Selective immobilization of carbon micro coils on patterned substrates and their electrochemical behavior on ITO substrate

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ABSTRACT

The selective immobilization of carbon micro coils (CMCs) has been investigated on patterned silicon substrates. A patterned silicon substrate was prepared by UV-irradiation under a photo mask onto amine-terminated monolayer on a silicon substrate. It was then dipped into a chloroform dispersion of CMCs which were ahead oxidized by phosphorous pentachloride. The selective, chemical anchoring of CMCs with high surface coverage was achieved on the amine-terminated pattern on the silicon substrate through amide covalent bonding. The uniform immobilization of CMCs on an indium tin oxide (ITO) substrate was accomplished through amide bonding between oxidized CMC and amine-terminated monolayer on the substrate. Such film of CMCs promoted the electric behavior of the ITO substrate.

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1. Introduction

Carbon micro coil (CMC) is one of carbon materials and has characteristic structural, mechanical and electronic properties: CMC is an amorphous material and exhibits properties of super-elasticity [1], electrical conductivity along the helical axis [2] and high hydrogen adsorption [3]. The unique character is also obtained even in embedding in polymer matrix [4]. CMCs pretreated by chemically binding polyvinyl alcohol (PVA) are compatibly dispersed in solvent and these hybridized CMCs promote the further reinforcement of properties of PVA matrix as compared to a simply blended system. These distinctive characteristics of CMCs are thus valid as a highly attractive material and on applications as sensors and devices.

Meanwhile, the immobilization on self-assembled monolayers (SAMs) has been the topic of extensive researches on both their fundamental importance for understanding interfacial properties and even for applications to manufacturing devices and sensors [5–8], and it have reported that the controlled assembly of another unique carbon material, single-walled carbon nanotube (SWCNT),

on a SiO$_2$ substrate is applicable for making networks of field-effect transistors [9]. Moreover, several self-assembling methods, including chemical immobilization [10,11] as well as adsorption [12–16] onto various prepatterned substrates, have been used to fabricate the patterned films of SWCNTs. Especially the method of chemical immobilization of SWCNTs has great potential for the functionalization and the modification of the patterned substrates [10].

On the other hand, there is no report of immobilization of CMCs on a SAM substrate except our previous paper [17], which reports the immobilization of CMCs on an amine-terminated SAM by chemical reaction of acid chloride moieties of CMCs. This procedure is beneficial and valuable for extensively developing the built-in of CMCs to composite devices. However, for the fabrication of devices, especially, of circuit systems, the complicate patterning is also required besides the uniform immobilization of carbon materials on substrates. Therefore, in the present work, the focus point is first the selective chemical attachment of CMCs onto an amine-terminated pattern on silicon substrate and the effective fabrication for patterning of CMCs. Among various patterning methods, photolithography is practical and industrially applicable, since it transfers a pattern of photo mask on the substrate by simple exposure [18].

The fabrication of composites with conductive materials (CMCs) and non-conductive material assures the conductivity depending on the content of CMCs in the composite [4]. The conductivity of the

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composites has been further improved through the pretreatment of CMCs. Then the fabrication of CMCs on conductive substrates should promote further conductivity of the substrates. However, such a report of CMCs on the conductive substrates is not found in our knowledge. The indium tin oxide (ITO) substrate is a suitable candidate of conductive substrates for electric application. In this work, the immobilization of CMCs was also performed on an ITO substrate by chemical binding between functionalized CMCs and SAMs on the ITO surface and the electric behavior of the ITO substrate was investigated.

2. Experimental

2.1. Materials

CMCs were prepared according to previously reported procedure [19]. Silicon substrate, ITO substrate, 3-aminopropyltriethoxysilane (APTES), PCl_5, anhydrous toluene, ethanol, chloroform, HNO_3 (60%), and membrane filter (pore size 0.2 μm) are all commercial products with commercial grade purity and used as purchased. Ultrapure water (>18.2 MΩ) was used throughout whole experiments. Oxidized CMCs (acid-treated CMCs) were prepared according to a previously reported procedure, where acid-treatment was carried out for 12 h, and they were characterized by infrared absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), thermal analysis, and scanning electron microscope (SEM) [17].

