

Surface Functionalization of Carbon Micro Coils and Their Selective Immobilization on Surface-Modified Silicon Substrates

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Surface functionalization of carbon micro coils (CMCs) was performed by acid treatment at different times. Nitric acid oxidation produced CMC with acidic functional groups, although morphology of CMCs was modified after the oxidation. The selective immobilization of as-prepared CMC from an aqueous dispersion was examined on differently surface-modified silicon substrates. It was confirmed that the acid-treated CMC was selectively immobilized on a silicon substrate by chemical bonding with amine-terminated self-assembled monolayers on a silicon substrate, while the pristine CMC was not.

Keywords: Carbon Micro Coil, Surface Functionalization, Acid Treatment, Self Assembled Monolayer, Immobilization, Silicon Substrate.

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1. INTRODUCTION

Although carbon materials have attracted huge interests over the past decade due to the potential applications arising from their advantageous mechanical and physicochemical properties, their poor dispersibility and chemical inertness have been an obstacle on the incorporation of these materials into composites or devices. Then an available route to solve these problems is the manipulation of surface functional groups on the carbon materials by physical or chemical treatments, as surface-bound functional groups can encourage the wettability, dispersibility and surface reactivity of carbon materials and the carbon/additive interfacial affinity within composite materials. For instance, a number of investigators have successfully employed oxidation reactions to activate carbon materials so as to possess acidic functional groups.^{1–6} Moreover, activated carbon nanotubes were applied to immobilization of metal and metal oxide nanoparticles on them.^{7,8}

Carbon micro coil (CMC) is produced by metal-catalyzed pyrolysis of acetylene at 700–800 °C and takes a spiral structure with coil diameter of micrometer order.^{9,10} It has been reported that CMCs are an amorphous material and have super-elastic properties; Elastic CMCs are

extended by 3–15 times and contracted to the original coil length.¹¹ CMCs also exhibit properties of high hydrogen absorption¹² and electromagnetic wave absorption,¹³ and polymer-grafting of CMC results in the improved dispersibility in mediums.¹⁴ These unique characteristics of CMCs are thus valid as a highly attractive material and on applications such as sensors and actuators. On the other hand, the immobilization of CMC on solid substrates is an important subject on the fabrication of devices, but there are no such reports until now to our knowledge.

In this work, the acid treatment of CMC was investigated, and its surface functionalization was characterized by means of several analytical techniques. Moreover, the immobilization of CMC on silicon substrates was carried out through chemical bonding of the functionalized CMC with the functional self-assembled monolayers (SAMs) on a silicon substrate.

2. EXPERIMENTAL DETAILS

CMC was prepared according to previously reported procedure.¹⁰ Octadecyltrichlorosilane, 3-aminopropyltriethoxysilane, phosphorus pentachloride, hydrogen peroxide, sulfuric acid (98%), nitric acid (60%), isopropyl alcohol, toluene, ethanol, dichloromethane (HPLC grade),

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carbon tetrachloride, 2,2,4-trimethylpentane, and hexane were commercial products and used as purchased. De-ionized water was used throughout whole experiments.

Acid-functionalization of CMC was carried out by oxidation of CMC with HNO_3 . CMC (30 mg) and HNO_3 (60 cm^3) were mixed in a flask equipped with a condenser. The mixture was heated at 90 °C in a silicon oil bath for different time periods of 7, 10, and 12 h with stirring at 140 rpm. After heated, the reaction mixture was filtered through a membrane filter (0.2 μm pore size). Then the residue on a filter was washed by water, until the filtrate remains in neutral. Finally, the rinsed residue (CMC with $-\text{COOH}$ functional group) was dried overnight in a vacuum oven at 60 °C.

Surface modification of silicon substrate was performed by preparation of SAMs on it.

2.1. Amine-Terminated Silicon Substrate

The silicon substrate was first cleaned by a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$, 3:1) according to standard procedure¹⁵ and immersed in a toluene solution of 3-aminopropyltriethoxysilane (10 mM) for 24 h, followed by thoroughly sonicating and rinsing with toluene, rinsing with ethanol, and then drying under N_2 gas. For preparing a damaged substrate, the amine-terminated substrate was UV-irradiated by a low-pressure mercury lamp (90 W) for 30 minutes.

