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# Surface Immobilization of Carbon Nanotubes by $\beta$ -Cyclodextrins and Their Inclusion Ability

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The surface immobilization of  $\beta$ -cyclodextrins on the surface of multiwalled carbon nanotubes (MWNTs) in an aqueous medium was achieved by covalent-binding of diamino-functionalized  $\beta$ -cyclodextrin with carboxylic acid-functionalized MWNTs via amide linkages using a water-soluble condensation agent at room temperature. The obtained product denoted as  $\beta$ -cyclodextrin-modified MWNTs was highly dispersible in an aqueous medium. The covalent surface functionalization of MWNTs by  $\beta$ -cyclodextrin was characterized by FTIR, TGA, EDS and TEM. The thermogravimetric analyses indicated that  $\sim$  70 wt%  $\beta$ -cyclodextrin was attached on the surface of MWNTs. Furthermore, the fluorometric analysis for adsorption of rhodamine 6G dye suggested that the formation of  $\beta$ -cyclodextrin-dye inclusion conjugate takes place prior to the adsorption of dyes on MWNTs and uniform dispersion of MWNTs.

Keywords: Carbon Nanotube, Diamino β-Cyclodextrin, Surface Immobilization, Water-Dispersible Carbon Nanotube, Fluorescence, Inclusion Ability.

### 1. INTRODUCTION

The carbon allotropes and their commercial massproduction has attracted and inspired scientists of all over the world to evaluate them for a wide range of applications.<sup>1-3</sup> Among the commercially available carbon allotropes, carbon nanotubes (CNTs) have exceptional applications in materials science, nanotechnologies and medicinal engineering owing to their unique electrical, mechanical, ultra-light weight and thermal properties.4-6 The excellent electron affinity and charge transfer capability make CNTs attractive for a number of various applications such as adsorbent, catalyst, bio-sensing electrode, solar cell, photo sensitizer, super conducting material, gas sensor, transistor, hydrogen storage and so on.7-12 However, the vital biomedical applications of CNTs are still underdeveloped due to major barriers i.e., limited reactivity and water-insolubility owing to their strong  $\pi - \pi$ stacking interaction and high aspect ratio.<sup>13-16</sup> Thus, extensive research is being undertaken to develop new dispersion techniques, which allow using CNTs in water, other polar-nonpolar solvents and in polymer matrix.<sup>17-27</sup>

Several covalent and non-covalent strategies have been attempted for the dispersion of CNTs in water and other organic solvents. In covalent approaches, carboxylate or azide-functionalized and halogenated CNTs have been effectively attached to the dispersing agents.<sup>15, 16, 28</sup> In noncovalent approaches, CNTs were effectively wraped by aromatic molecules, polymers and surfactants.<sup>29-31</sup> However, the demerit of using non-covalent interactions to fabricate hybrids of CNTs is that in a competitive reaction medium the adsorbed solubilizing molecules could be easily released from the CNTs surface.32, 33 Efforts are continuing to find simple, biocompatible and less expensive routes for functionalization of CNTs in order to elevate their dispersibility. Moreover, the surface modification of CNTs through covalent-noncovalent functionalization with supramolecular molecules is crucial for developing high performance materials based on CNTs and supramolecular materials.34

Cyclodextrins are cyclic host molecules, which are composed of glucose units and connected through  $\alpha$ -1,4glycosidic linkages.<sup>35</sup> Cyclodextrins have a characteristic torus truncated-cone shape structure with a hydrophilic exterior and a hydrophobic cylindrical interior. They are widely known for their unique ability to form inclusion

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complexes (ICs) with various molecules such as polymers, carbon allotropes, metals and hydrophobic molecules etc.<sup>36, 37</sup> These cyclodextrins serve well as good host molecules for the solubilization of fullerenes in water.<sup>38, 39</sup> Then the immobilization of cyclodextrin molecules to the surface of CNTs is an effective option for the approach of guest molecules to CNTs and thus for the enhancement of the interaction between guests and CNTs.<sup>40</sup>

