Surfactant and polymer-free electrochemical micropatterning of carboxylated multi-walled carbon nanotubes on indium tin oxide electrodes†

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We present a facile micropatterning method that is based on the electrochemically induced deposition of carboxylated multi-walled carbon nanotubes on an indium tin oxide electrode without using surfactants or polymers.

Carbon nanotubes (CNTs) have been widely used in a variety of areas, including molecular electronics,[1,2] sensors,[3] field-emission devices,[4] solar cells,[5] and fuel cells.[6] However, their practical applications are still very limited, which can be partially attributed to the difficulty of obtaining CNT micropatterns. Micropatterning of CNTs has been realized in two ways, namely, after CNT synthesis (*i.e.*, postmicropatterning) and during CNT synthesis.[7,8] The postmicropatterning method is more convenient for fabrication purposes, because lower processing temperatures and purified CNTs can be used. However, the very low solubility of CNTs in most solvents and the complexity of the micropatterning procedures make this method difficult to apply. Accordingly, simpler and more reliable micropatterning procedures are required to increase the applicability of CNTs.

To improve the solubility of CNTs, chemical modification and composite formation (with polymers) of the nanotubes have been employed.[9–11] Although various useful methods have been devised, the complex and non-cost-effective procedures involved limit their practical utility. Another strategy is to use highly carboxylated CNTs,[12–14] which are easily prepared *via* acid treatment and are dispersible even in aqueous solutions. The postmicropatterning method includes electrophoretic deposition,[15–18] electrochemical deposition,[19–24] transfer printing,[25] hydrophilicity-dependent adsorption,[26] and layer-by-layer assembly.[27] Among these procedures, electrophoretic deposition and electrochemical deposition are more suitable for mass fabrication and thickness control. Because electrophoretic deposition uses electrophoretic movement (*i.e.*, migration) of charged species, this deposition process is strongly dependent on the electric field, that is, on the electrode shape and the distance between the two electrodes. On the other hand, in the case of electrochemical deposition, the electrophoretic movement is minimized by using an excess of electrolyte. Uniform deposition is possible, irrespective of the electrode shape. Therefore, electrochemical deposition is more favorable for obtaining thickness-controlled CNT micropatterns.

Many electrochemical deposition methods have been developed, most of which are based on the electrochemically induced codeposition of CNTs with electroactive surfactants,[19] polyelectrolytes,[20] or conducting polymers.[22] However, the formation of these composite films may affect the intrinsic characteristics of the CNTs, and pure CNT films are preferred for a wide range of applications.

Here, we report a facile and versatile CNT-micropatterning method that employs the electrochemically induced deposition of carboxylated multi-walled CNTs (CMWCNTs) without using surfactants or polymers. A schematic diagram of the micropatterning method is shown in Fig. 1. Water electrooxidation at an indium tin oxide (ITO) electrode decreases the pH near the electrode. The carboxylate ions of the CMWCNTs are converted into carboxylic acid species. This conversion induces a change in the solubility of the CMWCNTs, which results in their deposition on a patterned ITO electrode. Prolonged water electrooxidation yields thick CMWCNT films on the ITO electrodes.

Electrochemically induced pH changes have been frequently used in electrochemical deposition, the cathodic method being more commonly applied than the anodic approach.[20,28] We attribute this trend to the fact that, compared to a pH decrease, an increase in pH can be more easily achieved by means of water or H^+ electroreduction and/or O_2 electroreduction at low overpotentials. However, only anodic deposition is possible in the case of CMWCNTs, because the

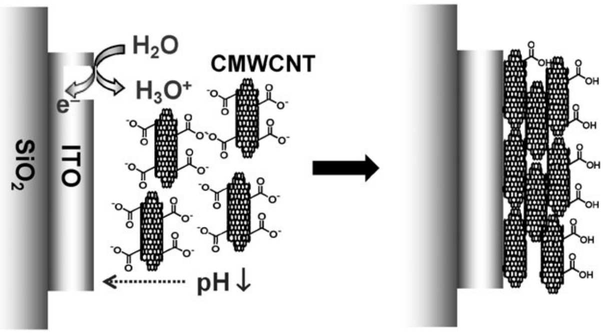

Fig. 1 Schematic representation of the electrochemical deposition of CMWCNTs on a patterned ITO electrode.

