig 5 The FTIR of the *t*-MWCNTs with adsorpted of whey peptides

Figure 5 was the FTIR of the *t*-MWCNTs with adsorpted of whey peptides.After the adsorption of whey polypeptide, in 1680cm^{-1}, 1510~1570cm^{-1} and 2900~3000 cm^{-1} comes a characteristic absorption peak of t-MWCNTs. Which 1680cm^{-1} corresponding to the C=O absorption peak of amide I band, 1510~1570 cm^{-1} corresponding to the N-H and C-N absorption peak of amide II band, 2900~3000 cm^{-1} corresponding to the telescopic absorption peak of $-CH_3$ groups in albumin and globulin. Figure 3 and Figure 5 Visual shows the change of functional groups of t-MWCNTs adsorption of whey polypeptide, which confirmed the adsorption effect between the whey polypeptide and t-MWCNTs.

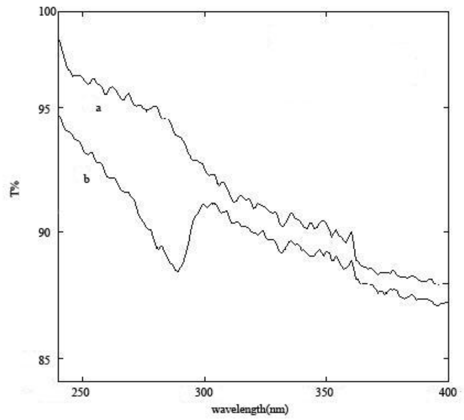

Fig 6 UV-reflectance of the *t*-MWCNTs with(b) and without(a) adsorpted of whey peptides

The reflection mapping in Figure 6 shows that the result of t-MWCNTs absorption of whey polypeptide using UV-integrating sphere measuring.A significant absorption peak was found in figure 6 at 280nm after t-MWCNTs adsorption whey peptides which was the characteristics absorption of peaks benzene ring.It may be attributed to some of the specific amino acid containing benzene ring exposed after hydrolysis of whey protein by enzymes. It could be proved that whey polypeptide were combined with the t-MWCNTs.Therefore, chemical adsorption was existed in the adsorption of whey polypeptide on MWCNTs

CONCLUSION

The adsorption efficiency of whey polypeptide on MWCNTs which was oxidated with nitric acid was much better than untreated one. The morphology of MWCNTs, such as surface area increases, the ports were opened, surface more pure, enhanced dispersibility in aqueous solution, had been improved after concentrated nitric acid treatment. New functional groups were introduced on surface, such as hydroxyl, carboxyl and so on. And these groups introduction of MWCNTs could be the major causes of the increased of adsorption efficiency. The adsorption efficiency was charactered by TEM, FTIR, and integrating sphere method. Interactions was found between whey polypeptide and t-MWCNTs which meant the presence of chemical adsorption beside physical adsorption.

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