國立交通大學

材料科學與工程學系

博士論文

層狀二維材料製備-由電漿電化學製備石墨氧化物、石墨烯及由焠火製備奈米片狀二硫化鉬

Production of two-dimensional layered materials－graphite oxide and graphene by plasma electrochemistry and MoS_2 nanosheets by quenching method

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Abbreviations

HOPG: highly ordered pyrolytic graphite

GE: recycled graphite

HG: high purity graphite

CP: cathodic plasma process

VPE: vapor plasma envelope

EG: expandable graphite

PEGO: plasma-expanded graphite oxide

PEEG: Plasma electrochemically exfoliated graphene

DI: deionized water

EPEGO: exfoliated PEGO

NMP: N-methyl-2-pyrrolidone

MB: Methylene Blue

GSs: Graphene sheets

MoS_2-DI: Exfoliation of solution of MoS_2 in DI water, without quenching.

MoS_2-DIQ: Exfoliation of solution of MoS_2 in DI water, with quenching.

MoS_2-KOH: Exfoliation of solution of MoS_2 in aqueous KOH, without quenching.

MoS_2-KOHQ: Exfoliation of solution of MoS_2 in aqueous KOH, with quenching.

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Abstract

The purpose of this work is to find out new approaches for one-pot synthesis of graphite oxide and graphene by plasma electrochemical exfoliation of graphite in a basic electrolyte solution in a short-reaction time with regards of environmental friendliness, energy/time saving, and low cost. First of all, we adopted a highly efficient cathodic plasma (CP) process in which the vapor plasma envelope calorific effect provides instant oxidation and expansion of graphite for producing plasma-expanded graphite oxides (PEGOs) from recycled graphite electrodes (GEs) or high purity graphite (HG), within a reaction time of 10 min without the need for strong oxidants or concentrated acids. X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy confirmed the dramatic structural change from GEs or HG to graphite oxides after the CP process. Furthermore, scanning electron microscopy and transmission electron microscopy revealed that the graphite oxide possessed a spheroidal morphology, with dimensions of 1–3 μm, as a result of melting and subsequent quenching during the plasma electrolysis process. We obtained a stable, homogeneous dispersion of PEGOs in N-methyl-2-pyrrolidone after sonication and filtering of the centrifuged PEGOs. We used these spheroidal graphite oxide particles as effective adsorbents for the removal of pollutants (e.g., Methylene Blue) from aqueous solutions. These PEGOs also served as good precursors for the preparation of graphite nanopletets.

Sequently, we have demonstrated a new and highly efficient plasma-assisted electrochemical exfoliation method, involving a plasma-generated graphite cathode and a graphite anode, for the production of graphene sheets from electrodes in a basic electrolyte solution in a short reaction time. The AFM images revealed a lateral dimension of approximately 0.5–2.5 μm and a thickness of approximately 2.5 nm, corresponding to approximately seven layers of graphene, based on an interlayer spacing of 0.34 nm. Additively, the influence of electrolytic concentration on morphological and structural properties of plasma-electrochemically exfoliated graphene is investigated and presented. Finally, we developed an efficient solution-based method for the production of few-layer MoS_2 nanosheets through exfoliation of bulk MoS_2 compounds that were subject to quenching in liquid N_2 and subsequent ultrasonication. AFM images of individual nanosheets revealed that the thickness varied from 1.5 to 3.5 nm and the lateral dimensions from 0.5 to 3.5 μm.

摘要:

此實驗的目的是要找出在相對基本的電解液中, 能夠快速用電漿電化學剝離法製造出石墨氧化物及石墨烯並且達到對環境友善、節省能源及時間與低成本的效果。首先, 我們在回收的石墨電極或高純度石墨採用高效率陽極電漿法以蒸汽熱電漿反應對石磨產生即時氧化及擴張隨後產出展開電漿石墨氧化物, 而此法可在不需要強氧化劑或高濃酸的條件下, 十分鐘的反應時間內完成。X-RAY 繞射分析、X-RAY 光電子圖譜或拉曼圖譜可檢測出在經過陽極電漿法後, 從石墨電極或高純度石墨到石磨氧化物的劇烈結構改變。此外, 掃描式電子顯微鏡與穿透式電子顯微鏡更可顯示出石墨氧化物擁有類似圓球狀的型態, 範圍尺度在 1-3μm 間, 這是在電漿電解法中融化並隨後冷卻的結果。聲裂法及離心過濾石墨氧化物後, 我們得到在 N-甲基吡咯烷酮中有穩定且同質均勻分布的展開石墨氧化物。應用上可將類圓球狀的石墨氧化物當作強吸收劑用來去除水溶液中的髒汙(例如:亞甲基藍)。他也是個好的製造石墨奈米小板之前驅物。隨後, 我們也說明如何由石墨陰陽極電漿電解剝離法在短時間內與簡單電解液的條件下產出石墨烯。原子力顯微鏡影像顯示出, 橫向尺度大約 0.5-2.5μm 及厚度約 2.5nm, 相當於七層石墨烯(每層約 0.34nm)的厚度。最後, 我們研究電解液的濃度如何影響電漿電化學剝離石墨烯的表面形態及結構最後我們發展出一個高效率液相製法使用 N_2 將塊狀 MoS_2 製備成 MoS_2 nanosheets, 由 AFM 的圖可以看出分開的 MoS_2 nanosheets 的厚度由 1.5 nm ~3.5 nm 且尺寸大小在 0.5μm ~3.5 μm 之間。。

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