Fast and reversible surface redox reduction in V_2O_5 dispersed on CN_x nanotubes†

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V_2O_5 nanofilms (NFs) uniformly distributed on N-doped carbon nanotubes (CNTs) exhibit significantly stable capacitive performance; the synthesized composites are promising as an instantaneous power supply in consumer electronics or electrical vehicles.

Electrochemical supercapacitors are currently widely investigated due to their interesting characteristics in terms of power and energy densities. Electrochemical supercapacitors make use of three main classes of materials: (i) carbon,[1–4] (ii) electronically conducting polymers[5–7] and (iii) metal oxides.[8–11] The last two kinds of system involve pseudo-Faradaic reactions, unlike carbon systems which use the double layer capacitance arising from the separation of charge at the interface between the solid electrode and the electrolyte. To realize the aim of renewable energy fulfilled by green technology, some efforts have been aimed at using a more environmentally friendly electrolyte than concentrated sulfuric acid. To this end, materials such as vanadium oxide are synthesized and tested in the presence of a neutral electrolytic solution. As a result of the multiple valence state of vanadium, vanadium pentoxide has versatile redox-dependent properties and finds wide applications in catalysis and electrochemistry.

Recently, hybrid nanocomposites containing carbon nanotubes (CNTs) have attracted much attention when each constituent component provides different functions for specific applications.[12] In our earlier publication,[13–15] we provided a simple and efficient route to prepare functional nanocomposites with well-dispersed RuO_2 nanoparticles (NPs) on vertically aligned N-doped CNT arrays directly grown on Si substrates. It was shown that uniform RuO_2 NPs can be formed around the sidewalls of N-doped CNTs over a large area using a simple sputtering method without any chemical pretreatment. It should be noted that chemical doping of CNTs is to activate regions along the tube walls and this will increase the surface reactivity.

To get fast and reversible supercapacitor performance for practical applications, V_2O_5 nanofilms (NFs) on N-doped CNTs and undoped CNTs are prepared in this work. From the resultant data, EC performances of V_2O_5 NFs on N-doped CNTs are significantly improved as compared with those on undoped CNTs. Effects of N-doping on structural properties and EC behavior are discussed.

The CNT growth was carried out in an inductively coupled plasma chemical vapor deposition (ICPCVD) system.[16] For V_2O_5 NFs deposition, arc-ion plating under Ar gas flow was performed for a deposition time of 30 min while the arc current was kept at 40 A.[17]

For structural analysis, a JEOL 6700 field-emission scanning electron microscope (FESEM) and a JEOL JEM-2100F field-emission transmission electron microscope (FETEM) were utilized. EC measurements were carried out using an Autolab potentiostat system in a three-electrode set up using Pt wire and Ag/AgCl/3 M KCl (207 mV *vs.* SHE at 25 °C) as the counter and reference electrodes, respectively. The electrolyte used was 2 M KCl at room temperature. Adjustment of the pH of the KCl electrolyte was carried out by adding 1 M $KHSO_4$ solution.

In Fig. 1(a), the cross-sectional SEM image of V_2O_5 NFs on undoped CNTs reveals the formation of continuous films. However, V_2O_5 NFs on N-doped CNTs are present as discrete particles as evident in Fig. 1(b). This infers the importance of

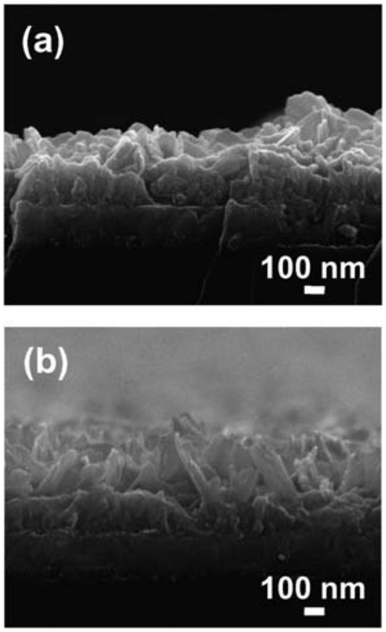

Fig. 1 Cross-sectional scanning electron microscope images of V_2O_5 on (a) undoped and (b) N-doped CNTs.

