

EFFECTS OF DIFFERENT ACID-TREATMENT ON THE NANOSTRUCTURE AND PERFORMANCE OF CARBON NANOTUBES IN ELECTROCHEMICAL HYDROGEN STORAGE

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The effects of various acids on the nanostructure and hydrogen storage performance of multi-walled carbon nanotubes (MWCNTs) were investigated. MWCNTs were sonicated in nitric acid (HNO_3), hydrogen peroxide (H_2O_2), sulphuric acid (H_2SO_4) and their mixtures. FTIR revealed that the ratio of oxygen-containing groups on the surface of CNTs depends on the type of oxidiser. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Thermal gravimetric analysis (TGA) showed an intact and stable nanostructure of MWCNTs treated by $\text{H}_2\text{O}_2+\text{HNO}_3$, with an improve functionality due to different kinds of pores. The Brunauer-Emmett-Teller (BET) surface area of MWCNTs treated by $\text{H}_2\text{O}_2+\text{HNO}_3$ increased to $343.1 \text{ m}^2/\text{g}$, as compared to 251.5 and $223.7 \text{ m}^2/\text{g}$ of the raw and $\text{HNO}_3+\text{H}_2\text{SO}_4$ treated MWCNTs, respectively. The MWCNTs treated by a mixture of $\text{H}_2\text{O}_2+\text{HNO}_3$ gave the highest discharge capacity of 72.6 mAh/g (electrochemical hydrogen storage of $0.27 \text{ wt.}\%$), as compared to a preferred mixture of $\text{HNO}_3+\text{H}_2\text{SO}_4$, which gave a discharge capacity of 3.0 mAh/g ; due to a structural damage of MWCNTs walls and low BET surface area. A $\text{H}_2\text{O}_2+\text{HNO}_3$ mixture promotes larger BET surface area and low reductive overpotential of hydrogen at the electrode.

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1. Introduction

Since a report on carbon nanotubes (CNTs) by Iijima [1] in 1991 an interest from scientific community has grown tremendously, on this carbon material. This nanomaterial has shown good potential as hydrogen storage media due to their extraordinary properties such as high active surface area and high electrical conductivity [2]. The hydrogen technology has high energy efficiency and reduces air pollution [3]. However, due to lack of a safe, effective and affordable hydrogen storage medium, its usage is limited [4]. Although CNTs have attracted attention as possible energy storage medium, their application has largely hampered by their poor dispersibility and bundling that exists among the nanotubes, due to strong intermolecular van der Waals interactions, which lead to the formation of aggregates [5]. In order to improve the chemical reactivity and interaction of CNTs with foreign molecules it is necessary to modify the surface of CNTs [6].

The introduction of surface oxides, carboxylic ($-\text{COOH}$), alcohol ($-\text{C-OH}$) and ketone ($-\text{C=O}$) [7], is a widely used approach to overcome the above mentioned problem. By tailoring the structural and electronic properties, the surface oxides can act as anchoring sites for the active surface species (metal ions, metal oxides, organic molecules, etc.) for specific catalytic reactions [8]. Oxidation of CNTs is more widely carried out by treatment with aqueous solutions of acids or oxidising agents, such as H_2SO_4 , HNO_3 , $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$, $\text{H}_2\text{SO}_4+\text{HNO}_3$, HCl , HF , KMnO_4 , $\text{KMnO}_4+\text{H}_2\text{SO}_4$, etc [7-11]. Chiang *et al.* [8] noted that the graphitic structure of CNTs is preserved if oxidised with a mild mixture of $\text{H}_2\text{SO}_4+\text{HNO}_3$. However, this was accompanied by

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thinning and shortening of tubes. In a recent oxidation study of CNTs by Mazov *et al.* [9], they have noted that the ratio of oxygen-containing groups on the surface of CNTs is less dependent on the type of oxidizer. They further noted less destruction of CNTs while using HNO_3 , as compared to mixture of $\text{HNO}_3+\text{H}_2\text{SO}_4$.