2.2. Methyl-Terminated Silicon Substrate

The cleaned silicon substrate was obtained by the same method¹⁵ and immersed in a SAM preparation mixture (20 mm^3 of octadecyltrichlorosilane, 20 cm^3 of 2,2,4-trimethylpentane, and 5 cm^3 of carbon tetrachloride) for 24 h and rinsed with hexane and isopropyl alcohol, followed by rinsing with water and drying under N_2 gas.

For immobilization of CMC on silicon substrates, the $-\text{COOH}$ group of CMC was first converted to acid chloride ($-\text{COCl}$) by adding stoichiometric excess of phosphorus pentachloride (1 mg) in dichloromethane (10 cm^3) and sonicating for 5 min. Surface-modified silicon substrates were then immersed in this reaction solution for 8 h, rinsed with dichloromethane and ethanol, and dried under N_2 gas.

Fourier transform infrared absorption (FT-IR) spectra of KBr pellets were recorded by using a Nicolet-6700 IR spectrometer. X-ray photoelectron spectroscopic (XPS) spectra were obtained on a theta probe ESCA VG scientific (2002) using a monochromatic $\text{AlK}\alpha$ source at a pressure of 2×10^{-9} mbar. Thermal gravimetric analysis (TGA) experiments were carried out using a Perkin Elmer instrument/Technology SII (Diamond TG/DTA) equipment, where 6 mg samples were heated at a scan rate of 10 °C/min from 25 to 800 °C under N_2 and air streaming. The surface morphology of samples was analyzed using a JEOL JSM-6500F scanning electron microscope (SEM)

at accelerating voltages of 0–15 kV. Static contact angles were measured by using a CAM 100. Reported values represent an average of at least three measurements per sample.

3. RESULTS AND DISCUSSION

3.1. Surface Functionalization of CMC

IR spectra of pristine and acid-treated CMCs are shown in Figure 1. Pristine CMC displayed an absorption band at 3450 cm^{-1} which was resulted from trace of water.¹⁶ Besides, the IR spectrum of acid-treated CMC exhibited additional bands at 1725, 1560 and 1214 cm^{-1} which could be assigned to $\text{C}=\text{O}$, COO^- and $\text{C}-\text{O}$ stretching vibration modes, indicating the coexistence of carboxylic acid and carboxylate groups.^{7,17} Thus, the FT-IR analysis proved the acid-oxidation of CMC.

The change of surface characteristics after surface functionalization of CMC is visualized in an inset in Figure 1. It is clear that the dispersibility of CMC in water increased after the surface functionalization. The hydrophobic nature of the pristine CMC became hydrophilic after acid treatment due to hydrophilic groups induced on the oxidation process.

XPS was used for characterization of CMCs. The C1s and O1s peaks of CMC after 7, 10, or 12 h acid-treatment are shown in Figure 2. The figure indicates that each peak is superimposed by some component peaks. Then the C1s and O1s peaks can be deconvoluted into five and three peaks, respectively, as seen in Figure 2. Their binding energies and area intensities with peak attributions^{18–21} are listed in Table I. Peak attributions indicated that peaks corresponding to hydrocarbon species were in 284–286 eV

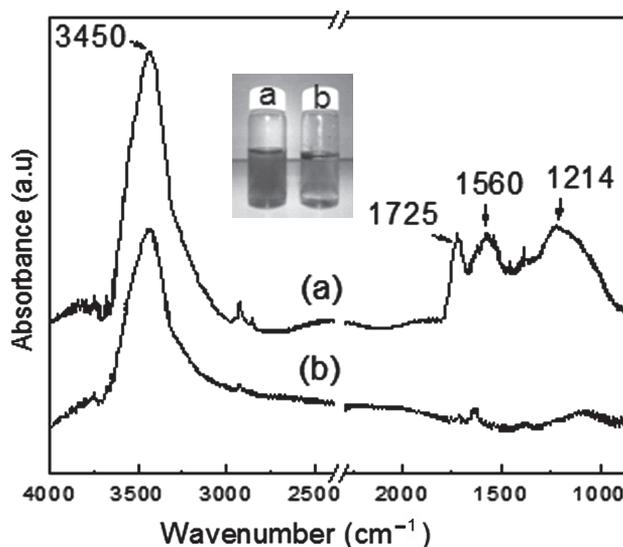


Fig. 1. FT-IR spectra of CMC. Inset: Photograph of CMC dispersion in water: (a) Acid-treated, (b) pristine.