 $\beta$ -cyclodextrin is most common, cheapest and most useful among commercially available cyclodextrins. Selective replacement of hydroxyl groups on  $\beta$ -cyclodextrin with other functional groups remarkably improves the reactivity, inclusion ability and solubility superior to the pristine  $\beta$ -cyclodextrin.<sup>41,42</sup> Although the presence of similar hydroxyl groups makes the selective modification of  $\beta$ -cylodextrin extremely difficult, the regioselective modification of  $\beta$ -cyclodextrin can be achieved by using geometry of reagents, which result in a selectively diffunctionalized  $\beta$ -cyclodextrin to improve water-solubility, inclusion ability and reactive functionality.<sup>43-45</sup> Thus the controlled covalent-noncovalent functionalization of CNTs with  $\beta$ -cyclodextrins improves their dispersibility without damage of their unique and characteristic properties.<sup>46-48</sup>

The principal aim of the present investigation was to covalently attach  $\beta$ -cyclodextrin along with the wall of CNTs. For this purpose, both  $\beta$ -cyclodextrin and CNTs were functionalized. Thus,  $\beta$ -cyclodextrin was modified with reactive amino functional groups and CNTs were functionalized to generate carboxylic groups on the surface. The amine functionality on the primary side of the  $\beta$ -cyclodextrin was effectively used, as it can react with carboxylic group of CNTs via amide linkage. The presence of  $\beta$ -cyclodextrin on the surface of CNTs can provide not only excellent water-dispersibility of CNTs but also the site for inclusion of guest molecules or ions. Therefore, the inclusion ability of  $\beta$ -cyclodextrin immobilized on CNTs was studied.

#### 2. EXPERIMENTAL DETAILS

#### 2.1. Materials

 $\beta$ -cyclodextrin was donated as a gift sample from Signet Chemical Corporation, Mumbai, and dried overnight under a vacuum oven at 60 °C before use. Diamino-functionalized  $\beta$ -cyclodextrin was synthesized and characterized according to the literature and our modified procedure.<sup>49,50</sup> Multiwalled CNTs (MWNTs) were purchased from Wako Pure Chemical Industries Ltd., (Taiwan) and purified by refluxing in concentrated (69%) HNO<sub>3</sub> for 2 days, followed by washing with concentrated hydrochloric acid and then water on a Millipore VC membrane (pore size = 0.1  $\mu$ m). 1-ethyl-3-(3-dimethylamino propyl) carbodiimide hydrochloride (EDC) and phosphotungstic acid were purchased from Sigma-Aldrich Chemical Co., Taiwan. Rhodamine 6G was a product of Acros

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Chemical Co, Japan. All other chemicals were commercial products of reagent grade and used without further purification. Water was purified by distillation and deionization using a Millipore Mili-Q Laboratory purification system (conductivity: 10  $\mu$ S/cm).

#### 2.2. Instruments and Measurements

FTIR spectroscopic measurements were recorded on a Nicolet-6700 spectrometer at  $10^{-4}$  resolution and 32 scans using a KBr pellet method. Thermogravimetric analyses (TGA) were done on a TGA Q500 instrument at a heating rate 10 °C/min in air atmosphere. The energy-dispersion X-ray spectrometric (EDS) measurements of powders on gold-coated carbon tape were performed on a JEOL JSM-6500F at an operation voltage of 20 kV. Transmission electron microscopic (TEM) images were obtained on a Hitachi H-700 equipped with a charge-coupled device camera, operating at an accelerating voltage of 100 kV. The specimens for TEM were prepared by directly dropping the dispersion of corresponding products onto the carbon-coated copper grids. Fluorescence spectra were recorded on a HITACHI F-3010 fluorometer with a 10 mm path cell.

#### 2.3. Carboxylic Acid Functionalization of MWNTs

Carboxylic acid-functionalized MWNTs (CNTs-COOHs) were obtained by refluxing 20 mg of purified MWNTs in 20 mL concentrated  $HNO_3/H_2SO_4$  (3:1, v/v) for 24 h after 2 h sonication.<sup>15</sup> After centrifuging, washing several times with water and drying overnight, the solid obtained was subjected to FTIR analysis to check the effective surface functionalization of MWNTs with carboxylic groups.