Although wide evaluations of the effects of acids oxidation on CNTs are known, an investigation of changes in physical and chemical properties [12] still remains unclear. Hence, the study has focus on investigating the effects of different acids treatments on the structure and performance of MWCNTs in electrochemical hydrogen storage.

2. Experimental

2.1 Preparation of Acid-treated MWCNTs

Acid treatments of the MWCNTs (Sigma Aldrich) were employed to generate a library of samples with different physical and chemical properties. Approximately 0.3 g of MWCNTs were sonicated at 25 °C in 200 ml of each of the following acids: H_2SO_4 (95 %), HNO_3 (55 %), H_2O_2 (30 %) and a mixture of the acids, $\text{H}_2\text{O}_2+\text{H}_2\text{SO}_4$, $\text{H}_2\text{O}_2+\text{HNO}_3$ and $\text{HNO}_3+\text{H}_2\text{SO}_4$ in a ratio of 1:3 (v/v). After 3 h of sonication, the acid-treated MWCNTs was diluted with 200 ml of distilled water and filtered through a 0.45 μm pore sized Nylon Membrane (Sigma Aldrich). The acid treated MWCNTs were then washed thoroughly with distilled water until a neutral pH is reached and dried at room temperature overnight. Finally, the detailed structures and the chemical compositions of raw MWCNTs and acid-treated MWCNTs were characterised by using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetry Analysis (TGA), X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis and Transmission Electron Microscopy (TEM).

2.2 Preparation of electrodes and their electrochemical measurements

The raw- and acid treated MWCNTs were used to fabricate the electrodes as follows: Approximately, 4 mg of raw- or acid treated MWCNTs was added into a solution of nafion (0.1 ml) and distilled water (3 ml). The mixture was sonicated for 15 min and then drop-dried on the surface of the GCE. Finally the electrode was dried in an oven at 80 °C for 2 h. The mass of the electrode was recorded before and after the fabrication, to determine the amount of the material on the electrode.

Electrochemical hydrogen storage capacities of fabricated electrode were studied using Bioanalytical Systems inc. (BAS) potentiostat driven by the epsilon EC (version 1.60.70), using a three-electrode system consisting of a glassy carbon electrode (GCE, 3.0 mm diameter) as working electrode, Ag/AgCl (saturated NaCl solution) as reference electrode and platinum wire as auxiliary electrode. Cyclic voltammetric (CV) measurements were carried out at 25 ± 1 °C, in a 6 M solution of KOH as the electrolyte (potential window of -1.4 to 0.2 V at a scan rate of 50 mV/s). The experiments of charging and discharging were carried out under the following conditions: The electrodes were charged for 120 s in a constant current of 3 mA and discharged under the same constant current.

3. Results and discussion

3.1 Characterisation

Fig. 1(A) shows the FTIR spectra of raw and acid treated MWCNTs. The spectra of raw MWCNTs show the absence of C-O, -CH and -OH functional groups [13]. However on acidification, the peak at 2984 cm^{-1} (-CH stretch, due to wet treatments [14]) and 1064 cm^{-1} due to C-O stretching becomes clearer [Fig. 1(A)]. Interesting to note is an increase in peak intensity of the C-O [Fig. 1(B)] and -CH stretch, when acids were changed, with an emergence extra peak at 3743 cm^{-1} , due to an -OH stretch. Two weak peaks also emerged at 1401 and 1241 cm^{-1} , which are due to the O-H bending deformation of carboxylic acid group and acidic C-O stretching, respectively [7, 15, 16]. A mixture of $\text{H}_2\text{O}_2+\text{HNO}_3$, was not used all previous acids treatments of MWCNTs [8, 9, 13, 17-19], yet it yields equally and even better results compared to the mixture

of $\text{HNO}_3+\text{H}_2\text{SO}_4$. Contrary to the report by Mazov *et al.* [9], the data shows that the ratio of oxygen-containing groups on the surface of CNTs depends on the type of acid/oxidiser.