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N incorporation on CNTs for spreading uniform extrinsic oxides such as V_2O_5 NFs.

In order to observe the different structural properties of N-doped and undoped CNTs, TEM analysis was performed as shown in Fig. 2. In Fig. 2(a), the N-doped CNTs exhibit a typical multi-walled CNT structure, whereas the majority of the CNTs found in the sample prepared with N addition showed bamboo-like structure. This can be intuitively understood, since the bonding of the nitrogen atom in a solid-state network is inherently non-planar with the presence of a lone pair of electrons, whereas the sp^2 bonding of the carbon atom is usually planar. As shown in Fig. 2(b), the average diameter of undoped CNTs is smaller than that of N-doped ones and the undoped samples only contain a couple of walls in the tube. Therefore, the addition of N_2 in the process gas not only enhances the nucleation of the CNTs, but also promotes the formation of bamboo-like structure.

After the composites of NTs and oxides were prepared, the uniform distribution of V_2O_5 NFs on N-doped CNTs was preliminarily examined by SEM images. To study the detailed structure evolution, the composites were further examined by TEM analysis, as shown in Fig. 3. In Fig. 3(a), the TEM image shows that V_2O_5 NFs are homogeneously covered with N-doped CNTs. By contrast, those NFs on undoped CNTs are present in the form of aggregates in Fig. 3(b). Also, the elemental mapping of vanadium was performed to clarify the morphological difference of V_2O_5 NFs on N-doped and undoped CNTs as shown in Fig. 3(c) and (d).

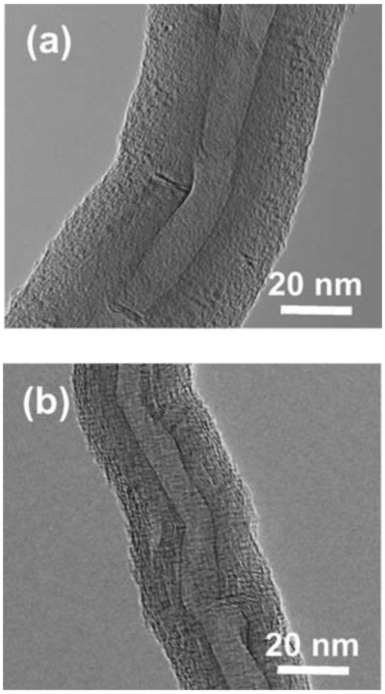

Fig. 2 Transmission electron microscope (TEM) images of V_2O_5 on (a) N-doped and (b) undoped CNTs.

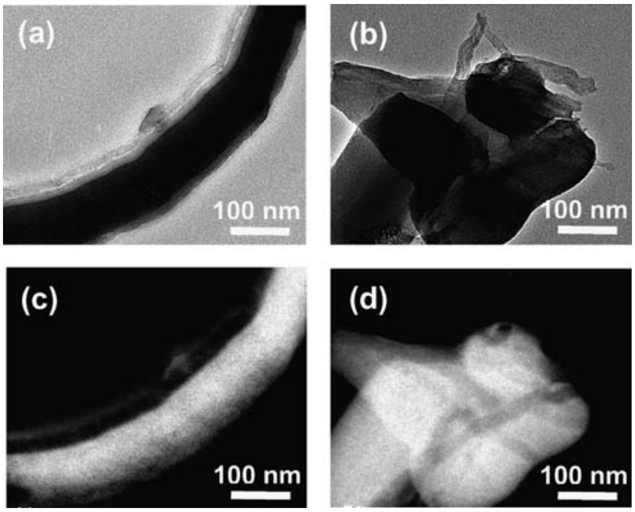

Fig. 3 TEM images of V_2O_5 on (a) N-doped and (b) undoped CNTs. Vanadium mapping of V_2O_5 on (c) N-doped and (d) undoped CNTs.

