# Facile synthesis of magnetic carbon nitride nanosheets and its application in magnetic solid phase extraction for polycyclic aromatic hydrocarbons in edible oil samples

Hao-Bo Zheng [a], Jun Ding [a], Shu-Jian Zheng [a], Gang-Tian Zhu [b], Bi-Feng Yuan [a], Yu-Qi Feng [a,*]

[a] Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, China
[b] Key Laboratory of Tectonics and Petroleum Resources (Ministry of Education), China University of Geosciences, Wuhan 430074, China

## ARTICLE INFO

## ABSTRACT

In this study, we proposed a method to fabricate magnetic carbon nitride (CN) nanosheets by simple physical blending. Low-cost CN nanosheets prepared by urea possessed a highly $\pi$-conjugated structure; therefore the obtained composites were employed as magnetic solid-phase extraction (MSPE) sorbent for extraction of polycyclic aromatic hydrocarbons (PAHs) in edible oil samples. Moreover, sample pre-treatment time could be carried out within 10 min. Thus, a simple and cheap method for the analysis of PAHs in edible oil samples was established by coupling magnetic CN nanosheets-based MSPE with gas chromatography-mass spectrometry (GC/MS) analysis. Limits of quantitation (LOQs) for eight PAHs ranged from 0.4 to 0.9 ng/g. The intra- and inter-day relative standard deviations (RSDs) were less than 15.0%. The recoveries of PAHs for spiked soybean oil samples ranged from 91.0% to 124.1%, with RSDs of less than 10.2%. Taken together, the proposed method offers a simple and cost-effective option for the convenient analysis of PAHs in oil samples.

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## 1. Introduction

Carbon nitride (CN) is a kind of metal-free polymer with many advantages, such as non-toxic nature, high stability, low cost, suitable band structure and easy preparation [1]. Therefore, CN nanosheets have drawn much scientific interest due to their potential applications in solar energy conversion, photosynthesis, electrocatalysis, bioimaging, and photocatalysis [2]. Some recent studies suggest CN is promising in sample pre-treatment techniques including solid-phase extraction (SPE) and solid-phase microextraction (SPME) owing to their versatile properties such as hydrophobicity, large $\pi$-conjugated structure and polar functional groups [3–7]. Among these techniques, CN nanosheets are also magnetized and served as sorbents in magnetic solid-phase extraction (MSPE). In this mode, powdery magnetic sorbents can be uniformly dispersed into a sample solution. At this point, the contact between the sorbents and the analytes increased greatly, which is beneficial to enhance the extraction efficiency and facilitate the mass transfer of analytes. Meanwhile, the sorbent can be reversibly agglomerated and re-dispersed in sample solution by the application of an appropriate magnetic field; thus, the phase separation could be conveniently conducted [8,9]. Compared with SPE or fiber-SPME, MSPE is a time-saving method; also the high backpressure caused by tightly packed SPE cartridges can be avoided [10], which expands its application in extracting analytes from environmental or biological samples.

In the reported studies, magnetic CN nanocomposites were obtained by an *in situ* growth method. Ultrasonically dispersed CN nanosheets were used as raw materials which mixed with water-soluble iron salts, then the depositing $Fe^{2+}$ and $Fe^{3+}$ ions were converted into $Fe_3O_4$ nanoparticles with controlled growth by using ammonia as a precipitating agent [4–6]. Nevertheless, procedures involved in the chemical modification were relatively tedious. In recent years, we reported an "aggregate wrap" strategy for the fabrication of magnetic sorbents [10–14]. When certain materials are co-mixed with $Fe_3O_4$ magnetite nanoparticles (MNPs) in proper solvent, the MNPs can be trapped spontaneously in the aggregates of the materials, leading to the formation of magnetic composites. This strategy was believed to be a simple and mild method for the preparation of magnetic CN nanosheets. Furthermore, we tested the feasibility of the magnetic CN

* Correspondence to: Department of Chemistry, Wuhan University, Wuhan 430072, PR China. Fax: +86 27 68755595.
E-mail address: yqfeng@whu.edu.cn (Y.-Q. Feng).

nanosheets in MSPE method for concentration of polycyclic aromatic hydrocarbons (PAHs) in edible oil samples. PAHs, a large class of toxic, mutagenic and carcinogenic compounds originated from incomplete combustion or pyrolysis of organic matter [15–17], are widespread in the environment. Due to the lipophilic nature of these compounds, fats and oils can be heavily contaminated with these xenobiotic substances [15,18–20]. Especially for edible oils, oilseed drying processes using direct firing for production of hot air or solvent extraction during their production may be an important source of contamination in a variety of edible oils [13]. Taken together, PAHs have adverse effect on the quality of edible oils; therefore, efficient methods for determination of PAHs in edible oils are highly needed.

In this study, a simple method for preparation of magnetic CN nanosheets was established, in which no chemical modification to the raw material was required, thus the pristine surface chemistries of materials remained. In addition, a method for the analysis of PAHs in edible oil samples was established by combination of MSPE using the prepared magnetic CN nanosheets as sorbents with gas chromatography-mass spectrometry (GC/MS) analysis.

## 2. Experimental

### 2.1. Chemicals and reagents

Urea, toluene, ethanol, n-hexane, ethyl acetate (EA), ethylene glycol (EG), ethylene diamine (ED), ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium chloride (NaCl), and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent (Shanghai, China). High performance liquid chromatography (HPLC) grade acetone was purchased from Fisher Scientific Company (Fair Lawn, NJ, USA). Before use, toluene was distilled from sodium shavings under the protection of $N_2$. Purified water was obtained with a Millipore Milli-Q apparatus (Bedford, MA, USA).