## 2.4. Immobilization of β-Cyclodextrins on Surface of MWNTs

The carboxylic acid-functionalized MWNTs were immersed into 30 mL of a freshly prepared 10 mM EDC solution to convert the carboxylic groups of MWNTs into active ester (2 in Scheme 2). After activation for 30 min, 100 mg of diamino  $\beta$ -cyclodextrin was added and the reaction mixture was allowed to stir for 24 h at room temperature. The excess of diamino  $\beta$ -cyclodextrin and byproducts obtained during the progress of reaction were removed by washing with water and dialyzing with a polymer membrane (MWCO 2 K) for 24 h. The product, denoted as  $\beta$ -cyclodextrin-modified MWNTs, was obtained by centrifugation and drying at 60 °C for 24 h. The procedure and the mechanism for the formation of this product are shown in Schemes 1 and 2, respectively.

#### 2.5. Sample Preparation for Fluorescence Measurement

A  $5.0 \times 10^{-5}$  M rhodamine 6G solution and a 25  $\mu$ g/mL  $\beta$ -cyclodextrin-modified MWNTs solution were prepared



β-Cyclodextrin Modified MWNT

Scheme 1. Synthetic scheme of chemical immmobilization of  $\beta$ -cyclodextrins on MWNT.

in water. The rhodamine 6G solution (1 mL) was added to different volumes (1–9 mL) of a  $\beta$ -cyclodextrin-modified MWNTs solution and then adjusted to a total volume of 10 mL by adding water. The mixtures were stirred and then allowed to equilibrate for 8 h before fluorescence measurements. Thus, the final concentration of rhodamine 6G was constant (5.0 × 10<sup>-6</sup> M) and the concentration of  $\beta$ -cyclodextrin-modified MWNTs was varied between 0–22.5  $\mu$ g/mL.

#### 3. RESULTS AND DISCUSSION

# **3.1.** Characterization of β-Cyclodextrins Immobilized on MWNTs

 $\beta$ -cyclodextrin-modified MWNTs were synthesized by the covalent attachment of diamino  $\beta$ -cyclodextrin with oxidized MWNTs (Scheme 1) through amide linkages using a water-soluble condensation agent, EDC. Figures 1(a) and (b) shows FTIR absorption spectra of pristine MWNTs



Scheme 2. Mechanism for the reaction of diamino  $\beta$ -cyclodextrin with oxidized MWNT by an activated ester intermediate.

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Fig. 1. FTIR absorption spectra of (a) pristine MWNTs (b) oxidized MWNTs, (c) diamino  $\beta$ -cyclodextrin and (d)  $\beta$ -cyclodextrin-modified MWNTs.

and oxidized MWNTs. The spectrum of oxidized MWNTs exhibited bands at 1720 and 1560 cm<sup>-1</sup> due to -C=O stretching and  $-COO^-$  antisymmetric stretching vibration modes, respectively, indicating the presence of carboxylic acid and carboxylate groups on the surface of MWNTs after treatment with acid mixture.<sup>15, 16, 51</sup> The bands at 3440 and 1640 cm<sup>-1</sup> come from traces of moisture.

The covalent amide linkages between MWNTs and modified  $\beta$ -cyclodextrin were confirmed from the FTIR spectra shown in Figures 1(c) and (d). In the spectrum of diamino  $\beta$ -cyclodextrin (Fig. 1(c)), the absorption bands were found at 3368, 2920, 1660, 1155, and 1029 cm<sup>-1</sup>, which could be assigned to typical absorption bands of  $\beta$ -cyclodextrin. Incidentally, the FTIR absorption spectrum of  $\beta$ -cyclodextrin-modified MWNTs (Fig. 1(d)) exhibited similar absorption bands to  $\beta$ -cyclodextrin, indicating the binding of  $\beta$ -cyclodextrin on MWNTs and the retaining of the pristine structure of  $\beta$ -cyclodextrin after the modification with MWNTs. Besides, there was disappearance of typical absorption bands (1720 and 1560  $cm^{-1}$ ) of oxidized MWNTs. Moreover, the typical band of amide I at 1674 cm<sup>-1</sup> was overlapped by the typical broad band of  $\beta$ -cyclodextrin. The results clearly suggest that carboxylic groups of MWNTs were completely exhausted by chemical reaction with diamino  $\beta$ -cyclodextrins, confirming the successful attachment of  $\beta$ -cyclodextrins onto the surface of CNTs through covalent amide linkages.