2.2. Preparation of APTES SAM on a silicon substrate [17]

A silicon substrate was first immersed in a piranha solution (H_2SO_4:H_2O_2 = 3:1) for 30 min and rinsed with water several times. Then the silicon substrate was again dipped in water for 30 min and dried by blowing N_2 gas. The silicon substrate was placed in a toluene solution of APTES (1%) for 24 h, followed by sonicating, rinsing with toluene and ethanol, and then drying under N_2 gas.

2.3. Patterning on a silicon substrate (patterned Si) [20]

A photo-masked, amine-terminated silicon substrate was exposed for 4 min under vacuum UV light generated from an excimer lamp (Ushio Electric, UER 20-172 V, λ = 172 nm, under the presence of dry N_2 gas). At this condition, two surfaces of amine-terminated and carboxyl/hydroxyl-terminated patterns are created on the silicon substrate.

2.4. Immobilization of CMCs on a patterned silicon substrate (CMC/patterned Si)

Oxidized CMCs, chloroform and stoichiometrically excess amount of PCl_5 were mixed, and the mixture was sonicated for 1 min for preparing acelated CMCs [17]. A patterned Si was then immersed into a 3 mg/cm^3 solution of acelated CMCs for 10 h, rinsed with ethanol and dried by blowing N_2 gas. Following these procedure and condition, immobilization of CMCs as reference experiments was also carried out by treating without PCl_5 on a patterned Si or by treating with and without PCl_5 on bare silicon substrates.

2.5. Preparation of an amine-terminated ITO substrate (APTES ITO)

An ITO substrate was first cleaned by washing with acetone and then immersing in ethanol through sonication for 10 min. Afterwards the substrate was immersed into an aqueous H_2O_2 (35 wt%) solution for 20 min, rinsed with water, and again immersed into

water for 10 min. The substrate dried by blowing dry N_2 gas was immersed in a toluene solution of APTES (1%) for overnight for the preparation of SAM, followed by sonicating, thoroughly rinsing with toluene and ethanol, and then drying under N_2 gas.

2.6. Immobilization of CMCs on an amine-terminated ITO substrate (CMC APTES ITO)

Oxidized CMCs were dispersed in chloroform. An APTES ITO was then immersed into a dispersion of CMCs (at 40 °C) for 10 h. After that, the substrate was rinsed with ethanol and dried by blowing N_2 gas.

2.7. Characterization

A patterned Si was prepared by using an instrument of photolithography at room temperature under N_2 atmosphere. The process from a patterned Si to a CMC/patterned Si was confirmed through a measurement of water contact angle by means of a simple photographic analysis. XPS spectra were obtained on a theta probe ESCA VG scientific (2002) using a monochromatic AlKα source at a pressure of 2×10^{-9} mbar. The surface morphology of samples was analyzed by using a Hitachi SEM at an accelerating voltage of 15 kV. Cyclic voltammetric (CV) measurement was carried out on an automatic polarization 3000 Hz system at scan rates of 25, 50 and 100 mV/s. The CV system consists of a reference electrode (Ag/AgCl (3 M KCl)), a counter electrode (Pt wire), and a working electrode (ITO substrate). Aqueous solutions of KNO_3 (1 M) and $K_3Fe(CN)_6$ (6 mM) in water were used as electrolyte species and redox species, respectively.

3. Results and discussion

3.1. Immobilization of carbon micro coils on patterned silicon substrates

To fabricate the amine-terminated pattern on a silicon substrate, amine-terminated monolayer was prepared on a silicon substrate and the pattern was produced on it by UV-irradiation using a photo mask. The chlorocarboxyl and carboxyl-CMCs are then immobilized on the patterned Si. The process of the reaction is represented in Scheme 1. The silicon substrates with different surface functions were evaluated by water contact angle. The bare silicon substrate (after the treatment with a piranha solution) was fairly hydrophilic with a water contact angle of less than 5°. After self-assembling of the APTES monolayer on a silicon substrate, the value of water contact angle was around 47°. The slightly lower water contact angle (42°) was obtained for the patterned Si (after UV-irradiation), because the patterning of the monolayer using UV-irradiation through the mask creates two surfaces of amine-terminated and carboxyl/hydroxyl-terminated patterns, as shown in Scheme 1, which have nearly similar hydrophilicity. The water contact angle of the patterned Si (CMC(PCl_5)/patterned Si) after immobilization (treated with PCl_5) was further reduced to 35° as compared to that of the patterned Si. The reason is probably due to the immobilization of hydrophilic CMCs on the patterned Si through chemical bonding (by chemical reaction between amine and acid chloride groups that were derived on Si substrate and CMC surface, respectively). These tendencies are similar to previous reports evaluated by a water contact angle goniometry [13].

