論文 / 著書情報
Article / Book Information

題目(和文)	カーボンナノウォールの表面改質と電気化学センサーへの応用
Title(English)	Study on surface modification of carbon nanowalls and their application to electrochemical sensors
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	Chemical science and engineering	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	(Engineering)
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Two-dimensional graphene-like carbon nanostructures have recently attracted a lot of practical interest due to their unique physical, electrical, and optical properties. Carbon nanowalls (CNW) belong to this category of functional materials that can be described as an open network of interconnected two-dimensional graphene sheets standing vertically on a substrate. Owing to the large surface area, highly active graphene edges, and fabricating without the use of catalysts, CNW has shown its fascinating application as electrode material for different electrochemical systems such as electrodes for batteries and supercapacitors, oxygen reduction, and recently electrochemical sensors and biosensors. Higher electrolyte permeability and reduction in ion resistance can be promoted by the opened structure of CNW film. However, functional properties of CNW can also be greatly influenced by the presence of structural defects and attached functional groups.

In this study, we propose two different approaches for modifying CNW surface for their potential applications in electrochemical sensing and biosensing field; Firstly, coating of CNW surface by transitional metal oxide (MnO_x) via anodic deposition technique and secondly, post plasma treatment of CNW with O_2/Ar plasma. At first step, synthesizing of CNW at different deposition times and their characterization was discussed. Plasma enhanced chemical vapor deposition in a CO/H_2 microwave discharge system was performed for fabricating CNW samples. Subsequent to this, synthesis of MnO_x/CNW was considered. Potentiostatic anodic deposition technique was applied for depositing of manganese oxides (MnO_x) onto the CNW surface at different deposition

times. It was shown that when deposition time is very short, the film has mostly original CNW structure with some nucleation spots of MnO_x. By increasing deposition time, the accumulation of MnO_x around the walls can be clearly confirmed. While, by further increase in deposition time, it is difficult to distinguish the border between CNW and MnO_x, which indicates that MnO_x can slightly infiltrate into the gaps between the walls. The average manganese oxidation state for the prepared electrodes was calculated based on deconvoluted O1s spectra and multiple splitting of Mn3s core level spectrum. As observed, electrodeposited MnO_x coatings exhibit mixed Mn valance states, where by increasing deposition time, the oxidation state of Mn increases. Cyclic voltammetry (CV) and amperometry techniques were performed to evaluate the sensor performance of MnO_x/CNW towards detecting hydrogen peroxide (H_2O_2). The prepared nanocomposite electrode exhibited high electrochemical activity for oxidation of H_2O_2 in phosphate buffer solution at an applied potential of +0.7V, showing a linear dependence on the concentration of H_2O_2 from 40μM to 10230μM, a high sensitivity (698.6 μA mM^{-1} cm^{-2}), and a detection limit of 0.55μM. The proposed hybrid CNW structure combined with the transitional metal oxide (MnO_x) demonstrated a great potential of CNW based composite electrodes in non-enzymatic electrochemical sensor application.

To further improve CNW performance as a metal-free electrochemical sensor through its intrinsic modification, O_2/Ar plasma with different O_2 flow ratios were applied to modify CNW surface. Our results revealed that the CNW treated in low oxygen flow rate (O_2/Ar: 0.1/10sccm) exhibited the highest concentration of incorporated oxygen on its structure, which consequently resulted in conversion of intrinsic hydrophobicity of CNW to hydrophilicity. Interestingly, however, further increase in oxygen flow rate did not increase the oxygen content of CNW structure, but instead it resulted in an increment in the defect and contributing less oxygen on CNW surface. We assume that when low density of oxygen species exists in the plasma treatment gas mixture, the amorphous carbon structures that exist on as-grown CNW surface are selectively etched and the potential active oxygen species are stabilized to the produced defect sites, therefore formation of oxygen functional groups occurs favorably. However, higher density of reactive

oxygen species can result in higher etching rate, which can consequently lead to increase the etch rate from both amorphous and sp^2 structures and prevent stabilization of oxygen in the defect positions, hence contributing less oxygen functional groups on the CNW structure. Electrochemical measurements revealed that the most hydrophilic CNW surface does not exhibit the highest electrochemical activity for the oxidation of H_2O_2. The highest amperometric response is observed for the CNW sample treated with O_2/Ar: 1.0/10sccm, which has lower oxygen content than CNW treated with O_2/Ar: 0.1/10sccm but still possessing hydrophilic characteristic and also owning more defective structure. These results can suggest the importance of both defects and oxygen-containing functional groups in electrochemical behavior of the electrodes as both defects and oxygen-containing functional groups can act as potential active sites for electrochemical reactions and oxygen-containing functional groups can enhance the hydrophilicity and surface area wetted by the electrolyte. The modified CNW in O_2/Ar: 1.0/10sccm plasma displayed wide linear response range for oxidation H_2O_2 from 50μM to 28000μM, low LOD, and sensitivity of 126.6μA/mM.cm^2. This study demonstrates that intrinsic modification of CNW by O_2/Ar plasma can result in enhancing CNW performance in electrochemical sensing systems as a metal-free electrode.