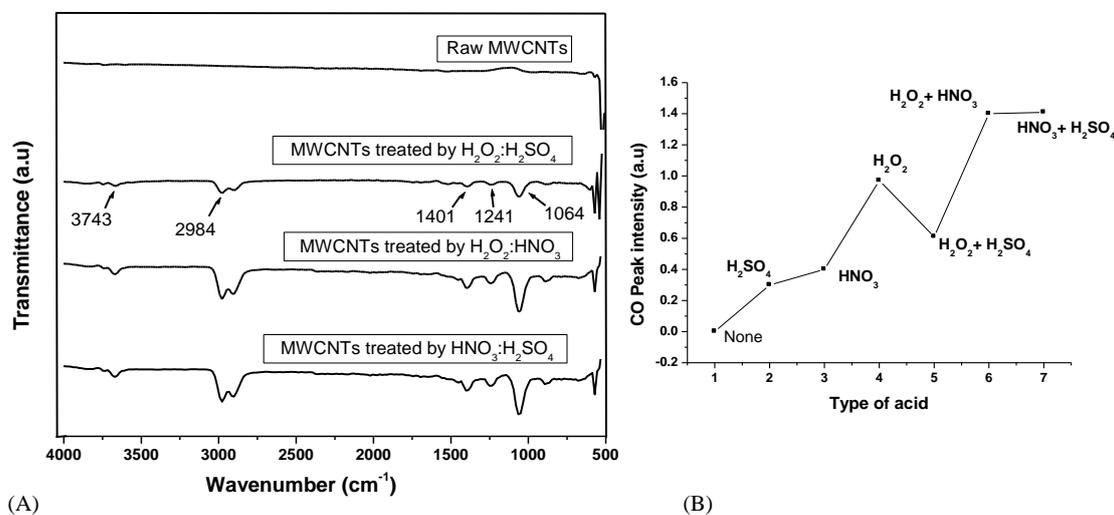


Fig. 1. (A) FTIR spectra of the acid-treated MWCNTs and (B) Effects of acid type on CO stretching (1064 cm^{-1}) peak intensity

Fig. 2 shows the XRD profiles of raw MWCNTs and acid treated MWCNTs. The intense diffraction peak at 26° two theta, in all samples is indexed to the C (002) plane reflection of the graphite [8, 13]. The sharpness of the peak on the MWCNTs treated by mixture of $\text{HNO}_3+\text{H}_2\text{SO}_4$ (Fig. 2) decreased as compared to the raw MWCNTs. This is attributed to the damaged structural walls of MWCNTs [15]. However, a mixture of H_2O_2 and HNO_3 or H_2SO_4 gave sharp and more intense peak (Fig. 2), which shows the formation of more ordered MWCNTs [19] with the graphitic structure remaining intact without significant damage [8].

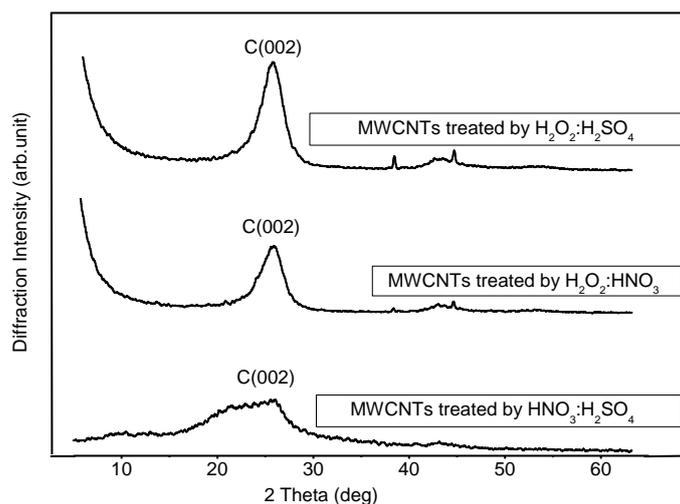


Fig. 2. XRD profiles of mixture of acids-treated MWCNTs

The TEM images are shown in figure 3. The raw MWCNTs (Fig. 3a) show the presence of amorphous particles inside the inner tube of the MWCNTs (shown by black circles). The TEM data shows that strong acid mixture ($\text{HNO}_3+\text{H}_2\text{SO}_4$) (Fig. 3c) damages the tubular structure of MWCNTs, with formation of amorphous carbon particles inside the tube. Similar results have