Differently functionalized substrates were further examined by XPS. In this instance, a bare Si, patterned Si and CMC(PCl_5)/patterned Si were analyzed. As seen in Fig. S1 (a wide scan profile), there was no N 1s peak on a bare Si substrate, but weak C 1s and strong O 1s peaks were observed. The presence of small amount of carbon atoms on a bare Si could imply remanence
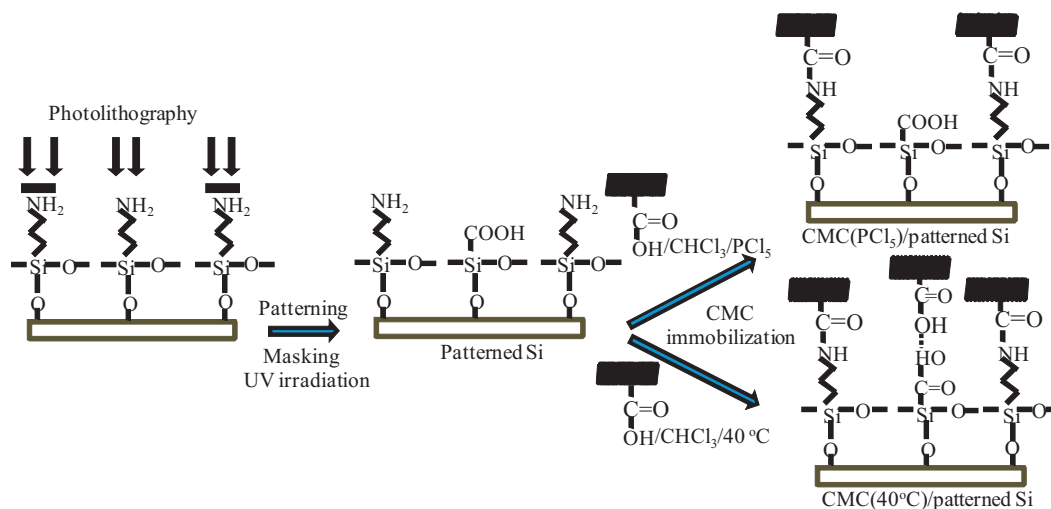
Scheme 1. Procedure of patterning and immobilization of CMCs on silicon substrate.

of some organic contaminants even after cleaning with a piranha solution. In the meantime, the strong oxygen peak indicates the generation of sufficient number of hydroxyl groups on a silicon surface.

However, on a patterned Si, a weak N 1s peak was observed, suggesting the successful attachment of amine-terminated group. A strong C 1s peak observed on a patterned Si can be attributed to carbons of APTES. These results indicate that SAM of APTES was successfully fabricated on a patterned Si. Although an XPS spectrum of a CMC(PCl$_5$)/patterned Si seems like that at a wide scan profile

of a patterned Si, the difference is obvious from the detail analysis of each peak, as shown in Fig. 1.

