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Graphene prepared by one-pot solvent exfoliation as a highly sensitive platform for electrochemical sensing

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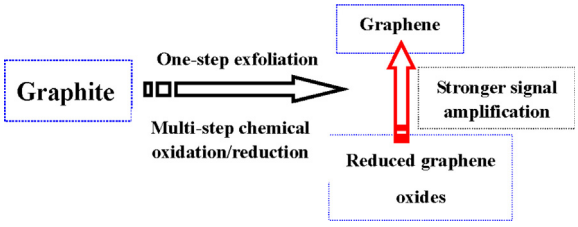
HIGHLIGHTS

- Graphene was prepared by one-step solvent exfoliation as superior electrode material.
- Compared with RGO, prepared graphene exhibited stronger signal enhancement.
- A widespread and highly-sensitive electrochemical sensing platform was constructed.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene was easily obtained *via* one-step ultrasonic exfoliation of graphite powder in *N*-methyl-2-pyrrolidone. Scanning electron microscopy, transmission electron microscopy, Raman and particle size measurements indicated that the exfoliation efficiency and the amount of produced graphene increased with ultrasonic time. The electrochemical properties and analytical applications of the resulting graphene were systematically studied. Compared with the predominantly-used reduced graphene oxides, the obtained graphene by one-step solvent exfoliation greatly enhanced the oxidation signals of various analytes, such as ascorbic acid (AA), dopamine (DA), uric acid (UA), xanthine (XA), hypoxanthine (HXA), bisphenol A (BPA), ponceau 4R, and sunset yellow. The detection limits of AA, DA, UA, XA, HXA, BPA, ponceau 4R, and sunset yellow were evaluated to be 0.8 μM, 7.5 nM, 2.5 nM, 4 nM, 10 nM, 20 nM, 2 nM, and 1 nM, which are much lower than the reported values. Thus, the prepared graphene *via* solvent exfoliation strategy displays strong signal amplification ability and holds great promise in constructing a universal and sensitive electrochemical sensing platform.

1. Introduction

Graphene is a two-dimensional, atomically thin lattice of sp^2-hybridized carbon with unique electronic, optical, mechanical, and thermal properties [1–6]. Due to its large surface area, high catalytic activity, and strong accumulation ability, graphene has been attracted increasing attention and widely used for electrochemical detection. In particular, the response signals and detection sensitivity of a large variety of species, such as catechol and hydroquinone [7,8], NADH [9], H_2O_2 [10], DNA [11], and Hg^{2+} [12], were reported to be remarkably enhanced on the surface of graphene-modified electrode. Among these studies, graphene was predominantly obtained *via* chemical oxidation of pristine graphite, especially according to Hummer's [13–15] or modified Hummer's methods [16–19]. However, the chemical oxidation based strategies have some intrinsic drawbacks. Firstly, a large

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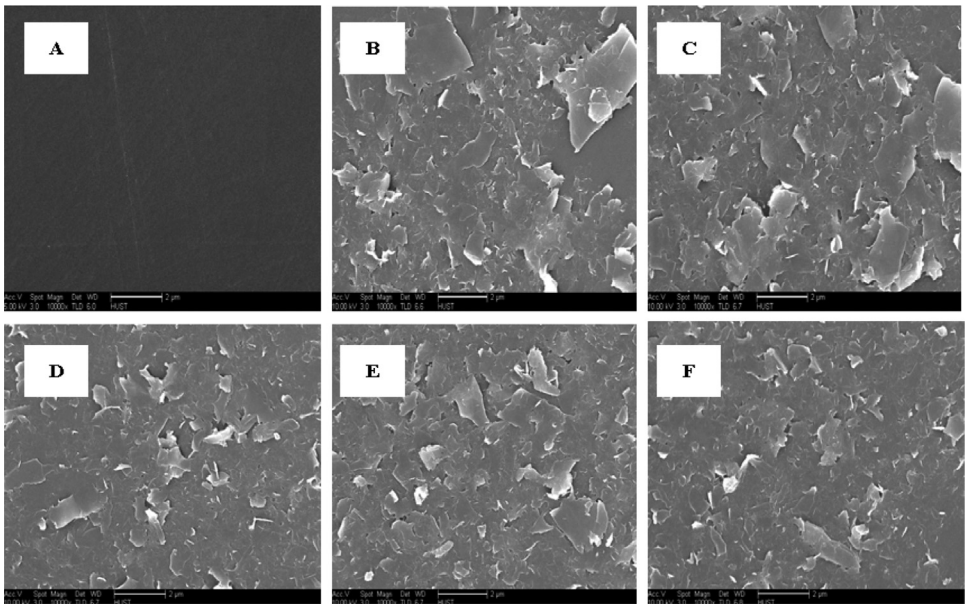

