



Electrochemical detection of trinitrotoluene in water samples based on a natural mineral attapulgite modified electrode[☆]



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ABSTRACT

This study reports an electrochemical approach for an assay of trinitrotoluene (TNT) in water samples. This assay is based on the electrochemical reduction of TNT at a natural mineral, attapulgite, modified glassy carbon (attapulgite/GC) electrode. To detect TNT, TNT is first accumulated on an attapulgite/GC electrode by holding the electrode at a constant potential of 0 V versus Ag/AgCl for 40 s in an aqueous TNT solution. Next, the attapulgite/GC electrode with accumulated TNT is transferred to a fresh PBS solution (0.1 M, pH 7.0, without TNT), where the TNT reduction current at -0.36 V versus Ag/AgCl in a linear sweep voltammogram (LSV) shows a linear response to TNT concentrations in the aqueous solution from 1 to 200 ppb with a correlation coefficient of 0.998 and a detection limit of 0.2 ppb at a signal/noise (S/N) of 3. Moreover, the attapulgite/GC electrode displays high stability, good anti-interference ability to certain common interferents in real water samples, and reliable detection precision. Along with the abundance, low price, and environmental friendliness of attapulgite, the developed electrochemical sensor for the TNT assay has great potential for the practical determination of TNT levels in real water samples.

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1. Introduction

2,4,6-Trinitrotoluene (TNT) is one of the most environmentally hazardous chemicals; even trace quantities of TNT can cause detrimental effects to the environment and human health [1–8]. Soil and water at sites where TNT has been manufactured, stored, or extensively used and tested are physically disturbed and persistently corrosive and contaminated. Furthermore, the environment contaminated with TNT is difficult to be remediated because of the chemically inert nature of TNT [9,10]. TNT is also a biological hazard, as environmental TNT is a mutagen and carcinogen that can be absorbed by the skin and gastrointestinal tract. Therefore, TNT is toxic to human health, causing anemia as well as abnormal functioning of the human liver, spleen, circulatory and immune systems, and can even cause cancer [5,11,12]. The U.S. Environmental Protection Agency recommends a maximum allowable level of TNT in drinking water to be 2 ppb [13]. Therefore, analytical methods used for sensing TNT are required to achieve a detection limit lower than 2 ppb.

Many conventional analytical methods have been used for detecting and assaying TNT, including high-performance liquid chromatography (HPLC), which is the approach recommended by the Environmental Protection Agency for assaying TNT [13], gas chromatography coupled with mass spectrometry (GC–MS) [14], and ion mobility spectroscopy (IMS) [15], etc. Along with these conventional methods, recently, several new techniques have been developed for detecting and assaying TNT, including colorimetry [16], surface-enhanced Raman spectroscopy (SERS) [17,18], fluorescence spectroscopy [19,20], and luminescent spectroscopy [21], among others. All of these methods enable a sensitive assay of TNT but require bulky expensive instruments, long assay time, and well-trained laboratory technicians. Thus, there is a need for a compact, low-cost, and simple approach for detecting and assaying TNT in the field.

An electrochemical approach can meet this need. Electrochemical techniques have many advantages, such as high selectivity, low detection limit, rapid analysis, portability, ease of use, and low cost [22–29]; in addition, these advantages can be employed for performing a TNT assay with high fidelity.

Electrochemical detection of TNT is based on the electrochemical reduction of the nitro group ($-\text{NO}_2$) in the TNT molecule to an amine group ($-\text{NH}_2$) [30]. The rate and extent of the electrochemical reduction of the nitro group significantly depends on the nature of the electrode material. The ideal electrode material should adsorb TNT and catalyze the electrochemical reduction of TNT. Many types of materials

[☆] This work is dedicated to Professor Hong-Yuan Chen on the occasion of his 80th birthday and in honor of his contributions to electroanalytical chemistry.

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have been investigated for the electrochemical reduction of TNT, including various carbon materials (such as glassy carbon [22], carbon nanotube [22], graphene sheet [19,23,25], nitrogen-doped graphene quantum dots [24], and boron-doped diamond [31]), gold [32], silica [33], and metal-oxides [34,35], etc. It has been determined that electrode materials with high adsorption ability for TNT can improve TNT detection sensitivity. For example, the electrochemical activity of TNT reduction on the ionic liquid-modified graphene (IL-graphene) was 51.4-folds higher than that on glassy carbon (GC) [22] because IL-graphene has a strong tendency to accumulate nitroaromatic compounds on its surface via π - π interaction between the two-dimensional planar structure of graphene and the nitroaromatic structure [36]. Moreover, the high electronic conductivity of IL-graphene can facilitate electron transfer during the electrochemical reaction process. Our recent work demonstrated that the doping of nitrogen in graphene can significantly enhance its electrochemical activity for TNT reduction, as indicated by the fact that the amplitude of the cathodic peaks of TNT reduction on nitrogen-doped graphene quantum dots (N-GQDs) is ~ 6.5 times higher than that obtained on graphene quantum dots (GQDs) [24]. The higher electrochemical activity of the N-GQDs for TNT reduction is ascribed to the enhanced TNT adsorption ability and improved electronic characteristics of N-GQDs. Our theoretical calculation indicated that nitrogen doping can reduce the energy gap of HOMO-LUMO (H-L gap) of the N-GQDs as well as enhance their electrochemical activity and electrical conductivity [24]. Moreover, nitrogen doping causes the delocalization of the highest unoccupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) spatial, leading to an improved adsorption of TNT. However, the synthesis of the N-GQDs is not straightforward and usually requires tedious procedures. Moreover, they cannot be synthesized in scalable and reproducible quantities.