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solubility of the carboxylate form of the nanotubes in neutral aqueous solutions is high whereas that of the carboxylic-acid form in acidic solutions is low. To increase the efficiency of water electrooxidation, high anodic overpotentials are required. The application of a potential greater than 2 V (*vs.* Ag/AgCl) at thin gold and platinum electrodes leads to metal dissolution, making it difficult to obtain CMWCNT films on these substrates. On the other hand, ITO electrodes are stable at high anodic potentials. However, they exhibit poor electrocatalytic properties for water electrooxidation. At potentials below 1.5 V, no CMWCNTs are deposited because of the low efficiency of the water electrooxidation reaction and the small pH decrease near the ITO electrodes. Thus, high anodic potentials must be applied to the ITO electrodes to obtain CMWCNT films.

CMWCNTs were prepared by acid treatment of the multi-walled CNTs (as reported previously),[12,14] and the electrochemical deposition was carried out in an aqueous solution containing 1 mg mL^{-1} CMWCNT and 1 mM KNO_3. Because high electrolyte concentrations may cause aggregation of the CMWCNTs, a low electrolyte concentration (namely, 1 mM) was used. Fig. 2 shows side-view SEM images of CMWCNT-modified ITO electrodes formed by applying a constant current of 600 μA cm^{-2}. Although potentiostatic deposition can also be used to obtain thickness-controlled CMWCNT films, the best results are achieved by using the galvanostatic procedure. By comparing TEM images of CMWCNTs and electrochemically deposited CMWCNTs, we observed that there was no significant difference in their shape and structure of CMWCNTs before and after electrochemical deposition (see ESI†). The coverage and thickness of the CMWCNT films increase with the applied current and potential. Higher anodic currents lead to an increase in the efficiency of the water electrooxidation reaction, which results in a lower pH value near the ITO electrode, thus accelerating the deposition process. Examination of the dependence of film thickness on deposition time revealed that the thickness increases with deposition time (Fig. 2d). It is worth noting that films thicker than 1 μm can be obtained after short deposition times. Interestingly, the curve in Fig. 2d shows a sigmoidal behavior. The top-view SEM image obtained after a deposition time of 100 s indicates partial coverage of the ITO electrode with the CMWCNTs (see Fig. 3a), whereas a thick CMWCNT film is obtained after 200 s (Fig. 2a and 3b). The results indicate that the amount of CMWCNT deposited during the first 100 s is very small compared to that deposited afterwards. At the beginning of the water electrooxidation reaction, the deposition of CMWCNTs is slow. After approximately 200 s, the deposition process becomes faster, before subsequently slowing again. Finally, the thickness levels off (see Fig. 2d).

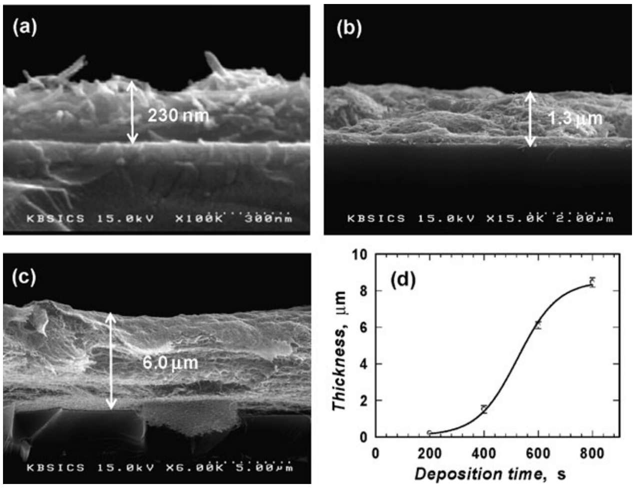

Fig. 2 Side-view SEM images of CMWCNT-modified ITO electrodes formed by applying a constant current of 600 μA cm^{-2} for (a) 200 s, (b) 400 s, and (c) 600 s in an aqueous solution containing 1 mg mL^{-1} CMWCNT and 1 mM KNO_3. (d) Dependence of the thickness of the CMWCNT films on the deposition time.

There is a possibility that the deposited CMWCNT films redissolve in a neutral aqueous solution. To check this possibility, the deposited films were dipped in water for 1 week, after which their thickness was measured. There were no significant changes in the film thickness. However, an ultrasonic treatment causes a rapid detachment of the CMWCNT films from the ITO surface.

Selective deposition of the CNTs is necessary to obtain appropriate micropatterns. To test the feasibility of selective deposition, two interdigitated ITO electrodes, patterned on a glass substrate, were used. A potential of 2.5 V was applied at one electrode. A uniform CMWCNT film was formed on the potentiostatically treated ITO substrate (see Fig. 4a and 4b), whereas no nanotubes were found on the glass surface (Fig. 4d). The electrochemically induced deposition method thus enabled us to selectively obtain uniform CMWCNT films on ITO electrodes. Recently, we reported that when an ITO electrode is simply dipped in a CMWCNT-containing aqueous solution, a very low surface coverage of CMWCNTs is formed on the ITO surface.[12] By the same mechanism, in the present experiments we observed a small degree of CMWCNT adsorption on the untreated ITO surface (Fig. 4c).