Apparently, N 1s and C 1s peaks on a CMC(PCl$_5$)/patterned Si could consist of multi components, since they are asymmetric. Then these peaks were divided into two components by the deconvolution procedure. Table 1 lists binding energy and atomic% of each component of Si 2p, C 1s, N 1s, and O 1s (XPS spectra of Si 2p were not shown). Two components (98.2 and 102.1 eV) of Si 2p on a bare Si are assigned to free Si and Si–OH, but a new component at 104 105 eV appears on a patterned Si and a CMC(PCl$_5$)/patterned Si
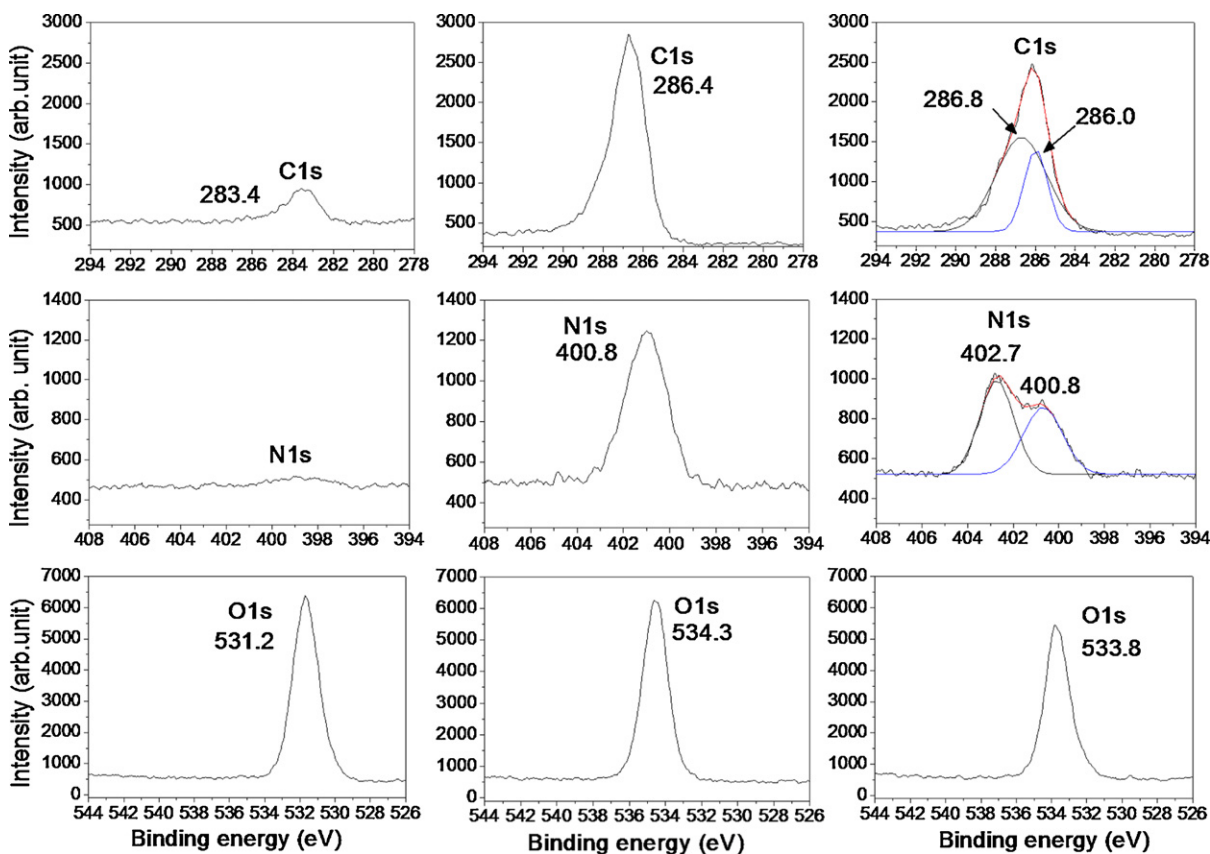

Fig. 1. XPS peaks on differently functionalized substrates. (left) bare Si; (middle) patterned Si; (right) CMC(PCl$_5$)/patterned Si. (top) C 1s; (middle) N 1s; (bottom) O 1s.

Table 1
Binding energies (B.E.) and percentages of atomic components from XPS of different Si substrates.

Element	Bare Si		Patterned Si		CMC(PCl$_5$)/patterned Si		Attribution
	B.E. (eV)	Atomic%	B.E. (eV)	Atomic%	B.E. (eV)	Atomic%	
Si 2p	98.2	32.7					Si (substrate)
	102.1	20.2					SiOH (substrate)
			105.0	27.4	104.1	18.3	Si–O–Si (APTES)
C 1s	283.4	11.5					Contamination (substrate)
			286.4	40.0	286.0	13.6	C (APTES)
					286.8	32.5	C (CMC)
N 1s			400.8	7.4	400.8	3.6	NH$_2$ (APTES)
					402.7	4.5	CONH (CMC)
O 1s	531.2	35.6	534.3	25.2	533.8	27.5	SiOH, Si–O–Si, CONH

instead of original Si 2p peaks on a bare Si, because of the formation of Si–O–Si after the sol–gel reaction with APTES.

Although the presence of a N 1s peak at 400.8 eV attributed to nitrogen atom of amine [21] indicates the formation of SAM of APTES on a patterned Si, a CMC(PCl$_5$)/patterned Si generates a new component at 402.7 eV attributed to nitrogen atom of amide [21], suggesting the immobilization of CMC. However, it should be noted that the CMC(PCl$_5$)/patterned Si remains also an amine N 1s component, due to the coexistence of free amine (ca. 44% = 100 × 3.6/(3.6 + 4.5)) without amidation with CMC. While carbon atom (286.4 eV) from alkyl chain of APTES SAM was found on a patterned Si, an another component (286.8 eV) was also observed in a CMC(PCl$_5$)/patterned Si owing to the attachment (ca. 70%) of new carbon species from the CMCs through covalent (amide) bonding with amine.

