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Facile synthesis of amide-functional reduced graphene oxides as modified quick, easy, cheap, effective, rugged and safe adsorbent for multi-pesticide residues analysis of tea

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ABSTRACT

Amide-functional reduced graphene oxide (amide-rGO) with different carbon chain length amino groups were successfully synthesized. The graphene oxides (GO) reduction as well as amino grafting were achieved simultaneously in one step via a facile solvothermal synthetic strategy. The obtained materials were characterized by X-ray diffraction, Raman spectroscopy, Fourier-transform infrared spectrometry and X-ray photoelectron spectroscopy to confirm the modification of GO with different amino groups. The adsorption performance of catechins and caffeine from tea acetonitrile extracts on different amide functional rGO samples were evaluated. It was found that tributylamine-functional rGO (tri-BuA-rGO) exhibited the highest adsorption ability for catechins and caffeine compared to GO and other amino group functional rGO samples. It was worth to note that the adsorption capacity of catechins on tri-BuA-rGO was 11 times higher than that of GO (203.7 mg g⁻¹ vs 18.7 mg g⁻¹). Electrostatic interaction, π - π interaction and surface hydrophilic-hydrophobic properties of tri-BuA-rGO played important roles in the adsorption of catechins as well as caffeine. The gravimetric analysis confirmed that the tri-BuA-rGO achieved the highest efficient cleanup performance compared with traditional dispersive solid phase extraction (dSPE) adsorbents like primary-secondary amine (PSA), graphitized carbon black (GCB) or C18. A multi-pesticides analysis method based on tri-BuA-rGO is validated on 33 representative pesticides in tea using gas chromatography coupled to tandem mass spectrometry or high-performance liquid chromatography coupled with tandem mass spectrometry. The analysis method gave a high coefficient of determination ($r^2 > 0.99$) for each pesticide and satisfactory recoveries in a range of 72.1–120.5%. Our study demonstrated that amide functional rGO as a new type of QuEChERS adsorbent is expected to be widely applied for analysis of pesticides at trace levels.

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1. Introduction

Tea is one of the most consumed beverages in the world because of its taste, aroma and health benefits [1]. Pesticide residues in tea have attracted more and more public concerns because they are one of the major toxic risks for human health [2]. Maximum residues limits (MRLs) of pesticide residues in tea have been established by several international organizations and countries [3]. However, direct analysis of multi-pesticide residues in tea at trace levels

can be very challenging owing to the complex tea matrices containing polyphenols, chlorophylls, high amount of caffeine, etc., which could easily be co-extracted and severely interfered with the trace pesticides analysis [4]. The sample preparation to remove the interferences from tea extracts is becoming the key procedure for pesticides analysis.

QuEChERS (quick, easy, cheap, effective, rugged and safe) method, firstly introduced by Anastassiades et al. in 2003, has achieved worldwide acceptance in multi-pesticide residues analysis that benefited from its simplicity and high throughput [5]. The cleanup technique based on dispersive solid-phase extraction (dSPE) to adsorb the interfering substances in the matrices, rather than the analytes, is critical for QuEChERS method. Commercial adsorbents primary-secondary amine (PSA), graphitized

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carbon black (GCB) and C18 are three most commonly used dSPE adsorbents to remove the interference substances. However, due to high co-extractive contents of tea, it is difficult to remove various interfering substances just using one kind of small quantity of these materials. The mixtures of two or three of adsorbents were required to achieve effective cleanup performance [6,7]. It is time consuming and labor intensive, especially for large number of samples analysis. Thus, developing new adsorbents with high affinity capacity towards different interference substances becomes very important and urgent for pesticides analysis.

Discovery of novel nanomaterials has provided new opportunity for sample preparation of trace analysts. Graphene based material has sparked much interest as promising adsorbent candidate because of its fascinating properties, like large surface areas, easy modification [8]. The oxygen-containing groups on the surface of graphene oxide (GO) can be modified with desirable organic groups to modulate hydrophilic-hydrophobic surfaces and to regulate effective adsorption sites, which can further tailor their adsorption performance. For example, 1,4-phenyldiboronic acid linked graphene oxide framework was reported as SPE adsorbent for phenylurea herbicides analysis [9]. Amine functionalized reduced graphene oxide using ammonia water as precursor was synthesized as cleanup sorbent for the determination of acidic pharmaceuticals in water [10]. Fatty acid in oil crops was adsorbed on amide graphene which exhibits better cleanup performance compared to other adsorbents [11]. Although there have been researches about the synthesis of amide graphene, it as a dSPE adsorbent for removal of tea matrix has not been reported before. Moreover, the synthesis of different carbon chain length amides functional graphene materials and their adsorption ability on tea matrix have not been investigated yet. The adsorption mechanisms of various tea matrices on amide graphene required further studied to pursue its promising application as an effective adsorbent.