PAHs standard solution was bought from J&K Chemical Ltd. (Tianjin, China). Benzo[a]pyrene-$d_{12}$ (I.S., BaP-$d_{12} \geq 98\%$) was bought from Sigma-Aldrich (St. Louis, MO, USA). The PAH standard solution contains chrysene (CHRY), benzo[a]anthracene (BaA), benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3–cd]pyrene (INPY), dibenzo[a,h]anthracene (DiahA) and benzo[g,h,i]perylene (BghiP), each at 0.2 mg/mL in methanol/methylene dichloride (1/1, v/v). The PAH stock solution and the I.S. stock solution were prepared in acetone (HPLC grade) at a concentration of 1 µg/mL. All the stock solutions were kept at $-20\,°C$ in darkness.

### 2.2. Preparation of magnetic carbon nitride nanosheets

MNPs were synthesized *via* a solvothermal process according to our previously reported method [10,12]. In detail, $FeCl_3 \cdot 6H_2O$ (5.0 g) was dissolved in EG (100 mL). NaAc (15.0 g) and ED (50 mL) were then added to the solution. After being vigorously stirred for 30 min, the homogeneous mixture was sealed in a teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to $200\,°C$ and maintained for 8 h, and then allowed to cool to room temperature. The product was magnetically collected, and washed with water/ethanol for several times. The washed product was then vacuum-dried at $60\,°C$ for 6 h.

CN nanosheets were synthesized *via* pyrolysis of a low-cost and abundant precursor of urea. Briefly, 20.0 g of urea was put in a porcelain crucible with a cover and heated under static air at $550\,°C$ for 4 h with a ramping rate of $2.5\,°C/min$. The resultant light yellow powder was washed with deionized water and acetone for several time then dried in a vacuum oven at $60\,°C$ [1].

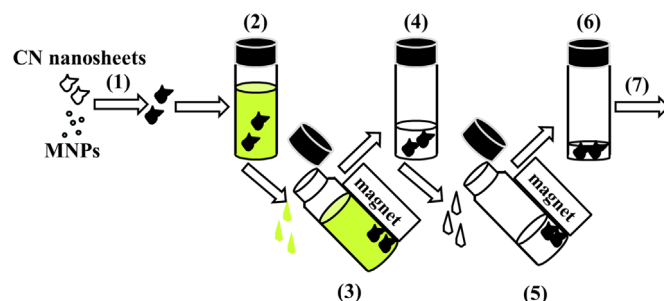Magnetic CN nanosheets were prepared by simple physical



**Fig. 1.** Schematic of proposed MSPE method: (1) preparation of magnetic CN nanosheets by physical blending, (2) sample loading and vortexing, (3) decanting, (4) washing, (5) decanting, (6) eluting, (7) GC/MS analysis.

blending. Briefly, CN nanosheets (500 mg) and MNPs (500 mg) were added to a mortar and ground into homogeneous fine powder. The powder was used for MSPE.

### 2.3. Sample preparation

Edible oil samples were purchased from a local supermarket in Wuhan (China). 20.0 g oil sample was weighted into a 100-mL volumetric flask, and appropriate volumes of PAHs standards (1 µg/mL) were added to the flask. Then the sample was dilute with n-hexane to the volume. A schematic representation of proposed MSPE method is shown in Fig. 1. Briefly, 10 mL oil sample solution was added into a 15-mL glass vial containing 40 mg magnetic CN nanosheets. Then the mixture was vortexed vigorously for 1.0 min. By applying an external magnet, the magnetic CN nanosheets were attracted toward the magnet rapidly. After discarding the supernatant, 1 mL n-hexane was added, and the mixture was vortexed for 0.5 min. The supernatant was discarded with the aid of an external magnet. Then PAHs were eluted from the magnetic CN nanosheets by 150 µL toluene with 1.0 min vortexing. Finally, 1 µL of desorption solution was used for the analysis by GC/MS.

It is worth noting that we employed two ways for the addition of internal standard in our experiments. When investigating the effect of experimental conditions on extraction performance of magnetic CN nanosheets toward the target compounds, the internal standard was added into the eluate at a level of 100 ng/mL to minimize the deviation of GC/MS analysis. When we were validating the proposed analytical method, the internal standard was added into the edible oil sample at a level of 10 ng/g before MSPE.

### 2.4. Instrumentation and analytical conditions

The MNPs, CN nanosheets and magnetic CN nanosheets were characterized using a JEM-2100F transmission electron microscope (TEM, JEOL, Japan). Magnetic characterization was carried out using a Physical Property Measurement System (PPMS, Quantum design) with fields up to 15,000 Oe a temperature of 300 K. Fourier transform infrared (FT-IR) spectra of the materials were determined by Thermo Nicolet AVTAR-360 (Madison, USA).

The GC/MS analysis was performed on a Shimadzu GCMS-QP2010 plus which was equipped with an AOC-20i+s autosampler (Kyoto, Japan). The GC separation was achieved on a fused silica capillary column Rtx®-5ms, crossbond® 5% diphenyl/95% dimethyl polysiloxane, 30 m (length) × 0.25 mm (i.d.) × 0.25 µm (film thickness) purchased from Restek (Bellefonte, USA). The oven temperature was held at $70\,°C$ for 2.0 min, then increased to $190\,°C$ at a rate of $15\,°C/min$ and held for 1.0 min, then increased to $260\,°C$ at a rate of $10\,°C/min$ and to $320\,°C$ at a rate of $5\,°C/min$. Finally it was held at $320\,°C$ for another 10.0 min. The injection volume was 1.0 µL in splitless mode. Helium (purity ≥ 99.999%)