been reported by Mazov *et al.*, [9] and Shirazi *et al.*, [15]. This treatment method further result in shorter nanotubes [12], resulting in low storage surface area. Treatment of MWCNTs with $\text{H}_2\text{O}_2+\text{H}_2\text{SO}_4$ (Fig. 3b) results in the formation of MWCNTs with smaller pore diameter. The surface of $\text{H}_2\text{O}_2+\text{HNO}_3$ treated nanotubes remains relatively smooth with less significant topological damage to the walls (Fig. 3a). This treatment has removed amorphous particles in the inner tube walls of MWCNTs, with formation of thinner walls. Related results were reported elsewhere, using nitric acid [9].

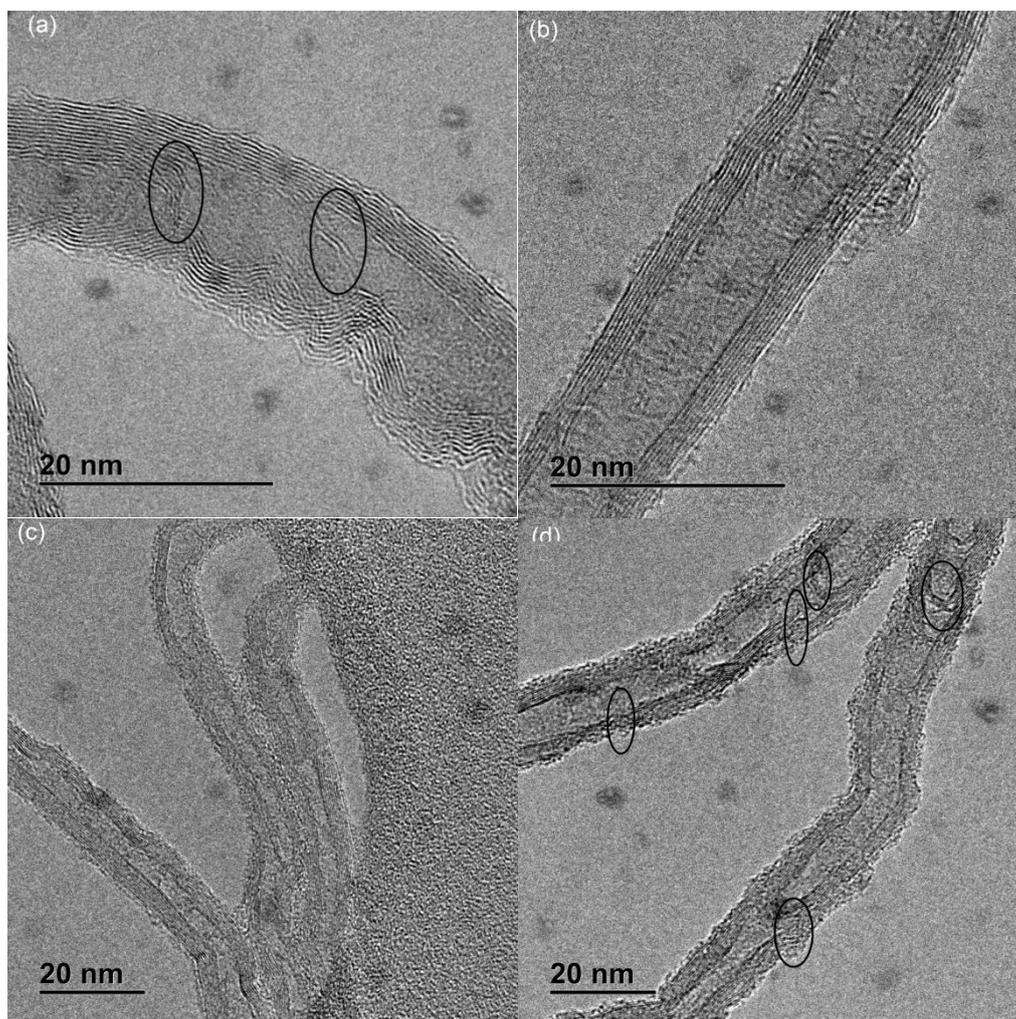


Fig. 3. TEM images of the (a) raw MWCNTs, MWCNTs treated by mixture of (b) $\text{H}_2\text{O}_2+\text{HNO}_3$ (c) $\text{H}_2\text{O}_2+\text{H}_2\text{SO}_4$ and (d) $\text{HNO}_3+\text{H}_2\text{SO}_4$.