Concerning to an O 1s peak, contributions of SiOH from a bare Si, Si–O–Si from a patterned Si, and C=O from a CMC(PCl$_5$)/patterned Si are mainly expected and, in fact, binding energies of the O 1s peak change among substrates. However, since the variation is not so large, it should be difficult to analyze components quantitatively. The results obtained from XPS support the formation of APTES SAM and the immobilization of CMCs with almost half of non-reacted (remaining) amine terminals. Those are consistent with ones from water contact angle which confirms the successful immobilization of CMCs on the patterned Si.

The surface morphologies of the patterned Si and CMC(PCl$_5$)/patterned Si were observed by SEM as shown in Fig. S2 and Fig. 2, respectively. Fig. S2 indicates that the pattern utilized consists of a rectangular closed area with frames of ≈50 μm width (long axis) and ≈100 μm (short axis). The frame is UV-nonirradiated area under the mask, namely, occupied by amine-terminated APTES groups, while a rectangular dark area is the UV-irradiated surface without amine-terminals. SEM images in Fig. 2 show that CMCs were attached only on the amine-terminated pattern in the patterned Si, while there were scarcely CMC fibrils in the irradiated (damaged) area, i.e. CMCs were repelled from this region. This is the further evidence of chemical bonding between amine group on the patterned Si and acid chloride on the oxidized CMCs. Similarly, on the CMC(40 °C)/patterned Si (treated at 40 °C without PCl$_5$) (see SEM images in Fig. 3), CMCs were attached on the amine-terminated area by chemical reaction between amine and carboxyl groups from the patterned Si and oxidized CMCs, respectively. In both cases, it can be clearly found that the selective immobilization of CMCs with high surface occupation successfully proceeds on amine-terminated pattern. However, in the latter case, few CMC fibrils were also observed on the irradiated area, possibly through the hydrogen bonding of oxidized CMCs with carboxyl/hydroxyl groups that were induced on silicon substrate during UV-irradiation [20], as illustrated in Scheme 1.
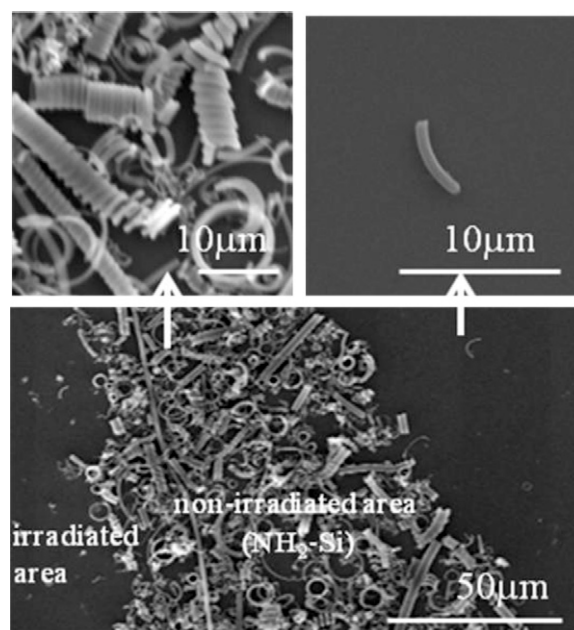

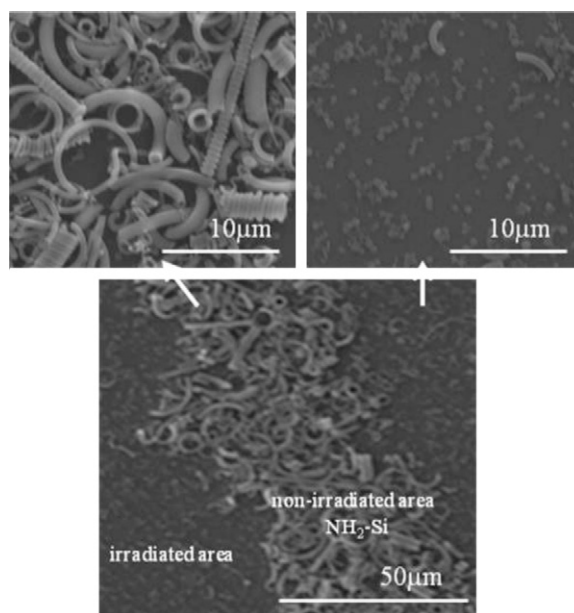**Fig. 2.** SEM images of CMC(PCl$_5$)/patterned Si.