Herein, we report the use of the nanometer-sized natural mineral, attapulgite, as a novel substrate to accumulate TNT and as a unique electrode material to electrochemically detect TNT. Attapulgite is a hydrated magnesium silicate consisting of double chains of Si-O, which are further linked by a layer of octahedral magnesium atoms in 6-fold coordination, forming a network of strips that are joined together only along the edges [37–46]. The natural mineral has advantages of non-toxicity, good biological compatibility, low cost, abundance in nature, and in particular, high surface area ($169 \text{ m}^2/\text{g}$ [38]), and has been extensively used in the fields of pharmaceutical industries [39,40], nanocomposite preparations [42], environmental absorbents [46], catalyst supports [37,43–45], etc. Our results indicate that TNT can be strongly adsorbed on the surface of attapulgite and exhibits high electrochemical reduction characteristics. The dependence of the electrochemical reduction current on TNT concentration can be used to sensitively sense TNT in water samples as low as 0.2 ppb, which is considerably lower than the maximum allowable level of TNT (2 ppb) in drinking water recommended by the U. S. Environmental Protection Agency [13].

2. Experimental section

2.1. Fabrication of the attapulgite modified electrode

Prior to use, attapulgite (Jiuchuan Clay Company, Xuyi, China) was purified according to the previously reported procedures [41]. In brief, it was ground in a KM-10 planetary mill (Nanjing University Instrument Plant, China) at 800 rpm for 2 h. The ground sample (1 g) was then treated with 100 mL of HCl (8 M) at 80°C for 2 h and cooled to ambient temperature. The suspension was filtered through a $0.65\text{-}\mu\text{m}$ microporous nylon membrane and thoroughly washed with double distilled water. The product was dried at 80°C for 12 h in air to obtain the purified sample (white powder). X-ray (XRD) diffraction patterns of the purified attapulgite show peaks at ~ 8.5 , 13.9 , 19.8 , and 28.1° (Fig. 1A), which are characteristic patterns of pure attapulgite and correspond to (110), (020), (400), and (040) plane, respectively. All of these diffraction peaks are the same as those of the reference patterns collected for attapulgite (JCPDS 29-0855). The transmission electron microscopic (TEM) image indicates that attapulgite has a rod-like morphology with an average size of $20\text{--}50 \text{ nm}$ in width and $0.5\text{--}1 \mu\text{m}$ in length (Fig. 1B). The zeta potential (ζ) of the purified attapulgite was measured to be approx. $-28 \pm 2 \text{ mV}$. The polydispersity index (PDI) of the attapulgite was estimated to be ~ 0.35 based on dynamic light scattering (DLS) measurements.

Prior to fabricating the modified electrode, the glassy carbon electrode (GC, 3 mm in diameter, CH Instruments) was sequentially polished with metallographic abrasive paper (No. 6) and slurries of 0.3 and $0.05 \mu\text{m}$ alumina to create a mirror finish. The GC electrode was then sonicated for approximately 1 min in absolute ethanol and then double-distilled water to remove traces of alumina grit from the electrode surface. After being rinsed thoroughly with double distilled water, the GC was dried in air at ambient temperature. For the fabrication of the attapulgite modified GC electrode, attapulgite was first dispersed in phosphate buffer solution (PBS, pH 7.0) by ultrasonication (at a concentration of 1 mg/mL). The suspension ($8 \mu\text{L}$) was later mixed with Nafion ($2 \mu\text{L}$), and finally the mixture ($5 \mu\text{L}$) was cast onto the surface of the GC electrode with a microsyringe. The solvent was allowed to be evaporated in air at ambient temperature. This electrode is denoted as the attapulgite/GC electrode. The scanning electron microscopic (SEM) image shows that the attapulgite can be uniformly distributed on the electrode surface and form a layer of even film (Fig. 1C). This feature is very useful for the nanostructures being used as a substrate for the adsorption of TNT because the uniform nanostructure can significantly increase the effective surface of the electrode and enhance the loading of TNT, thereby improving the electrochemical response. The attapulgite on the surface of the GC electrode is fairly stable because the electrochemical response of the attapulgite/GC electrode after 200 cycles of continuous scanning in PBS remained almost unchanged except for a slight decrease at the initial five cycles (decrease by

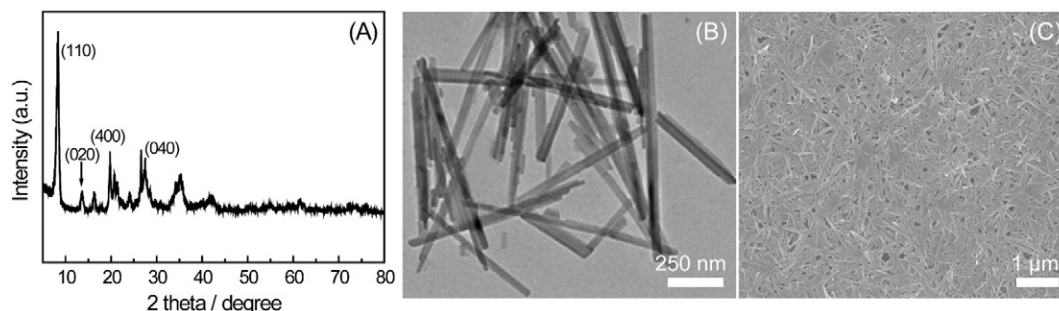


Fig. 1. Typical XRD patterns (A), and TEM image of the purified attapulgite (B). (C) The SEM image of the attapulgite modified glassy carbon electrode surface.

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