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# Fabricated ultrathin magnetic nitrogen doped graphene tube as efficient and recyclable adsorbent for highly sensitive simultaneous determination of three tetracyclines residues in milk samples

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## ABSTRACT

In this work, ultrathin magnetic nitrogen doped graphene tube (mNi@N-GrT) is synthesized via a template free graphitization process. The mNi@N-GrT as magnetic solid phase extraction adsorbent is used to extract three tetracyclines (TCs), showing the best extraction ability and adsorption capacity than graphene, MWCNT and magnetic MWCNT (NiFe<sub>2</sub>O<sub>4</sub>/MWCNT). The tubular structure of mNi@N-GrT can avoid the aggregation problem, provide higher active surface area and larger conjugated system. The doping of N atom will generate structural defects which will be adsorption sites for three TCs. Furthermore, the mNi@N-GrT with magnetic properties is beneficial to the recovery and recycle. The limits of detections (LODs) (S/N = 3:1) are in the range of 1.29–2.31 ng mL<sup>-1</sup> with average recoveries from 91.6 to 109.7% in milk samples. The results demonstrate that the mNi@N-GrT is a hopeful adsorbent in the MSPE of TCs in real samples.

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## 1. Introduction

Tetracyclines (TCs) are a kind of broad-spectrum antimicrobial drugs, widely used as agriculture, human and veterinary medicines to prevent bacterial diseases [1]. However, the improper use of TCs can result in unsafe residues in animal based foods [2,3] causing potential adverse effects, such as antibiotic resistance and allergic reactions. In order to ensure the food safety, WHO and Ministry of Agriculture of China have established the maximum allowable level of single or total TCs as 0.1 mgL<sup>-1</sup> in milk [4]. Therefore, it is of great concern to develop sensitive, economical methods for the determination of TCs. So far, various methods for the detection of TCs have been reported in the literature, such as liquid chromatography–tandem mass spectrometry [5], capillary electrophoresis [6], electrochemical aptasensor [7], and ion chromatographic [8]. Among these methods, HPLC is the most frequently used owing to its effective and simultaneous analysis.

Food origins are with complicated matrices, it is critical to use a reliable and efficiency pretreatment method to avoid matrix interference and improve sensitivity. Solid phase extraction (SPE) cartridges containing different adsorbents [9,10] have widely used for the extraction of TCs in complex matrices. However, SPE car-

tridges have its own disadvantages, such as easily affected by impurities, and single use. Compared to SPE cartridges, magnetic solid-phase extraction (MSPE) have more advantages. The magnetic adsorbent can be dispersed in sample solution for the extraction and recycled by external magnetic field without centrifugation or filtration process. It makes the pretreatment process efficient, low consumption and eco-friendly [11,12]. Thus, the proper adsorbent is the key factor in the MSPE process.

Over the past few decades, the carbon nanotube and graphene were reinvested magnetic properties (Fe<sub>3</sub>O<sub>4</sub>) and used as adsorbent for magnetic solid-phase extraction, such as magnetic MWCNTs were used as adsorbent for analysis of herbicides [13], pesticide [14] and medicine [15]; magnetic graphene used as adsorbent for MSPE of the sulfonamide antibiotics [16], 3D-IL@mGO used as adsorbent for MSPE of 16 polycyclic aromatic hydrocarbons [17], and Fe<sub>3</sub>O<sub>4</sub>NPs@GO employed for pre-purification and pre-concentration paclitaxel [18]. The magnetic carbon materials have shown good pre-concentration ability, but also have respective disadvantages, such as the synthesis methods of CNTs and graphene were high energy dissipation, high costs and complicated. Furthermore, the magnetic property of carbon material was reinvested through extra steps. Those deficiencies limit the widespread applications of magnetic carbon materials. Hence, we aim to develop a one-step strategy for the synthesis of magnetic nitrogen doped graphene tube, which was facile, environment-friendly and less expensive.

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Herein, we adopt a template free graphitization strategy for the formation of tubes from inexpensive dicyandiamide (DCDA) as precursor, Ni nanoparticles as catalysts and water as solvent. During the graphitization process, metal ions  $\text{Ni}^{2+}$  turn into metal Ni nanocatalysts [19,20], and then the nanocatalysts further catalyze the DCDA to form nitrogen doped graphene tubes. The tubes are used as effective MSPE adsorbent and simultaneous determination of three TCs (Oxytetracycline, Chlortetracycline-HCl, Tetracycline hydrochloride) residues in milk samples by high performance liquid chromatography (HPLC), showing satisfactory extraction performance. We also studied the adsorption mechanism between  $\text{mNi@N-GrT}$  and TCs to elucidate their adsorption behaviors in detail.