One of the convincing and visual evidences for surface modification of MWNTs with  $\beta$ -cyclodextrins was the water-dispersibility of these nanotubes. A comparison of the dispersibility is shown in Figure 2. Same quantities of three samples of pristine MWNTs, oxidized MWNTs and  $\beta$ -cyclodextrin-modified MWNTs were suspended in water and stirred for half an hour and left as it is. Within few minutes the pristine MWNTs settled down to the bottom of the petri dish, whereas the oxidized MWNTs did not precipitate at short time like one hour but settled down



**Fig. 2.** Dispersibility of (a) pristine MWNTs, (b) oxidized MWNTs and (c)  $\beta$ -cyclodexrin-modified MWNTs.

after 5 h. In the case of  $\beta$ -cyclodextrin-modified MWNTs, the MWNTs were stable without visible precipitates in the aqueous system even after several months.

To further confirm the surface modification of MWNTs, the obtained product was analyzed by TGA and compared to the starting materials i.e., diamino  $\beta$ -cyclodextrin, pristine MWNTs and oxidized MWNTs. Figure 3 shows the TGA curves of pristine MWNTs, oxidized MWNTs, diamino  $\beta$ -cyclodextrin and  $\beta$ -cyclodextrinmodified MWNTs. As shown in Figures 3(a) and (b), pristine MWNTs and oxidized MWNTs underwent weight loss at the temperature range of 500-700 °C. On the other hand, diamino  $\beta$ -cyclodextrin (Fig. 3(c)) displayed weight loss in three steps including the weight loss of hydrated water and was completely decomposed up to 500 °C. On a TGA curve of  $\beta$ -cyclodextrin-modified MWNTs (Fig. 3(d)), the weight loss happened through some steps up to 630 °C. The observed weight loss after 500 °C on the TGA curve of  $\beta$ -cyclodextrin-modified MWNTs can be attributed to the loss of diamino  $\beta$ -cyclodextrin alone. Hence, the weight content of covalently bonded diamino  $\beta$ -cyclodextrin in  $\beta$ -cyclodextrin-modified MWNTs was determined from weight% in the TGA curve at 500 °C and evaluated to be about 70 wt%.

EDS analysis was also carried out on pristine MWNTs, oxidized MWNTs and  $\beta$ -cyclodextrin-modified MWNTs, and the results are given in Figure 4. The EDS results



**Fig. 3.** TGA curves of (a) pristine MWNTs, (b) oxidized MWNTs, (c) diamino  $\beta$ -cyclodextrin and (d)  $\beta$ -cyclodextrin-modified MWNTs.

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Fig. 4. FE-SEM combined EDS of (a) pristine MWNTs, (b) oxidized MWNTs and (c) β-cyclodextrin-modified MWNTs.

were quite convincing in the sense that the carbon content reduced from pristine MWNTs to oxidized MWNTs and  $\beta$ -cyclodextrin-modified MWNTs with a corresponding increase in the elemental content of oxygen.

The visual and direct confirmation for the immobilization of  $\beta$ -cyclodextrins on the surface of MWNTs comes from TEM images. Figure 5 shows TEM images of pristine MWNTs, oxidized MWNTs, and  $\beta$ -cyclodextrin modified MWNTs without and with staining by phosphotungstic acid. From the comparison between TEM images of pristine MWNTs (Fig. 5(a)) and oxidized MWNTs (Fig. 5(b)), it was found that the reflux treatment with acid mixture affected the purification of MWNTs beside the surface oxidation of MWNTs; the acid treatment removed extra metal catalysts, amorphous carbons and carbon nanoparticles, which were formed during the course of production of MWNTs.