Fig. 3. SEM images of CMC(40 °C)/patterned Si.

Table 2
Binding energies (B.E.) and percentages of atomic components from XPS of bare and CMC APTES ITO substrates (M:Si, Sn, In).

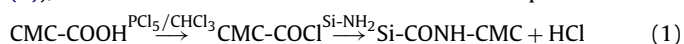| Element	Bare ITO			CMC APTES ITO		
	B.E. (eV)	Atomic%	Attribution	B.E. (eV)	Atomic%	Attribution
Si 2p	102.4	34.3	S̲i̲, S̲i̲OH	99.1	19.9	S̲i̲–O (APTES)
C 1s	283.1	11.8	Contamination	284.3	45.0	C̲ (APTES), C̲ (CMC)
N 1s				395.5	8.4	N̲H₂ (APTES), CON̲H (CMC)
O 1s	531.7	53.9	MO̲H	529.1	26.7	MO̲H, Si–O̲, CO̲NH

Table 3
Potentials and currents on oxidation and reduction processes from CV on bare and CMC APTES ITO substrates at different scan rates.

Sample	$E_{Red.}$ (V)	Current (mA)	$E_{oxd.}$ (V)	Current (mA)
Bare ITO (sc 25 mV/s)	+0.31	0.28	+0.18	−0.32
Bare ITO (sc 50 mV/s)	+0.32	0.39	+0.16	−0.43
Bare ITO (sc 100 mV/s)	+0.43	0.51	+0.03	−0.57
CMC APTES ITO (sc 25 mV/s)	+0.33	0.33	+0.16	−0.36
CMC APTES ITO (sc 50 mV/s)	+0.34	0.47	+0.15	−0.49
CMC APTES ITO (sc 100 mV/s)	+0.35	0.65	+0.12	−0.66

The reaction of immobilization was further tested using bare silicon substrates treated with PCl₅ and at 40 °C without PCl₅ by the same procedure as discussed above. In both cases, there were no CMC fibrils on the silicon substrates, indicating the unable attachment of CMCs due to the lack of amine groups on substrate (see Fig. S3). Proceeding the same way but using pristine CMCs and an amine-terminated silicon substrate, the same result was previously observed [13]. The absence of CMCs on the silicon substrate obtained from the latter two cases suggests that CMCs on the CMC/patterned Si are combined by chemical bonding with functionalized silicon substrate, i.e. this combination provides the strong immobilization between them, agreeing with the results obtained from the water contact angle and XPS.

It can be confirmed that the selective immobilization of CMCs was performed on the patterned Si by the selective chemical reaction but not on bare Si. However, it should be noticed that the selective attachment of CMCs on the patterned Si occurred more on the treatment of CMCs with PCl₅ than on the treatment of CMCs at 40 °C without PCl₅. The reaction in the former case is due to the conversion of –COOH groups on the oxidized CMCs into –COCl groups by PCl₅, i.e. due to the favorable reaction of –COCl groups with amine groups on the non-irradiated area, as described in Eq. (1). On the treatment of CMCs at 40 °C without PCl₅ on the patterned Si, the anhydration reaction occurs at moderate temperature (Eq. (2)), while the reaction does not occur at room temperature.

$$CMC\text{-}COOH \xrightarrow{PCl_5/CHCl_3} CMC\text{-}COCl \xrightarrow{Si\text{-}NH_2} Si\text{-}CONH\text{-}CMC + HCl \quad (1)$$

$$CMC\text{-}COOH \xrightarrow{Si\text{-}NH_2/CHCl_3/40\,°C} Si\text{-}CONH\text{-}CMC + H_2O \quad (2)$$