## 2. Experimental

### 2.1. Reagents and chemicals

Dicyandiamide ( $\text{C}_2\text{H}_4\text{N}_4$ , DCDA), Nickel acetate tetrahydrate ( $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$ ) are analytical reagent, Oxytetracycline (OTC,  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_9$ ), Chlortetracycline-HCl (CTC,  $\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{O}_8\cdot\text{HCl}$ ), Tetracycline hydrochloride (TCC,  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\cdot\text{HCl}$ ) were bought from Aladdin Biological Co., Ltd (Shanghai, China). HPLC grade of  $\text{CH}_3\text{OH}$  and acetonitrile (ACN) were purchased from Sinopharm Company (Shenyang, China).

### 2.2. Instruments

The HPLC analyses were studied by Shimadzu LC-16 system (SPD-16 UV-vis detector). The Micro-structure of  $\text{mNi@N-GrT}$  was studied by transmission electron microscopy (TEM, TecnaiG220, FEI, USA) and field emission scanning electron microscope (SEM, HITACHI SU8000, Japan). The carbon content of  $\text{mNi@N-GrT}_2$  was measured by elemental analysis (Eurovector EA3000, Italy). The chemical composition and electronic state of  $\text{mNi@N-GrT}$  was determined by X-ray photoelectron spectroscopy (XPS Thermo ESCALAB 250Xi, USA). The crystalline phase of  $\text{mNi@N-GrT}$  was confirmed by X-ray diffraction (XRD, Siemens D5000, Germany). Raman spectra of  $\text{mNi@N-GrT}$  were obtained by Laser Confocal Micro-Raman Spectroscopy (LabRAM XploRA, HORIBAJOBINYVONS.A.S, France). The surface area of  $\text{mNi@N-GrT}$  was measured by  $\text{N}_2$  adsorption/desorption isotherm with a Micromeritics Tristar 3020 (Norcross, USA). The magnetic prosperity of  $\text{mNi@N-GrT}$  was measured by vibrating sample magnetometer (VSM, Lakeshore 7407, USA) at room temperature. The pH value was measured by pH meter (PHSJ-4F Model, Shanghai instrument electric science instrument, China).

### 2.3. Preparation of $\text{mNi@N-GrT}$

The  $\text{mNi@N-GrT}$  was prepared according to the previous report with modification [20]. The DCDA (8.973 g) and  $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$  (4.195 g) were dissolved in 500 mL double-distilled water, and stirring constantly for 24 h at  $60^\circ$ . Then the water was evaporated at  $70^\circ$  in oven and obtained pale green dry products. The pale green products were ground to fine powder, following a annealing at  $1000^\circ\text{C}$  for 1 h in  $\text{N}_2$  with a ramp-rate of  $8^\circ\text{C min}^{-1}$ . The moles ratio of DCDA and  $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$  were optimized. The ratio was 4:1, 6:1, 9:1, which were denoted by  $\text{mNi@N-GrT}_1$ ,  $\text{mNi@N-GrT}_2$ ,  $\text{mNi@N-GrT}_3$ .

### 2.4. MSPE procedures

First, the 10.0 mg of  $\text{mNi@N-GrT}$  were dispersed into working solution ( $5\text{ mg L}^{-1}$  solution of TCC, OTC and CTC) or sample solution and incubated 10 min by a shaker. After extraction, the

mixture solution was transferred to a centrifuge tube, the adsorbent remained in the tube and the supernatant was discarded with the help of the external magnet. The analytes were desorbed with 2 mL methanol containing 1%  $\text{HCOOH}$  under vortex for 5 min, the collected eluate was filtered through a NYLON 66 ( $0.45\ \mu\text{m}$ ) filter membrane before HPLC analysis.