In the case of  $\beta$ -cyclodextrin-modified MWNTs without staining (Fig. 5(c)), it was difficult to distinguish the surface immobilization of MWNTs with  $\beta$ -cyclodextrins, although some haziness could be observed on the surface of MWNTs, ascribed to the functionalization with diamino  $\beta$ -cyclodextrin. In the case of a TEM image of  $\beta$ -cyclodextrin-modified MWNTs stained with phosphotungstic acid (Fig. 5(d)), black stains (high contrast spots) were observed on the surface of MWNTs which could be due to the adsorption of phosphotungstic acid on the amide linkages or diamino  $\beta$ -cyclodextrins. It could be also be confirmed from the TEM images that the acid treatment and the surface immobilization of MWNTs did not damage the surface of MWNTs.

## 3.2. Inclusion Ability of $\beta$ -Cyclodextrins Immobilized on MWNTs

One of the efficient methods to confirm the functionality (especially inclusion ability) of  $\beta$ -cyclodextrin on the surface of CNTs is to find out whether any organic molecule can be included into the  $\beta$ -cyclodextrin cavity and probed by means of a suitable technique. Thus, the fluorescence emission of rhodamine 6G excited at 480 nm in aqueous solutions of  $\beta$ -cyclodextrin-modified MWNTs was compared to those in aqueous solutions of diamino  $\beta$ -cyclodextrin, pristine MWNTs and oxidized MWNTs. The results of these measurements are shown in Figure 6. The maximum emission intensity was observed at 554 nm for all systems.

In the presence of diamino  $\beta$ -cyclodextrin, the fluorescence intensity of rhodamine 6G increased with increasing in concentration of diamino  $\beta$ -cyclodextrin (Fig. 6(A)).

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Fig. 5. TEM images of (a) pristine MWNTs, (b) oxidized MWNTs, (c)  $\beta$ -cyclodextrin-modified MWNTs without staining and (d)  $\beta$ -cyclodextrin-modified MWNTs staining with phosphostungstic acid.

This phenomenon is due to the formation of inclusion complex, where the rotation of the rhodamine 6G molecule is hindered and the relaxation of the solvent molecules is considerably decreased. Both of these effects can result in a decrease in the vibrational deactivation. The inclusion of rhodamine 6G in the non-polar cavity of  $\beta$ cyclodextrin protects the dye emission from quenching by water molecule. The cavity of cyclodextrins behaves similar to organic solvents, which offer the non-polar surrounding for the included molecules. This alternative microenvironment can provide the favorable polarity for enhanced quantum efficiencies and hence the increase in the intensity of fluorescence. Since rhodamine 6G is not a small molecule to include into a single  $\beta$ -cyclodextrin unit, it can be included into two  $\beta$ -cyclodextrin units (Scheme 3(a)), thus forming a 2:1 complex with  $\beta$ cyclodextrin and leading to the increase in fluorescence intensity.52

Meanwhile, the fluorescence intensity was reduced in the presence of pristine MWNTs, oxidized MWNTs and  $\beta$ -cyclodextrin-modified MWNTs (Figs. 6(B)–(D)). The fluorescence hypochromism of rhodamine 6G by nanotubes can be explained by the overlapping of aromatic rings in

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rhodamine 6G on six-ringed structure of the nanotube surface. This is expected for pristine CNTs in the aqueous solution, since the strong  $\pi-\pi$  stacking (Scheme 3(b)) is the main probable interaction between rhodamine 6G and the surface of CNTs and it results in the fluorescence quenching. Similar fluorescence hypochromism of rhodamine 6G on oxidized MWNTs and  $\beta$ -cyclodextrinmodified MWNTs indicates the fact that though the covalent functionalization of CNTs has taken place with the modification of the  $\pi$  structure on their surface, the CNTs still retain the essential property of the nanotubes.