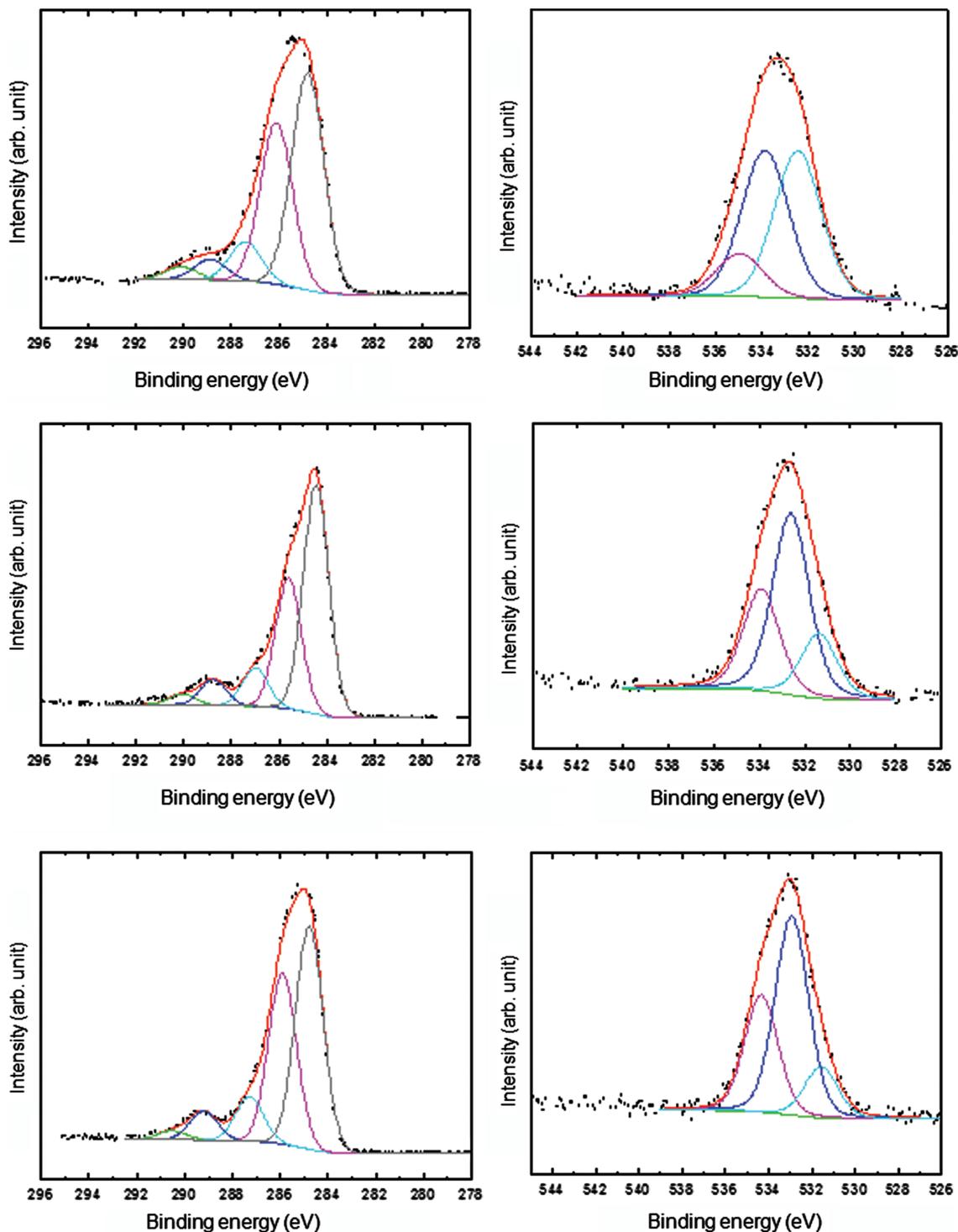


Fig. 2. C1s (left) and O1s (right) XPS spectra after 7 h (top), 10 h (middle) and 12 h (bottom) acid-treatment and their peak deconvolution.