3.2. Immobilization of carbon micro coils on ITO substrates

The bare and CMC-immobilized APTES ITO substrates (CMC APTES ITO) (the scheme of the preparation was shown in supporting information, Scheme S1) were also evaluated by XPS as shown in Fig. S4 and Table 2. An N 1s peak was observed for a CMC APTES ITO, as expected, while there was no corresponding peak on the bare substrate. Meanwhile, XPS peaks of other elements (Si, C, and O) were varied in binding energy and atomic%, after APTES SAM was fabricated on a bare ITO substrate and CMCs were immobilized on it. Si 2p, C 1s and O 1s peaks on the bare ITO are attributed to Si, SiOH, contaminations and MOH (M:Si, Sn, In), similar to the case on a silicon substrate. However, it must be paid attention that the values of atomic% of elements (Si, C, N, and O) on the CMC APTES ITO are almost similar to those on the CMC(PCl₅)/patterned Si (see Table 1). Thus the XPS analysis indicates successful immobilization of CMCs on SAM substrates, independently on the species of substrate.

CV measurement at different scan rate was carried out using a bare ITO and a CMC APTES ITO as a working electrode and utilizing redox molecules such as K₃Fe(CN)₆, which provide a convenient electron transfer between the solution and the electrode surface [22]. The surface morphology of CMC APTES ITO (shown in supporting information Fig. S5) demonstrates that CMCs were attached uniformly on ITO substrate. As shown in Fig. 4, K₃Fe(CN)₆ displayed almost completely the oxidation–reduction behavior on the bare ITO and CMC APTES ITO electrodes. Observed values of potential and current for oxidation and reduction processes occurred at different scan rates (sc) are listed in Table 3.

In the case of a bare ITO electrode, when sc was increased, the reduction potential increased as well as the current but the oxidation potential and current decreased. The tendency of the potential–current behavior on the CMC APTES ITO electrode was
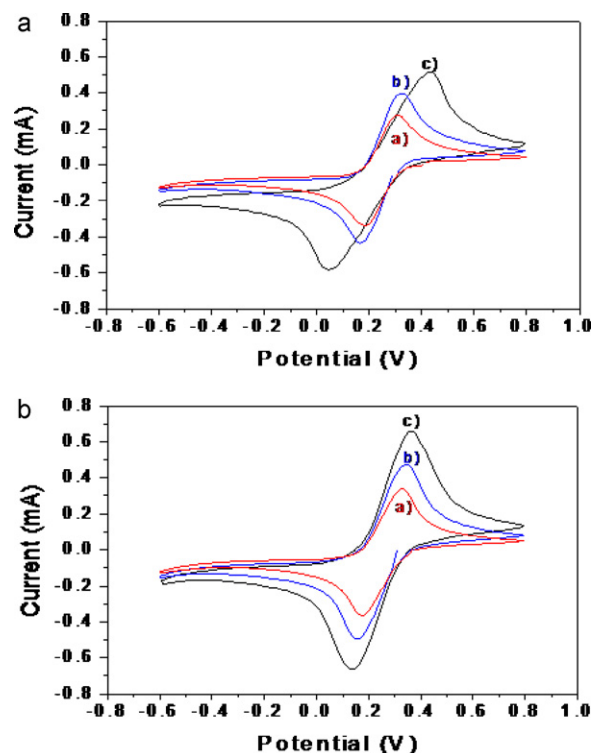

Fig. 4. CV analysis of ITO substrates at different scan rates. (A) Bare ITO, (B) CMC APTES ITO. (a) 25, (b) 50, (c) 100 mV/s.

similar to that on the bare ITO. However, compared to the bare ITO, the value of reduction current generated on the CMC APTES ITO was greatly increased (27% in maximum) and the oxidation current was correspondingly decreased (17% in maximum). The possible reason is that the CMC fibrils promote the electron transfer between CMCs and ITO electrode, i.e. CMC APTES ITO improves electrochemical signal more than bare ITO. Otherwise the value of redox current increases with increase in surface area of electrode, since the immobilization of CMCs increases the surface area of ITO electrode.

4. Conclusions

A highly selective pattern of CMCs has been successfully fabricated on a silicon substrate by using a photolithographic procedure and selective chemical reaction of acylated CMCs with amine-terminated SAM on a silicon substrate. This immobilization method provides strong binding between the CMCs and the substrates, resulting in high surface density on the amine-terminated region of silicon substrates. Namely, this method is highly selective and efficient to control the immobilization of CMCs on the substrates. Moreover, the ITO electrode was reinforced its electrical property by the immobilization of CMCs. Further development of these procedures may lead to a simple and effective method for the selective attachment and alignment of individual CMCs, which is important to their practical applications such as energy, sensing and semiconductive devices.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2011.09.058.

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