For comparison, we also attempted to obtain CMWCNT films *via* electrophoretic deposition. However, we failed to attain uniform and reproducible layers by using the same solution as that employed in the electrochemical deposition. Moreover, it was difficult to apply electrophoretic deposition to micropatterned ITO electrodes.

To evaluate the electrocatalytic properties of CMWCNT-modified ITO electrodes, we obtained cyclic voltammograms in an acetate buffer containing catechol or hydroquinone (Fig. 5). At bare ITO electrodes, high overpotentials are required to trigger catechol and hydroquinone electrooxidation, whereas typical quasireversible cyclic voltammograms

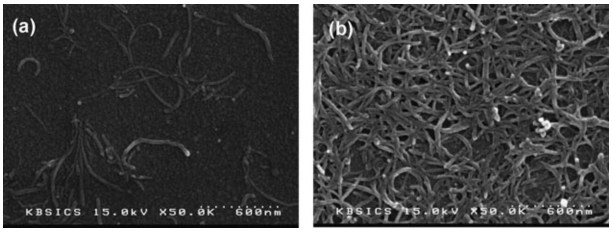

Fig. 3 Top-view SEM images of CMWCNT-modified ITO electrodes formed by applying a constant current of 600 μA cm^{-2} for (a) 100 s and (b) 200 s.

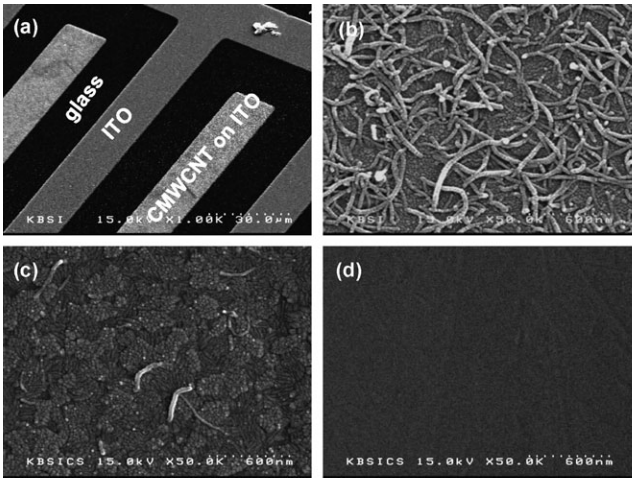

Fig. 4 (a) SEM image of selectively deposited CMWCNT films on ITO (the films were formed on one of two interdigitated ITO electrodes, *via* electrochemical deposition, by applying a potential of 2.5 V for 1500 s). (b–d) Magnified SEM images of (b) an ITO electrode to which a potential was applied, (c) an ITO electrode to which no potential was applied, and (d) a glass surface.

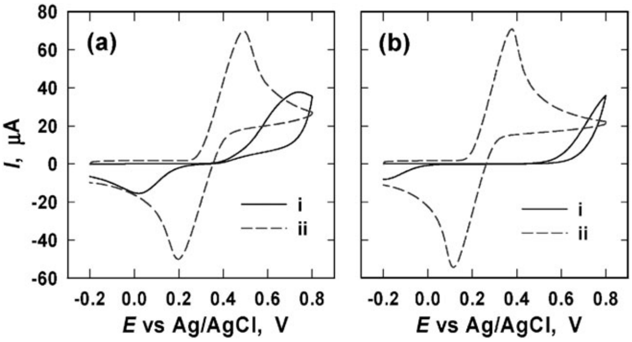

Fig. 5 Cyclic voltammograms of (i) bare ITO and (ii) CMWCNT-modified ITO electrodes at a scan rate of 20 mV s^{-1} in 0.10 M acetate buffer (pH 4.5) containing (a) 1 mM catechol and (b) 1 mM hydroquinone. The electrodeposition was performed potentiostatically at 2.5 V for 1000 s.

are obtained at CMWCNT-modified electrodes. This result demonstrates the good electrocatalytic behavior of the modified electrodes.

In summary, we have developed a new and facile CNT micropatterning method that affords uniform and thickness-controlled CNT films without using additives, such as surfactants or polymers. In the proposed method, water-dispersible CMWCNTs are deposited on an ITO electrode *via* an electrochemically induced pH change that occurs near the electrode as a result of water electrooxidation. Galvanostatic control offers reproducible film formation and, importantly, thick CNT films can be formed with a short time. This simple micropatterning method could play a crucial role in improving the practical applications of CNTs.

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