Herein, GO was functionalized with different carbon chain length amino groups by one step solvothermal treatment. The adsorption abilities of catechins, caffeine as well as pigments on resulting amide-functional reduced graphene oxides (amide-rGOs) were investigated. We clarified the influence of surface charge, surface hydrophilic-hydrophobic properties of the amide-rGO samples on the adsorption performance of catechins and caffeine. The material was further used as adsorbent in modified QuEChERS procedure. By combined with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) or gas chromatography coupled to tandem mass spectrometry (GC-MS/MS), a method for the determination of 33 pesticide residues in tea was proposed. It is expected that the functional graphene based materials are attractive for novel analytical chemistry.

2. Experimental

2.1. Chemical and materials

Graphite powder, NaCl, anhydrous ethanol, ethylene glycol, amino water and ethylenediamine were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). *n*-Butylamine, *tert*-Butylamine, tributylamine, Dodecylamine and Octadecylamine were obtained from Aladdin Industrial Corporation. PSA, GCB and C18 were purchased from Tianjin Bonna-Agela Technologies (China). HPLC grade acetonitrile were purchased from Merck (Darmstadt, Germany). Deionized water was obtained by using a Milli-Q system (Millipore, Milford, USA).

The standard compounds of 33 pesticides were provided by Agricultural Environmental Protection Institution of Tianjin, China. The purity of the pesticides standards were >99.0%. The standards of (–)-epigallo-catechin-gallate (EGCG) and caffeine were purchased

from Sigma-Aldrich company. All standard solutions were stored at 4 °C in dark vials. The MRLs of pesticides in this work were established by EU, Japan and China were summarized in Table 1.

Green tea samples purchased from local market were used as blank samples or spiked samples for recovery assays. Before the recovery assays, the samples were tested and confirmed for the absence of targeted pesticides.

2.2. Synthesis and characterization of amide-functional reduced graphene oxides

GO was synthesized from natural graphite flake by the modified Hummers method [12]. Reduced graphene oxides functionalized with different amino groups were prepared via a facile solvothermal synthetic strategy (Fig. 1). Typically, 0.4 g GO was dispersed into 60 mL ethylene glycol with the aid of bath ultrasonication. After further addition of 0.05 mmol of ammonia water (A), ethylenediamine (EA), *n*-butylamine (*n*-BuA), *tert*-butylamine (*tert*-BuA), tri-butylamine (tri-BuA), dodecylamine (DA) or octadecylamine (OA), the dark brown mixture was transferred to a Teflon lined autoclave for solvothermal reaction at 180 °C for 15 h. After reaction, the precipitate was centrifuged and washed repeatedly with ethanol and deionize water until its pH reached 7. The synthesized rGO was named as A-rGO, EA-rGO, *n*-BuA-rGO, *tert*-BuA-rGO, tri-BuA-rGO, DA-rGO and OA-rGO.

The structures of GO and amide-functional rGO samples were characterized by the X-ray diffraction (XRD) and Raman spectra. Wide-angle XRD patterns were recorded on a Rigaku Ultimate IV diffractometer using Cu K α radiation (40 kV, 40 mA, 10° min⁻¹ from 10 to 80°). Raman spectra were obtained using Labor Raman HR-800 with laser excitations at 514.5 nm. The surface functional groups were observed by X-ray photoelectron spectroscopy (XPS) and fourier transform infrared spectroscopy (FTIR). XPS measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. FTIR spectra of the samples were recorded on a Thermo Nicolet 380 spectrometer. The zeta potential, element analysis and water contact angle measurement were conducted to discuss the adsorption mechanism. Zeta potential of samples were measured by Nano-ZS ZEN3600 (MALVERN Instrument) at 25 °C. Elemental analyses were performed with Vario MICRO CHN elemental analyser (EA). The water contact angle measurement was conducted on a JC2000C1 Contact Angle Measurement (Shanghai Zhongchen Technical Apparatus Co., China).

2.3. Sample preparation

2.3.1. Preparation of tea acetonitrile extract

A thoroughly grinding green tea powder (2.0 g) was added into the mixture of 2 mL water and 10 mL acetonitrile, and then extraction was performed with the help of a homogenizer at 12,000 rpm for 2 min. After that, 2.5 g of NaCl was introduced and vortexed for 1 min, followed by centrifugation at 4000 rpm for 10 min. 2 mL of the supernatant was ready for use.

2.3.2. Adsorption experiment

The adsorption of catechins and caffeine from tea acetonitrile extract was conducted on amide-rGO samples. 100 mg amide-rGOs was added into 2 mL tea acetonitrile extract, vortexed for 2 min, followed by centrifugation at 5000 rpm for 10 min. The supernatant was prepared for analysis. The adsorption capacities of catechins and caffeine were measured via HPLC analysis. In comparison with amide-rGOs, the adsorption on GO and other commercial adsorbents (like PSA, GCB, C18) were investigated under the same

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