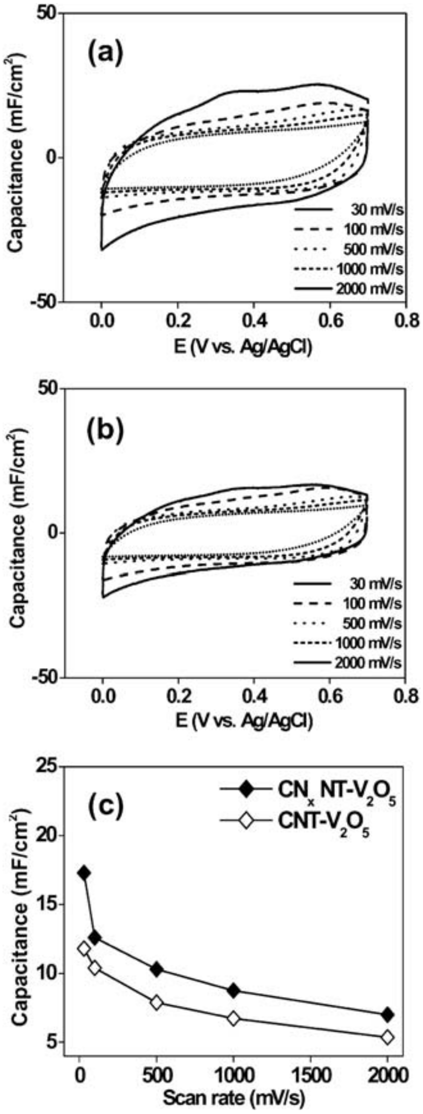

Fig. 4 Capacitance–voltage (*C*–*V*) diagrams of V_2O_5 on (a) N-doped and (b) undoped CNTs at various sweep rates. (c) The specific capacitance as a function of scan rate for comparison of nanocomposites of V_2O_5 deposited on N-doped and undoped CNTs (electrolyte: 1 M KCl and 1 M $KHSO_4$).

Fig. 4 exhibits the effect of N incorporation on the capacitance–voltage (*C–V*) curves of CNTs with different loadings of V_2O_5 NFs at scan rates of 30 to 2000 mV s^{-1} in 1 M KCl and 1 M $KHSO_4$. As displayed in Fig. 4(a) and (b), the capacitance of V_2O_5 NFs on N-doped CNTs is higher than that on undoped CNTs. For comparison, the specific capacitance of V_2O_5 NFs deposited on N-doped and undoped CNTs as a function of scan rate has been clearly elucidated as shown in Fig. 4(c). The cycle lifetime test was also measured. The *C–V* curve in ESI† Fig. S1(a) shows the capacitive behavior of V_2O_5 NFs on N-doped and undoped CNTs at a scan rate of 500 mV s^{-1} for one cycle. There is little apparent difference of capacitive performance of V_2O_5 NFs on N-doped and undoped CNTs; however, the difference becomes more marked after 1000 cycles tested (ESI† Fig. S1(b)). Therefore, N incorporation activates the capacitive properties of CNTs and the capacitance enhancement becomes significant as more V_2O_5 NFs are adhered to CNTs.

From these investigations, the effect of N incorporation is very important for enhancing the capacitive properties of V_2O_5 NFs. V_2O_5 NFs are trapped and arranged in an orderly fashion on the sidewalls of CNTs as verified from EM images. Based on the statements of Ewels and Glerup, graphene and pyridine-like defects are generated after N doping CNTs.[18] Those two defects are significantly associated with the structural properties and EC performances of CNTs. Without N-doping, the surface of CNTs is apt to be electrochemically inactive; namely, V_2O_5 NFs gathering on CNTs lead to poor capacitance. But capacitive performance will be effectively improved after N doping into CNTs due to the hydrophilic interface generated by preferential defect sites. Moreover, N-doped CNTs exhibit only metallic behavior[19] and this is also advantageous for promoting the improvement of energy-storage efficiency. Therefore N-doping is a simple manipulation which can provide a prompt response ability in supercapacitor applications.

Rapid capacitive performances of V_2O_5 NFs on N-doped CNTs have been evidenced. In structural properties, cross-sectional SEM and TEM images show that N-doped CNTs are good supports for the uniform distribution of V_2O_5 NFs. In capacitive behavior, N-doped CNTs covered with uniformly dispersed V_2O_5 NFs give rise to a significantly stable capacitive performance after long-term testing for 1000 cycles. Such synthesized composites of N-doped CNTs covered with V_2O_5 NFs could act as efficient instantaneous power supplies in consumer electronics or electrical vehicles.

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