Chromatographic separation of TCs was performed on a SB-C18 column (Agilent,  $4.6\ \text{mm} \times 150\ \text{mm}$ ,  $5\ \mu\text{m}$ ). The mobile phase was ACN: oxalic acid ( $0.01\ \text{mol L}^{-1}$ , pH 3) (25:75, v:v), flow rate was  $0.7\ \text{mL min}^{-1}$ , detection wavelength was at  $272\ \text{nm}$ , injection volume was  $20\ \mu\text{L}$ .

### 2.5. Preparation of samples

Raw milk ( $\text{milk}_1$ ), pure milk ( $\text{milk}_2$ ) and skimmed milk ( $\text{milk}_3$ ) were obtained from the local supermarket in Shenyang. Firstly, 2.5 mL milk was added into 5 mL  $\text{Na}_2\text{EDTA-McIlvaine}$  buffer solution (pH 4.0,  $0.1\ \text{mol L}^{-1}$ ), vortexed for 5 min and centrifuged for 5 min at 4000 rpm. Then, the extraction process was repeated twice with 2.5 mL of  $\text{McIlvaine}$  buffer-EDTA solution, the supernatant were reunified and diluted to 10 mL with  $\text{McIlvaine}$  buffer-EDTA solution. It was filtered through  $0.45\ \mu\text{m}$  filter membrane and stored at  $5^\circ\text{C}$ .

$\text{Na}_2\text{EDTA-McIlvaine}$  buffer solution (pH 4.0,  $0.1\ \text{mol L}^{-1}$ ) was prepared by dissolving 16.81 g  $\text{Na}_2\text{EDTA}$ , 6.86 g  $\text{Na}_2\text{HPO}_4$ , and 5.9 g citric acid monohydrate in 500 mL double-distilled water [3], the solution was stored in a refrigerator before use.

## 3. Results and discussion

### 3.1. Characterization of $\text{mNi@N-GrT}$

The morphology of  $\text{mNi@N-GrTs}$  with different molar ratio of DCDA to metal was studied by SEM and TEM. The Fig. 1a demonstrates the  $\text{mNi@N-GrT}_2$  with uniform hollow tube morphology. The magnification SEM (Fig. 1b) shows that the  $\text{mNi@N-GrT}_2$  is well-aligned, with interior hollow voids feature. The diameters are ranging from 200 to 500 nm, which present open channels for the transport of TCs. As shown in the insert image of Fig. 1b, the  $\text{Ni}^{2+}$  is transformed into Ni nanoparticles during the pyrolysis process, and Ni nanoparticles act as catalyst for the  $\text{mNi@N-GrT}$  growth. As shown in the SEM image of  $\text{mNi@N-GrT}_1$  (Fig. 1c), the excess Ni nanoparticles are produced and agglomerated on the graphene tubes, the tube are shorter due to the deficient of DCDA. Otherwise, the  $\text{mNi@N-GrT}_3$  (Fig. 1d and the insert image) get longer, the surfaces covered with folds and grooves, and the diameters are expanded to 900 nm. Fig. 1e is the TEM image of  $\text{mNi@N-GrT}_2$ , the walls of  $\text{mNi@N-GrT}_2$  are ultrathin and almost transparent, and the thickness of the  $\text{mNi@N-GrT}_2$  is about 8 nm. The carbon content is further explored by elemental analysis, indicating the carbon content of  $\text{mNi@N-GrT}_2$  is about 49.977 wt%. The uniform hollow tube structure and abundant carbon matrix can enhance the contact area and channel between adsorbent and TCs, which are favorable for the extraction.

As shown in Fig. 1f, the crystalline phases of  $\text{mNi@N-GrT}_2$  were studied by X-ray diffraction (XRD) patterns. The peaks at  $12.6^\circ$  and  $26.2^\circ$  are correspond to graphite carbon (001) and (002) plane, indicating the formation of graphite-like material [21,22]. Other three peaks at  $44.3^\circ$ ,  $51.8^\circ$ , and  $76.2^\circ$  are assigned to the (111), (200) and (220) planes of Ni [23,24] which confirmed the  $\text{Ni}^{2+}$  ions has been transformed into Ni nanoparticles.

The XPS analysis confirmed the presence of Ni, C, O and N elements in  $\text{mNi@N-GrT}_2$  (Fig. S1a). As shown in C 1s spectra (Fig.S1b), the peak at 284.8 eV ascribe to C-C/C=C bonds which is indicative of the  $\text{sp}^2$  hybridized graphite-like carbon atom in graphene.

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