range, and peaks due to oxidized carbon species (e.g., C3($-\text{C}=\text{O}$), C4($-\text{COOH}$)) existed between 287–289 eV. Meanwhile, the O3 peak was attributed to the $-\text{C}=\text{O}$ species (i.e., carboxyl and carbonyl groups). Thus, the presence of C4 and O3 peaks indicates that carboxylic acid groups are formed on CMC surfaces by acid treatment. The relative area intensity of C4 and O3 against C1 + C2

after 10 h treatment was stronger than that after 7 h, but it was only slightly intensified after 12 h. On the other hand, the nitrogen-containing species (N1s) decreased during oxidation, and the lowest intensity was found after 12 h treatment (see Table I). The eventual disappearance of nitrogen atom implies the replacement of nitrogen-containing species by the oxidized groups on CMCs. It can

Table I. Binding energies (BE) and area intensities of deconvoluted C1s, O1s, and N1s peaks on XPS of CMC acid-treated for different time periods.

Peak no.	7 h treatment		10 h treatment		12 h treatment		Attribution
	BE	Area intensity	BE	Area intensity	BE	Area intensity	
C1s							
C1	284.7	5800.3	284.4	6044.5	284.7	6964.6	Delocalized hydrocarbon
C2	286.1	4315.7	285.5	3824.5	285.9	5350.0	Localized hydrocarbon
C3	287.4	1043.4	286.9	1128.4	287.2	1384.7	$\pi^* \rightarrow \pi$ shake up for C2, $-C=O$
C4	288.8	543.6	288.7	702.2	289.2	899.2	$-COOH$
C5	290.1	332.3	290.0	291.5	290.5	274.5	$\pi^* \rightarrow \pi$ shake up for C1
C4/(C1 + C2)		0.053		0.071		0.073	
O1s							
O1	532.4	2522.0	531.3	1131.5	531.5	995.0	$-OH$
O2	533.8	2509.6	532.6	3175.6	532.9	3873.3	Unattributed oxides
O3	534.9	727.5	533.9	1788.5	534.3	2280.7	$C=O$
O3/(C1 + C2)		0.071		0.181		0.185	
N1s							
N1	400.0	162.9	400.0	212.8	400.6	265.6	Unattributed
N2	401.6	533.6	401.0	214.5	401.5	151.0	Unattributed
(N1 + N2)/(C1 + C2)		0.069		0.043		0.034	

be supported from XPS data that the oxidized groups are induced by the oxidation of nitrogen-containing species on CMC surface upon the treatment of CMC with nitric acid for 10 h or more.

To clarify the chemical change caused by the oxidation process, the thermal behavior of CMC was evaluated by the TGA method. At the elevated temperature, oxygen-containing groups are unstable and subsequently decomposed. Then the degree of oxidization is expected to be characterized as a variation in weight loss of CMCs. At first, TGA measurements were carried out under air. Although the pristine CMC did not lose its weight below 580 °C, the weight loss of acid-treated CMC began from the beginning of measurement and reached about 20% at 560 °C, as seen in Figure 3(A). This weight loss is considered to be due to a decomposition process of organic groups which were induced on CMC by acid-treatment. After reached a threshold temperature, the CMC decreased its weight rapidly to zero because of air oxidation. The threshold and end temperatures of air oxidation were 560 and 590 °C, respectively, for acid-treated CMC, while those of pristine CMC were 580 and 620 °C, respectively. These results indicate that CMC reduces its thermal stability by acid treatment.

