A novel approach to conformal functionalization of carbon nanowalls by cyclic operation of PECVD and plasma treatment

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Abstract: Incorporating oxygen in carbon nanowalls (CNW) structure has been considered a key technology to enhance the active sites for electrochemical reactions. It is also beneficial to improve the permeability of the electrolyte solution. However, this is still a great challenge to functaionalize the deep parts of the surface of CNW by post plasma treatment. Herein, we report a cyclic operation of plasma enhanced chemical vapor deposition (PECVD) and plasma treatment to fabricate CNW with oxygen functional groups not only on the top surface but also in the deep pores. In this method, a CO/H_2 and O_2/Ar microwave discharge systems for PECVD and plasma surface treatment, respectively, was periodically applied to synthesize and treat CNW cyclically.

Keywords: Carbon nanowalls, Plasma treatment, oxygen functional groups

1. Introduction

Owing to the large surface area, catalyst-free synthesis, and high density of sharp edges with open boundaries, carbon nanowalls (CNW) have shown their fascinating applications in different electrochemical systems [1-3]. Although, the 3D interconected porous network of CNW can promote an easy access of electrolyte ions to CNW surface to interact with, the hydrophobic nature of CNW restricts the electrode-electrolyte interaction [4]. In an attempt to enhance the intrinsic electrochemical sensing ability of CNW, we previously studied the surface functionalization of CNW by O_2/Ar plasma to introduce both oxygen functional groups and structural defects on its surface. An enhancement in electrochemical sensing properties of CNW samples after O_2/Ar plasma treatment was clearly observed and it showed the highest value for the sample with both optimum hydrophilicity and defective structure, due to increase in both accessible surface area wetted by the electrolyte and electrochemical active sites [5]. Inspired by our previous research acheivement, we aimed to further functionalize CNW in the deep parts of the walls. For this purpose, we introduce a novel inter-synthesis cyclic plasma treatment method to fabricate CNW with conformal oxygen functional groups in the deep parts of the walls. This research may provide a new avenue for conformal functionalization of CNWs with higher wall heights and thus their application in energy and power fields.

2. Experimental

CNW was fabricated on silicon plate (9 × 9 × 0.5mm) using microwave plasma enhanced chemical vapor deposition (MPECVD) as shown in Fig.1. The applied MPECVD system in this study was powered by 2.45 GHz microwave (APPLIED SCIENCE AND TECHNOLOGY, INC AX 2000). Firstly, substrate was placed into the reactor chamber and the chamber was pumped down to 1Pa. Then sequentially CO/H_2 and O_2/Ar mixtures were introduced at a constant flow rates at 23/2sccm and 0.1/10sccm, respectively and the chamber pressure was kept at 250Pa. CNW synthesis and treatment was done by the same method as reported in our previous work with this difference that total synthesis time of 60s was devided into 12 cycles, each cycle containing 5s synthesis by CO/H_2 and 5s plasma treatment by O_2/Ar [5]. Fig. 2 illustrates the schematic representation of inter-synthesis cyclic plasma treatment method. After synthesizing, the substrate was taken out of the chamber to characterize the CNW sample. The morphology of CNW sample was observed using a field emission scanning electron microscopy (JSM-7500F) operated at voltage of 5.0kV and beam current of 10μA. Raman spectroscopy was performed to study the structural properties of the CNW sample by JASCO NRS-4100 at an excitation wavelength of 532nm.

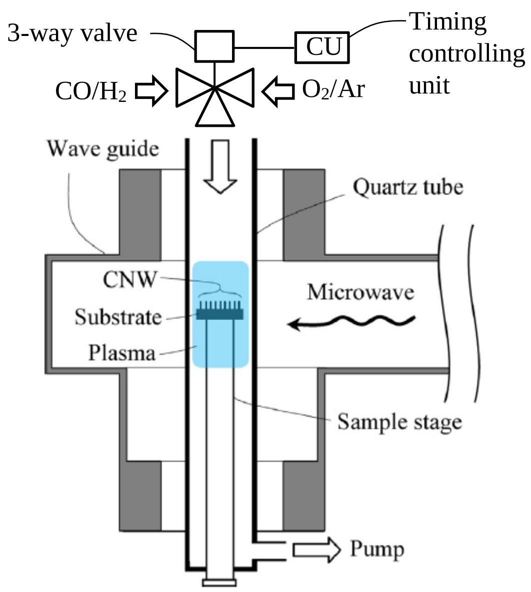

Fig.1. Schematic representation of MPECVD system

3. Result and discussion

Fig. 3 shows SEM top surface and cross-section images of CNW prepared by inter-synthesis cyclic plasma treatment method and compared with CNW prepared without cyclic plasma treatment. Growing of CNW perpendicularly to the substrate can be revealed by cross-