Fig. 1. SEM images of GCEs modified with NMP (A), G@12h (B), G@24h (C), G@36h (D), G@42h (E) and G@48h (F), scale bar: 2 μm.

amount of strong oxidizing reagents such as concentrated H_2SO_4, $KMnO_4$, and $K_2S_2O_8$ are typically involved, leading to environmental pollution and hazardous operations. Secondly, the preparation process is generally complicated and consists of multiple pre- and post-treatments. Finally, the destruction of the intrinsic sp^2 hybridized structure of graphite can be easily happened during the chemical oxidation, affecting the properties of the resulting graphene materials.

Compared to the chemical oxidation strategy, liquid-phase exfoliation has been proven to be a convenient and efficient approach to prepare graphene [20]. The major challenge is selecting suitable solvent molecules to reduce the strong van der Waals attractions between the layers of bulk graphite. Moreover, exfoliation is often accelerated by introducing external forces, and the widely-used technique is ultrasound. Shear forces and cavitation that resulting from ultrasound attack graphite layers and further improve the exfoliation efficiency. Until now, solvents such as *N*-methyl-2-pyrrolidone (NMP) [20,21] and dimethylformamide (DMF) [22] were successfully used to prepare graphene. However, the application of graphene prepared by solvent exfoliation in electrochemical sensing remains limited.

In this work, graphene was prepared through one-step ultrasonic exfoliation using NMP as solvent, and its application in electrochemical sensing was systematically investigated. With prolonged ultrasonic time, the exfoliation efficiency and the graphene yield are initially increased and then reach the plateau. Compared with the reduced graphene oxides (RGO) prepared by chemical exfoliation of graphite, the such prepared graphene significantly enhanced the oxidation signals of a wide variety of species, such as ascorbic acid (AA), dopamine (DA), uric acid (UA), xanthine (XA), hypoxanthine (HXA), bisphenol A (BPA), ponceau 4R, and sunset yellow. These encouraging results may pave the

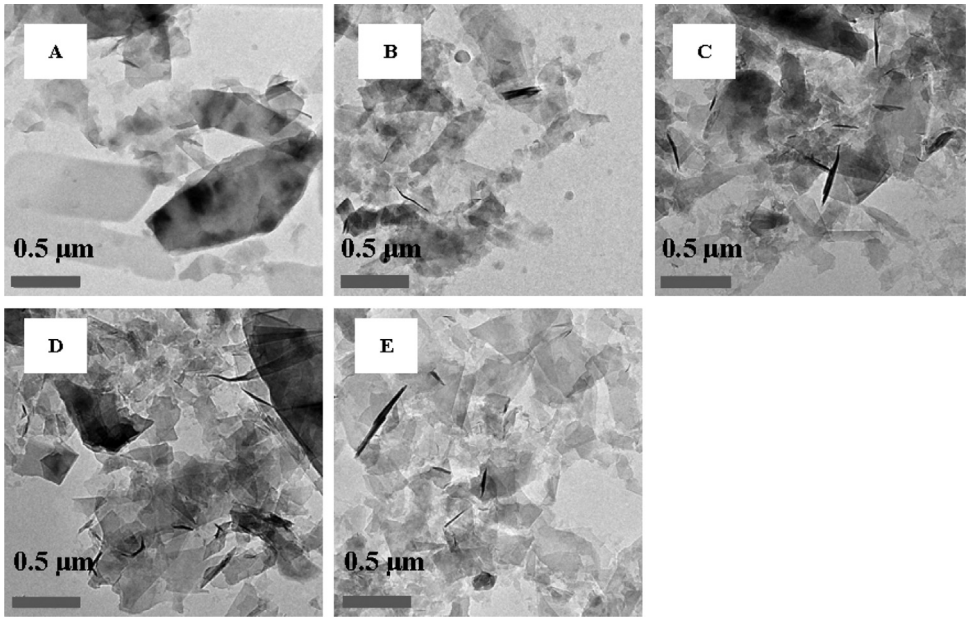

Fig. 2. TEM images of G@12h (A), G@24h (B), G@36h (C), G@42h (D) and G@48h (E), scale bar: 0.5 μm.