To remove the influence of oxidative atmosphere, TGA measurement was also performed under nitrogen gas (Fig. 3(B)). Pristine CMC remained nearly constant weight even with heating up to 800 °C under this condition. Meanwhile, acid-treated CMCs resulted in reducing weight with the elevation of temperature: The oxidized CMCs showed a small weight drop around 118 °C that is assigned to the loss of physisorbed water and small molecules. The weight loss of oxidized CMC began from 118 °C and continued up to 800 °C. These results can be compared to those of related carbon materials. On the investigation of the

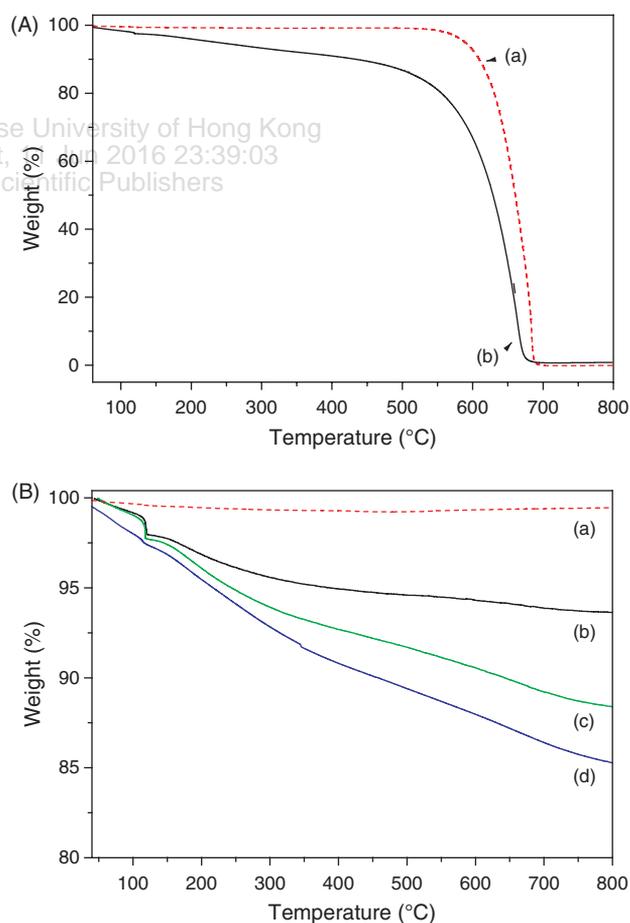


Fig. 3. (A) TGA curves under air atmosphere. (a) Pristine CMC, (b) acid-treated CMC (12 h). (B) TGA curves under nitrogen atmosphere. (a) Pristine CMC, (b) acid-treated CMC (7 h), (c) acid-treated CMC (10 h), (d) acid-treated CMC (12 h).

gradual thermal decomposition of preoxidized activated carbon, the number of carboxylic compounds on it was diminished to almost zero by heat treatment around 800 °C under vacuum.²² Additionally, multi-walled carbon nanotubes after the oxidation by HNO₃ contained a large number of functionalized sites, and the decomposition of them occurred around 580 °C and almost finished at 800 °C under inert condition.²³

The larger the procession of oxidization on CMC, the greater the weight loss became. For comparison, the degree of weight loss for each CMC was calculated in the range from 118 to 800 °C. The percentage of weight loss in CMC was 4.9, 8.8, and 11.9% for 7, 10, and 12 h treatment, respectively. These loss rates are consistent with the rates of COOH against hydrocarbon that were evaluated from XPS analysis described above (Table I). Then the amount of oxides as COOH groups calculated from the weight loss was estimated as 1.1, 1.9, and 2.6×10^{-3} mol/g for 7, 10, and 12 h treatments, respectively. From the titration measurement, it was reported that the amount of oxides was 1.34×10^{-3} mol/g for CMC after nitric acid treatment of 10 h.²⁴ The present result is considerably consistent with the previous report. As compared to the related nano-carbon material, the amount of carboxyl groups for multi-walled carbon nanotube was 3.7×10^{-3} mol/g after 48 h acid-treatment.²⁵ This value implies that one COOH moiety could be induced per approximately 18 carbon atoms. The amount of COOH groups in the oxidized CMC is about 1/3 ~ 1/2 of that in the multi-walled carbon nanotube, but it is considered that the oxidation is sufficient for further experiments.