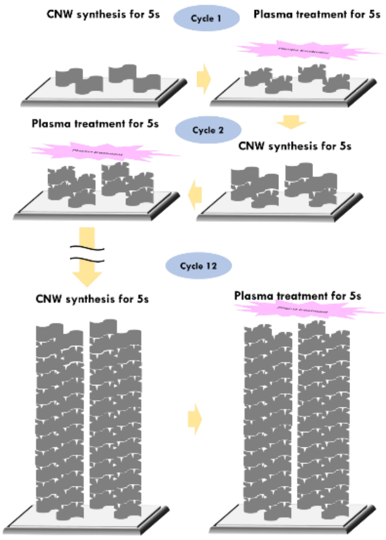

Fig.2. Schematic representation of depositing CNW by cyclic operation of PECVD and plasma treatment (1 cycle: CNW synthesis for 5s, plasma treatment for 5s).

section images. However, CNW earns layer by layer structure as synthesis is paused for 5seconds during the treatment time. In addition, more branched structure can be observed for the CNW prepared with cyclic plasma treatment method.

(a) (b)

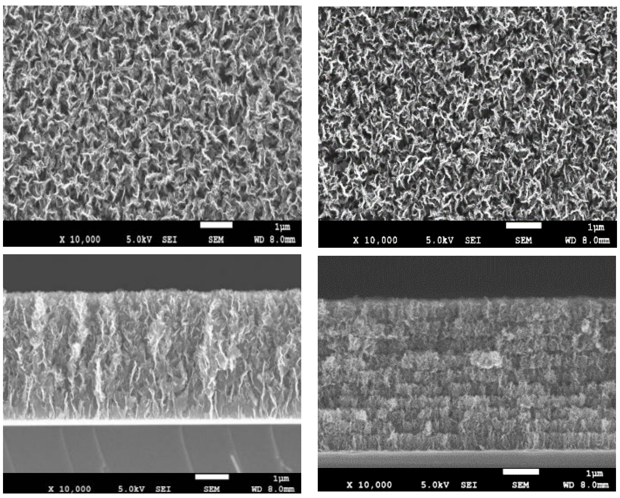

Fig.3. SEM top surface and cross-section images of CNW deposited (a) without plasma treatment with 60s deposition time and (b) inter-synthesis cyclic plasma treatment method with 12 cycles (each cycle: CNW synthesis for 5s, plasma treatment for 5s)

To understand the structural characteristic of CNW synthesized by cyclic plasma treatment method, Raman spectroscopy was applied (Fig. 4) and it compared with the Raman spectra of CNW films without any plasma treatment and post plasma treatment with O_2/Ar: 0.1/10sccm. As disclosed in Fig. 4, the cyclic plasma treatment method doesn’t induce significant differences in the Raman spectra of CNW, indicating preserving the basic structure of the material. The ratio between the intensity of D and G bands (I_D/I_G) is used as the quantitative analysis technique to estimate the degree of disorder in graphene lattice. It is seen that as-grown CNW without any plasma treatment has the I_D/I_G of 1.65, which decreases to I_D/I_G of 1.5 after post plasma treatment with O_2/Ar: 0.1/10sccm. However, it displayed a significant increase in I_D/I_G of CNW prepared with cyclic plasma treatment method (I_D/I_G= 2.2). It can be suggested that post plasma treatment results in selective etching and removing amorphous carbon on the surface of as-grown CNW and substitution of oxygen to defect sites, hence decreasing the I_D/I_G. While, as it confirmed by SEM cross-section images, the layer by layer and highly branched structure of CNW produced by cyclic plasma treatment enhances the edge plane structure on CNW, therefore leading to an increment in I_D/I_G.

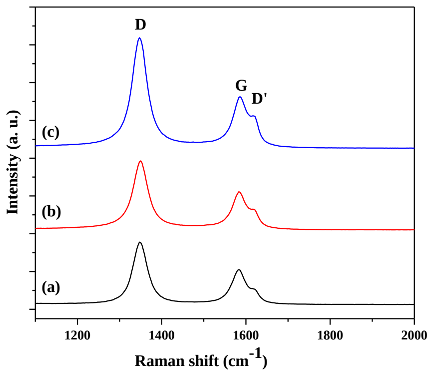

Fig.4. Raman spectra of CNW films (a) without any plasma treatment with 60s deposition time (b) post plasma treatment with 10s O_2/Ar:0.1/10sccm plasma , and (c) CNW prepared by inter-synthesis cyclic plasma tretament method with 12 cycles (each cycle: CNW synthesis for 5s, plasma treatment for 5s)

4. Conclusion

In this study, we proposed an inter-synthesis cyclic plasma treatment method to fabricate CNWs with conformal oxygen functional groups. SEM images revealed perpendicular growth of CNW on substrate with layer by layer and highly branched structure. Raman analysis showed an increase in I_D/I_G from 1.65 to 2.2, which can be assigned to increase in defective edge planes. This reaserch may provide a new pathway for fabricating CNW with conformal oxygen functional groups which can be beneficial for vast ion diffusion.

5. References

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