The nitrogen adsorption-desorption isotherms of the acid treated MWCNTs is shown in figure 4. The hysteresis loop are close to type-IV isotherm and show a sharp capillary condensation step at a relative pressure ranging between 0.8 and 0.99, indicative of a typical mesoporous structure. The BET surface area of the MWCNTs treated by H_2SO_4 and $\text{HNO}_3+\text{H}_2\text{SO}_4$ decreased to 250.59 and 223.72 m^2/g respectively, compared to the raw MWCNTs (251.48 m^2/g). The decrease in the surface area is due to structural damage as depicted by XRD and TEM images. Interestingly, the BET surface area of MWCNTs treated by $\text{H}_2\text{O}_2+\text{HNO}_3$ increased to 343.09 m^2/g . The sample showed higher pore volume and wider pore size distribution (Fig. 4, insert and Table 1). Based on this and TEM results, it is justified that the mesoporous $\text{H}_2\text{O}_2+\text{HNO}_3$ treated MWCNTs may endow the possibility of combining different functionality provided by different kinds of pores. Mesoporous can afford higher specific surface area and active sites for electrochemical energy storage leading to high performance.

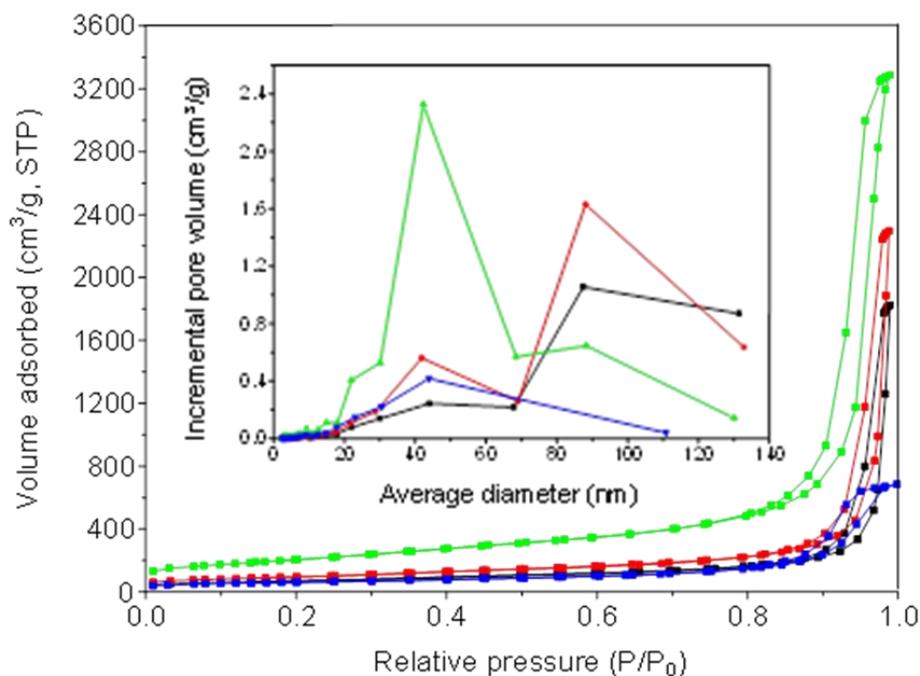


Figure 4. N_2 adsorption and desorption isotherms and BJH pore size distribution of (a) raw MWCNTs (black line), MWCNTs treated by mixture of (b) $H_2O_2+HNO_3$ (red line) (c) $H_2O_2+H_2SO_4$ (green line) and (d) $HNO_3+H_2SO_4$ (blue line)