Morphologies of CMC before and after acid treatment at different time periods were compared on SEM images. As seen in Figure 4(a), a large variety of spirals with different pitches and diameters exist in pristine CMC, and the distribution of spirals seems not to vary so much even after acid treatment for 7 and 10 h. The varied image of spirals was observed in a SEM photograph (Fig. 4(b)) of CMC after 12 h treatment, where rather uniform spirals were found. It was noticed that the oxidized CMCs shrank to small diameter, when compared to pristine CMC. This modification on morphology of CMC can be caused by hydrogen bonding between carboxylic acids induced on the spiral in a CMC. In fact, the variation to alkaline condition namely the deprotonation from carboxylic acid recovered the morphology of spirals because of the break of hydrogen bonding and the occurrence of electrostatic repulsion. It was observed with reproducibility on SEM that the spirals of 12 h acid-treated CMC were fairly thermal-damaged to be segmentized after heated up to 800 °C for TGA measurement under nitrogen atmosphere, as shown in Figure 4(c). Meanwhile, spirals of pristine CMC have scarcely changed to be segmentized even after heated up to 800 °C.

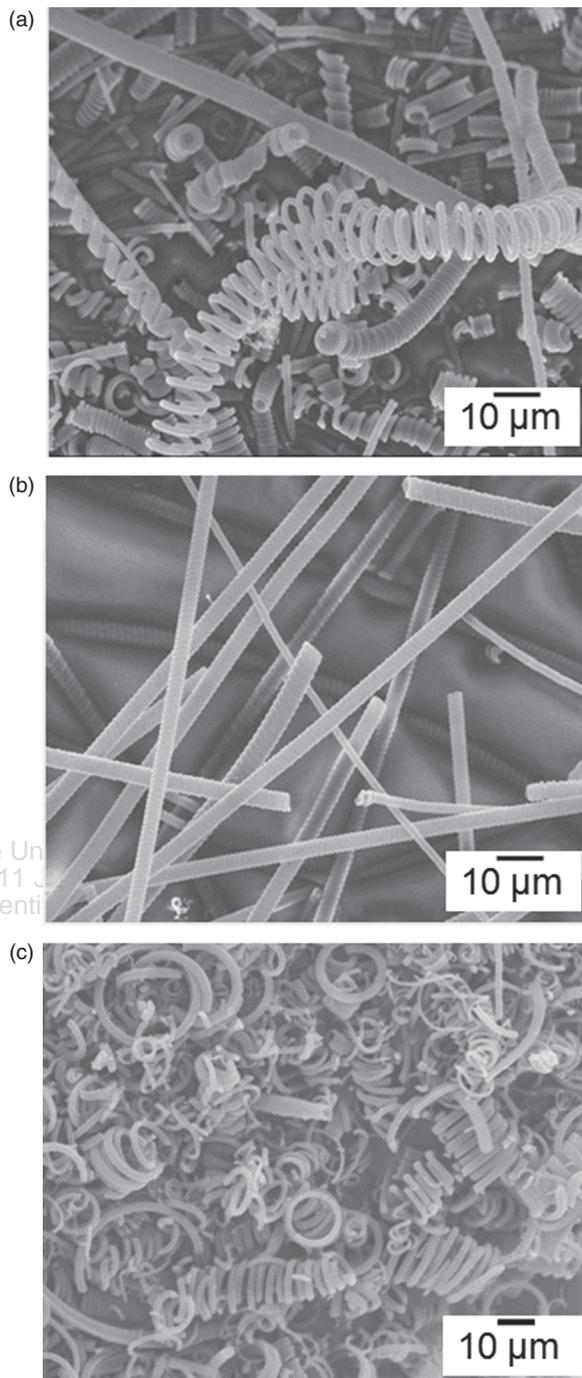


Fig. 4. SEM images. (a) pristine CMC, (b) acid-treated CMC (12 h), (c) acid-treated CMC (12 h, after heated up to 800 °C for TGA measurement under nitrogen atmosphere).

3.2. Selective Immobilization of CMC on Surface-Modified Silicon Substrates

Surface characteristics of differently modified silicon substrates were confirmed by water contact angle measurement.²⁶ The water contact angles on pristine, SAM-modified, and UV-irradiated (damaged) silicon substrates are listed in Table II. The contact angles are

Table II. Water contact angles on silicon substrates.

