博　士（環境科学）　賀　　建　軍

学位論文題名

Fabrication, behaviors and applications of graphitic nano-carbon based electrodes

（グラファイト構造ナノカーボン電極の製作、挙動解析及び応用に関する研究）

学位論文内容の要旨

Due to their wide potential window, excellent chemical inertness, and high electro-catalytic activity, graphitic carbons have been found wide ranges of applications in both analytical and industrial electrochemistry. Effective surface areas, degrees of the edge atoms, and impurities of the graphitic carbons have been the key parameters determining the electrochemical efficiency of the graphitic carbon based electrodes. It has been experimentally demonstrated in this study that high-performance graphitic carbon electrodes are obtainable through nano-sizing and/or boron-doping of the graphitic carbons. In this study, high-performance graphitic carbon electrodes with highly purified single-walled carbon nanotubes, boron-doped nano-graphite, and electrochemically reduced graphene as the functioning elements have been successfully created and their unique electrochemical behaviors and the potential applications have been extensively studied.

This thesis consisted of five chapters. In chapter 1, a brief introduction to the typical graphitic carbons was described. In chapter 2, sheets consisted of entire single-walled carbon nanotubes (SWNTs) were used as the functioning elements for creating electrodes for the electrochemical measurement of ethidium bromide. The SWNT-sheet based electrode exhibited a fast electron transfer process on the electrode surface via the cyclic voltammetry with $K_4Fe(CN)_6$ as electrochemical probes. This SWNT-sheet based electrode showed also a high sensitivity toward ethidium ions, a typically harmful, aromatic backboned chemical. The SWNT-sheet

based electrode was capable of accumulating ethidium ions to a higher concentration based on π–π and electrostatic interactions and therefore was capable of detecting ethidium ions with a detection limit of 1.0×10^{-8} M. In chapter 3, boron doped graphitic nano-particles were used as the functioning elements for creation of electrodes for the direct detection of uric acid in biological samples. The electrode obtained in this manner was capable of oxidizing ascorbic acid at lower potentials; this provided a desirable solution to the interfering problem encountered in the detection of uric acid in biological samples caused by ascorbic acid. The detectable concentrations for uric acid ranged from 5.0 to 130 μM. The applicability of the electrode was experimentally demonstrated by the successful direct detection of uric acid in real urine samples. Nano-sizing together with boron-doping have enhanced the electro-catalytic activity of the electrode towards ascorbic acid; a high degree of the edge atoms was also created after the nano-sizing and boron-doping treatment; and as a result, the electrode was capable of oxidizing ascorbic acid at lower potentials. In chapter 4, fully exfoliated graphitic oxide (GO) was prepared by using a modified Hummers method. The GO was then electrochemically reduced to graphene to preparing super-capacitors with the thickness for the electrode is only few atoms thick. The resultant electrode showed a specific capacitance of 246 F/g; which is about 210% and182% higher than that of the electrode obtained using thermally reduced graphene and chemically reduced graphene, respectively, as the functioning elements. After the electrochemical reduction, in the C1s XPS spectra, the peak corresponding to O=C–OH was not observed and for C–O–C the peak area was reduced from 40.1% to 19.2%; while for C–OH, the peak area was increased from 7% to 19.7%. This distribution for the residual functional groups in graphene obtained by the electrochemical reduction was different in quantity to that of the residual functional groups in graphene obtained by using thermal and chemical reduction. In chapter 5, the overall achievements obtained in this study were summarized and the possibilities for further applications were discussed. All these research achievements are highly beneficial to the fields of both analytical and industrial electrochemistry and environmental science.

学位論文審査の要旨

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学位論文題名

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（グラファイト構造ナノカーボン電極の製作、挙動解析及び応用に関する研究）

In this study, high-performance graphitic carbon electrodes with highly purified single-walled carbon nanotubes, boron-doped nano-graphite, and electrochemically reduced graphene as the functioning elements were created and their electrochemical behaviors and the possible applications were studied. First, the candidate used sheets consisted of highly purified single-walled carbon nanotubes (SWNT) as the functioning elements to create working electrodes for the selective detection of pollutant chemicals. The working electrode obtained in this manner showed high selectivity for detection of chemicals of planer structures, such as ethidium ions, the typically carcinogenetic chemicals with a detection limit of 1.0×10^{-8} M. The targeted chemicals were accumulated by the SWNT-sheet based electrodes due mainly to the so-called π–π interactions. Second, the candidate used boron doped graphitic nano-particles as the functioning elements to create electrodes for the direct detection of uric acid in biological samples. The electrode obtained in this manner was capable of oxidizing ascorbic acid at lower potentials; this provided a desirable solution to the interfering problem encountered in the detection of uric acid in biological samples caused by ascorbic acid. The detectable concentrations for uric acid ranged from 5.0 to 130 μM. Nano-sizing effects together with boron-doping effects have enhanced the electro-catalytic activity of the electrode towards ascorbic acid, and as a result, the electrode was capable of oxidizing ascorbic acid at lower potentials. Finally, the candidate used the electrochemically reduced graphene as the key elements for preparing super-capacitors with the thickness for the electrode is only few hundred nano-meter thick. The resultant electrode showed a specific capacitance of 246 F/g; which is about 210% and182% higher than that of the electrode obtained using thermally reduced graphene and chemically reduced graphene, respectively, as the functioning elements. After the electrochemical reduction, in the C1s XPS spectra, the peak corresponding to O=C–OH was not observed and for C=O the peak area was reduced from 40.1% to 19.2%; while for C–OH, the peak area was increased from 7% to 19.7%. This distribution for the residual functional groups in graphene obtained by the electrochemical reduction was different in quantity to that of the residual functional groups in graphene obtained by using thermal and chemical reduction. In conclusion, the candidate, in this study, had demonstrated that the graphitic nano-carbon based electrodes with wide potential window, excellent chemical inertness, and high electro-catalytic activity were obtainable by optimizing the effective surface areas, degrees of the edge atoms, and the impurities of the graphitic carbons. The electrodes created by the candidate were found to have wide ranges of applications in both analytical chemistry and environmental sciences. In addition, the candidate showed familiarity with, and critical understanding of the relevant literatures; the methods adopted were appropriate to the subject matter and properly applied; the research findings were suitable set out, accompanied by adequate exposition and discussion, and the quality of English and the general presentation were satisfactory. The recommendation by the examination committee was that "the degree be awarded".