Table 1: Surface characteristics of the raw- and acid-treated MWCNTs

Sample: MWCNTs treated by	BET surface area (m^2g^{-1})	Peak pore volume (cm^3g^{-1})	Peak pore sizes (nm)
None	251.48	1.95	30.98
H_2SO_4	250.59	2.09	33.30
HNO_3	328.25	2.03	24.74
H_2O_2	313.61	1.99	25.46
$H_2O_2+HNO_3$	343.09	2.91	33.96
$H_2O_2+H_2SO_4$	736.58	4.94	26.83
$HNO_3+H_2SO_4$	223.72	1.06	18.97

The TGA profiles of raw- and acid-treated MWCNTs are shown in figure 5. A clear weight loss of MWCNTs treated by $HNO_3+H_2SO_4$ was observed after 200 °C, relative to all other samples. This decrease is attributed to the damaged walls of MWCNTs as demonstrated by XRD and TEM results. However, the $H_2O_2+HNO_3$ treated MWCNT gave a better and improve stability relative to raw-MWCNTs and $HNO_3+H_2SO_4$ treated MWCNTs. This clearly shows that no defects occurred during functionalisation, hence the materials achieve high thermal stability.

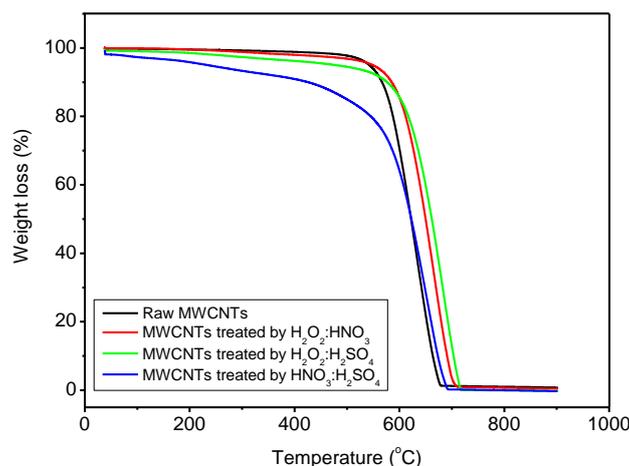


Fig. 5. TGA profiles for the raw- and acid-treated MWCNTs

3.2. Electrochemical hydrogen storage of raw and acid treated MWCNTs electrodes

Fig. 6 shows CV of (a) raw MWCNTs, mixture of (b) $\text{H}_2\text{O}_2+\text{H}_2\text{SO}_4$, (c) $\text{H}_2\text{O}_2+\text{HNO}_3$ and (d) $\text{HNO}_3+\text{H}_2\text{SO}_4$ treated MWCNTs electrodes. The results show the current respond peak at -450 mV, due to the hydrogen uptake by raw MWCNTs during the electrode charging process. Its discharge process occurred at -350 mV. The current responds of single acids treated MWCNTs showed lower current response, however, MWCNTs treated by mixture of $\text{H}_2\text{O}_2+\text{HNO}_3$ (Fig.6c), showed higher current response, accompanied by a peak shift to a less negative overpotential. It shows that the reductive overpotential of hydrogen at this electrode is lower and the reduction process is accomplished more easily [20]. The electrode further shows a prominent rectangular shape compared to all others (Fig.6c). This findings correlate with structural properties as confirmed by FTIR, XRD, TEM and BET data. The results of $\text{H}_2\text{O}_2+\text{HNO}_3$ treated MWCNTs demonstrate that their adsorptive capacity for hydrogen species in water depends on the type of functional group present on the surface and available active sites [21, 22]. Thus functionalisation procedure promotes larger rate constants as reported elsewhere [16]. In this study FTIR data revealed that more oxygenated species dominates the surface.

