Electrochemical on-surface synthesis of a strong electron-donating graphene nanoribbon catalyst

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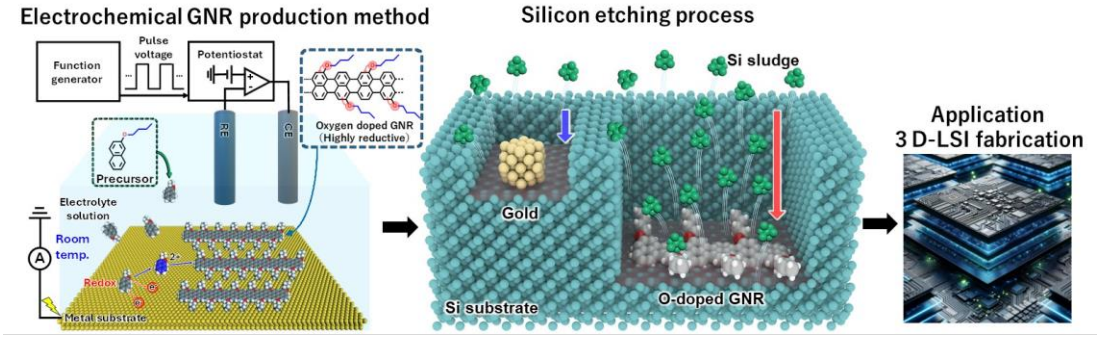
Edge functionalization of graphene nanoribbons (GNRs) by introducing electron-donating or withdrawing substituents into their backbones is crucial for their applications in electronic, magnetic, and energy fields. However, edge-functionalization through the on-surface synthesis can be challenging. This is mainly due to the decomposition of functional groups at temperatures ranging from 300 to 500°C and limited monolayer GNR growth based on metal catalysis. To solve the problem, we developed an electrochemical technique for on-surface GNR synthesis that overcomes these limitations to produce edge-functional GNRs. Our approach involves regioselective ionic polymerization and oxidation-based dehydrogenation, which occur at the electric double layer (EDL), liquid-solid interface. Our technique allows GNR growth at <80°C and layer-by-layer growth, which was previously impossible.

This study demonstrated the successful use of electrochemical on-surface synthesis to produce oxygen-doped GNRs with 5-AGNR widths and butoxy substituents using the asymmetric precursor, 2-butoxynaphthalene. We discovered a unique nonlinear growth mechanism for GNR synthesis. The di-cation form of the asymmetric precursor, produced through a two-electron oxidation process via high voltage application, becomes an active intermediate for GNR growth, suggesting a previously unknown heterochiral di-cationic polymerization mechanism. This research demonstrates that electrochemically synthesized GNRs are highly effective catalysts for silicon chemical etching in the semiconductor industry, surpassing the efficiency of previously used noble metal catalysts.



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