Additional insights were obtained from the analysis of the fluorescence intensity depending on concentration of MWNTs. It could be seen from Figure 7 that the emission intensity at 554 nm of rhodamine 6G decreased for all the three systems, that is, pristine MWNTs, oxidized MWNTs and  $\beta$ -cyclodextrin-modified MWNTs. However, the profile of the decrease was different for all three. For cases of pristine and oxidized MWNTs, the intensity decreased through two-step process with increasing the concentration of MWNTs. The concentration of the inflection point between two linear gradients was 15 and 2.5  $\mu$ g/mL for pristine and oxidized MWNTs, respectively. Moreover, the



nonpolar-nonpolar and π-π interaction

Scheme 3. Schematic illustration of the formation of  $\beta$ -cyclodextrin-dye inclusion complex and the adsorption of dyes on MWNTs.

pristine and oxidized MWNTs solutions aggregate after some time.<sup>53</sup> In contradistinction to above, there were modes of dye adsorption on CNTs. three linear slopes for  $\beta$ -cyclodextrin-modified MWNTs  $\beta$  graphene structure, the first adsorption should be the

observed. These results indicate that there are different

two inflection points at 2.5 and 15  $\mu$ g/mL among the \_\_\_\_\_On the pristine MWNTs with the homogeneous



Fig. 6. Fluorescence spectra (excited at 480 nm) of rhodamine 6G ( $5 \times 10^{-6}$  M) in aqueous solutions of (A) diamino  $\beta$ -cyclodextrin, (B) pristine MWNTs, (C) oxidized MWNTs and (D)  $\beta$ -cyclodextrin-modified MWNTs at different concentrations: (a) 0, (b) 2.5, (c) 5.0, (d) 7.5, (e) 10.0, (f) 12.5, (g) 15.0, (h) 17.5, (i) 20.0 and (j) 22.5 µg/mL.

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Fig. 7. Change in fluorescence intensity at 554 nm of rhodamine 6G  $(5 \times 10^{-6}M)$  as a function of concentration of (a) pristine MWNTs, (b) diamino  $\beta$ -cyclodexrin, (c) oxidized MWNTs and (d)  $\beta$ -cyclodextrinmodified MWNTs in water.

physisorption of dyes followed by the second adsorption by strong  $\pi - \pi$  stacking interaction (Scheme 3(b)). Since the oxidized MWNTs have many functional groups (carboxylic acids and other oxidized units) on the surface of MWNTs, cationic rhodamine 6G can electrostatically bind with carboxylic acids on MWNTs at the initial stage. Sequentially, the dye may give rise to  $\pi - \pi$  stacking interaction with the surface of CNTs, since the slope of the second step is similar to that of the pristine MWNTs. The formation of conjugates between rhodamine 6G and  $\beta$ -cyclodextrin-modified MWNTs may differ from other systems,<sup>54</sup> because main functional groups (carboxyl groups) of MWNTs are exhausted to form amide bonds with  $\beta$ -cyclodextrin. Therefore, the possible adsorption is mainly the inclusion into the  $\beta$ -cyclodextrin non-polar cavity (Scheme 3(c)) with the minor physisorption/ $\pi$ - $\pi$  stacking interaction. Such adsorption is saturated up to 15  $\mu$ g/mL, because the quenching (hypochromism) of the emission is not progressive above this concentration. Thus, the excellent water-dispersibility of  $\beta$ -cyclodextrinmodified MWNTs and inclusion ability of  $\beta$ -cyclodextrins on the surface of MWNTs is very useful in a biological medium to probe the guest molecule in vitro or vivo studies.55

### 4. CONCLUSIONS

The fabrication of water-dispersible hybrid materials denoted as  $\beta$ -cyclodextrin-modified MWNTs was achieved by a simple, conventional covalent bond formation technique. The successful attachment of  $\beta$ -cyclodextrin on the surface of MWNTs was effectively characterized by conventional techniques like FTIR, TGA, EDS and TEM analyses. This synthetic method provided an enough number of  $\beta$ -cyclodextrin units on the surface of MWNTs. The combination of cyclodextrins and MWNTs allows using the properties of both components in aqueous medium. On one hand this procedure afforded the easy dispersion

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of CNTs in water, and on the other it provided nanocavities of  $\beta$ -cyclodextrin on the surface of the MWNTs for the inclusion of selected guest molecules. The nanocavities can include organic molecules, which are sufficiently small to 'fit' into the  $\beta$ -cyclodextrin cavity, as exemplified by the inclusion of rhodamine 6G, and the results support the potential of these hybrid materials for specific sensing based on CNTs.

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