Type of silicon substrate	Contact angle
Pristine	$56 \pm 1^\circ$
Methyl-terminated	$107 \pm 2^\circ$
Amine-terminated	$81 \pm 1^\circ$
CMC-immobilized amine-terminated	$67 \pm 1^\circ$
UV-irradiated (damaged)	$5.0 \pm 0.4^\circ$

high in order of pristine < amine-terminated < methyl-terminated substrates, and they are not inconsistent with previously reported values.^{27–29} This fact reveals hydrophobicity of methyl-terminated substrate as compared

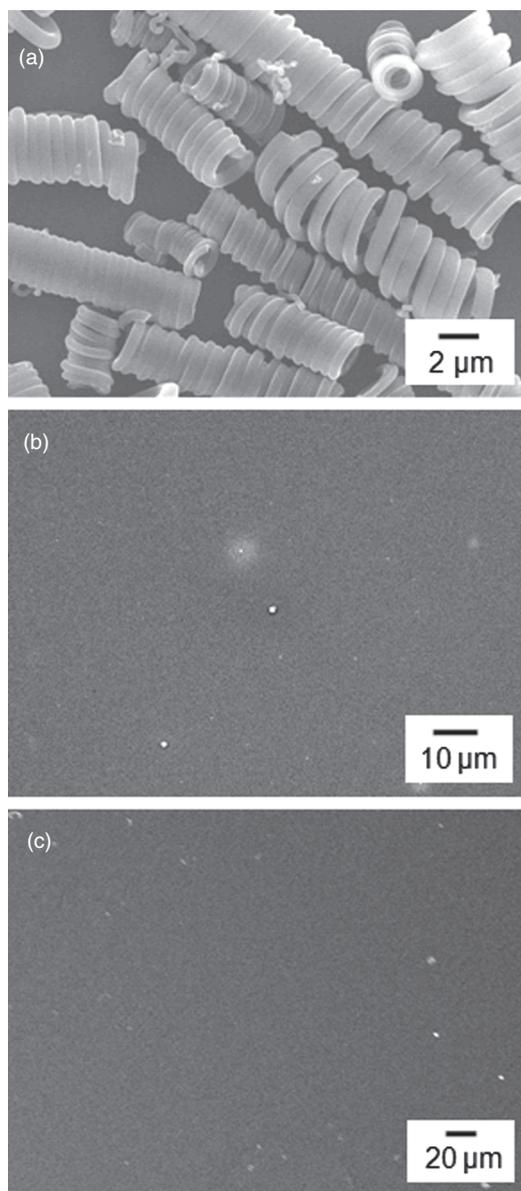


Fig. 5. SEM images after CMC immobilization procedure. (a) Acid-treated CMC on an amine-terminated silicon substrate, (b) acid-treated CMC on a UV-irradiated (damaged) silicon substrate, (c) pristine CMC on an amine-terminated silicon substrate.

to amine-terminated and pristine substrates. Incidentally, a UV-irradiated (damaged) substrate displayed high hydrophilicity ($5.0 \pm 0.4^\circ$), which is attributed to the removal of amine-terminated SAM and the formation of silicon hydroxide on the silicon substrate.

The immobilization procedure of oxidized CMC, as described in the experimental section, was carried out on amine-terminated, methyl-terminated, and UV-irradiated (damaged) substrates. In comparison, immobilization of pristine CMC on an amine-terminated substrate was also performed. Figure 5 shows SEM images of such substrates. The images undoubtedly confirmed that the immobilization of oxidized CMC could be achieved abundantly on the amine-terminated silicon substrate but not on the methyl-terminated and the UV-irradiated substrates along with the pristine CMC on the amine-terminated substrate. It should be noticed on the variation of water contact angle from non-immobilized to immobilized substrate (see Table II) that the CMC-immobilization changed the surface character to be more hydrophilic than the pre-immobilization state due to acid-functional groups on CMC. Thus the immobilization of CMC on silicon substrates was selectively controlled via an amide binding reaction between a