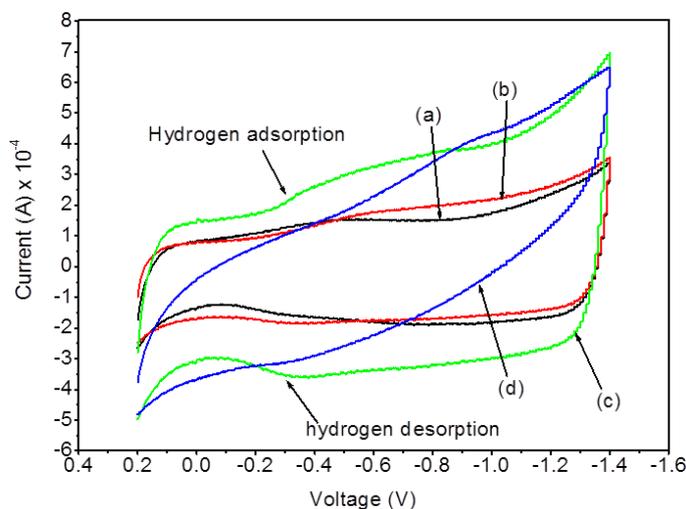


Fig. 6. CV curves of (a) raw MWCNTs, mixture of (b) $\text{H}_2\text{O}_2+\text{H}_2\text{SO}_4$, (c) $\text{H}_2\text{O}_2+\text{HNO}_3$ and (d) $\text{HNO}_3+\text{H}_2\text{SO}_4$ treated MWCNTs.

The charge-discharge capacity studies revealed that H₂O₂+HNO₃ treated MWCNTs electrode gave the discharge capacity of 72.6 mAh/g, relative to that of H₂O₂+H₂SO₄ and HNO₃+H₂SO₄, which gave 52 mAh/g and 3.0 mAh/g, respectively (Table 2). Although, H₂O₂+H₂SO₄ showed high BET surface area (736.58 m²g⁻¹) compared to H₂O₂+HNO₃ treated MWCNTs (343.09 m²g⁻¹); other factors contributed to better discharge capacity such as better structural stability, a combination of both small and large pore channels and thin MWCNTs walls (the electrolyte can easily penetrate inside the tubes, which is crucial for electrochemically gathering of hydrogen [23]). The H₂O₂+H₂SO₄ treated MWCNTs consist mainly of small pore channels, hence lower discharge capacity. Since large pore channels permit rapid electrolyte transport, while the small pores provide more active sites for chemical reactions [24], a combination of both small and large channels results in a good material for energy applications. In the case of HNO₃+H₂SO₄, since hydrogen could be stored between the graphene layers, damage to the graphite structure of the MWCNTs would reduce the amount of stored hydrogen.

Table 2: Electrochemical data for the MWCNTs samples^a

Sample no.	Sample: MWCNTs treated by	Discharge capacity (mAh/g)	Hydrogen storage (wt.%) ^b
1	None	8.23	0.03
2	H ₂ O ₂	15.15	0.06
3	H ₂ SO ₄	41.97	0.17
4	HNO ₃	50.51	0.19
5	H ₂ O ₂ +H ₂ SO ₄	52.36	0.20
6	H ₂ O ₂ +HNO ₃	72.63	0.27
7	HNO ₃ +H ₂ SO ₄	2.98	0.01

^aAll data were repeated three times. ^bThe amount of hydrogen stored was calculated as follows: ((discharge capacity x 2.02 wt.%) / 540 mAh/g) [25].

4. Conclusion

In summary the type of surface functional groups depends on the type of acid/oxidiser used, with the amount of surface functional groups increasing with the choice of acid mixture. Treatment of MWCNTs with H₂O₂+HNO₃ mixture improve and maintain good and stable structural walls, with formation of thinner tubes as revealed by TEM, XRD and TGA data. The H₂O₂+HNO₃ treated MWCNTs showed mesoporous walls, with a much improved BET surface area of 343.1 m²g⁻¹, relative to 223.7 m²g⁻¹ of HNO₃+H₂SO₄. The HNO₃+H₂SO₄ treated MWCNTs showed a structural damage and poor stability as revealed by TEM, XRD and TGA results. In addition, an improved structure of MWCNTs led to high discharge capacity of 72.6 mAh/g for H₂O₂+HNO₃ treated MWCNTs relative to all other samples. The study demonstrated that the surface properties and hydrogen storage of MWCNTs can be improved by treatments with H₂O₂+HNO₃ (1:3 v/v).

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