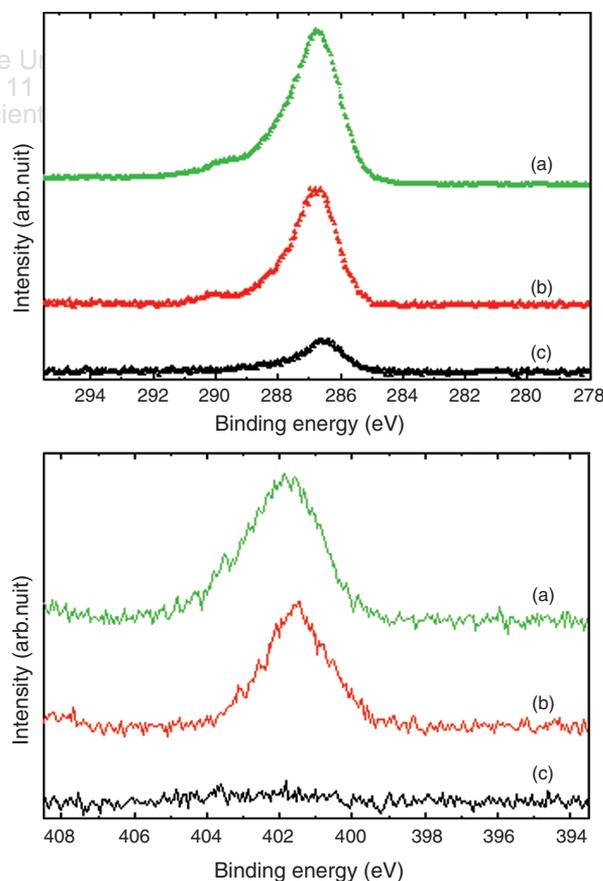


Fig. 6. C1s (top) and N1s (bottom) XPS spectra of silicon substrates. (a) CMC-immobilized amine-terminated, (b) amine-terminated, (c) UV-irradiated (damaged).

–COCl group of oxidized CMC and an –NH₂ group of amine-terminated substrate. In this connection, such chemical reaction does not occur on other combination of CMC and substrate.

C1s and N1s peaks in an XPS spectrum of CMC-immobilized amine-terminated silicon substrate were compared with those of amine-terminated and UV-irradiated (damaged) silicon substrates. The results are shown in Figure 6. Area intensities of C1s and N1s peaks of amine-terminated silicon substrate were found 6997.2 and 1594.3, respectively. Meanwhile, the corresponding intensities after CMC immobilization were 10349.1 and 2116.5, respectively. Then the intensity ratio of C1s against N1s is 4.39 and 4.89, respectively, for substrates before and after CMC immobilization. Increase in the relative ratio indicates the existence of abundant C atoms on the substrate due to the binding of CMC, that is, the successful immobilization. Note that a C1s peak diminished and an N1s peak disappeared by UV irradiation on amine-terminated substrate. This resulted from the decomposition of most alkyl amine on the substrate by UV irradiation. The decomposition of alkyl amine and the possible formation of hydroxide are consistent with the high hydrophilicity of the substrate from the contact angle result and support the impossibility of CMC immobilization on this substrate (see SEM result in Fig. 5(c)).

4. CONCLUSION

It was demonstrated that CMC was functionalized by the treatment with nitric acid. The oxidation on CMCs was found to proceed with the treatment time and almost accomplish after 12 h treatment. Although the amount of –COOH groups produced by the oxidization on CMC is less than that on the multi-walled carbon nanotube, it should be sufficient for further utilizations. It is noticed that the acidification slightly changes the morphology of CMC and diminishes its toughness. However, the morphology can be recovered by the alkalization of CMC, and the latter character may be valuable on the degradation of used CMC. The success of the surface-acidification in the present report leads to the huge possibility of further functionalization via the anchor of the carboxylic acid moiety on the CMC surface.

The immobilization of CMC was examined on various substrates, that is, different types of hydrophilic substrates and a hydrophobic substrate. It was confirmed that the acidified CMC was selectively immobilized only on an amine-terminated silicon substrate by the chemical reaction with –COCl groups which were chemically induced on the CMC surface. Thus the selective anchoring of CMC was achieved on the adequately functionalized substrate.

Then this procedure is beneficial and valuable for extensively developing the applications of CMC in composite devices.

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