

# Electrochemical behavior and voltammetric determination of ammonium dinitramide using a graphene film modified glassy carbon electrode



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## ABSTRACT

A graphene modified glassy carbon electrode (GMGCE) was developed to investigate the electroreduction of ammonium dinitramide (ADN) using cyclic voltammetry and differential pulse voltammetry techniques. ADN was reduced with higher rates at low potentials on GMGCE compared to GCE. The GMGCE exhibited fast response towards ADN with a detection limit of  $2.0 \times 10^{-6}$  M and a linear range of  $2.5 \times 10^{-6}$  to  $8.5 \times 10^{-4}$  M. The possible interference from several common ions was tested. The proposed method was successfully applied in the determination of ADN in water samples.

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## 1. Introduction

Ammonium dinitramide (ADN) [Scheme 1](#) is a powerful, environmental-friendly oxidizer developed in 1990s for use in composite solid rocket propellants [1–4]. It is an ionic compound containing the ammonium ion and a new oxide of nitrogen, the dinitramide anion ( $-N(NO_2)_2$ ). Dinitramides have been considered a promising candidate for replacing today's dominant oxidizer, ammonium perchlorate. However, stability issues have troubled the development of an ADN based fuel [5].

The discovery of graphene (GR) in 2004 by Geim and Novoselov [6] has generated great interest among researchers to explore their unique electrical, physical, mechanical and chemical properties to develop high performance devices. Researchers have been exploring the potential of graphene in a wide range of applications such as, nanoelectronics [7,8], sensors [9–11], field emission [12,13], displays [14], batteries [15,16], polymer matrix composites [17], nanoscale reactors [18] and electrodes [19,20].

Graphene including two-dimensional nanostructure hold great promise for the development of miniaturized chemical and biological sensors because of (1) greater adsorptive capacity due to large

surface area to volume ratio, (2) ability to tune electrical properties of the nanostructure by adjusting the composition and size and (3) the ease of configuration as chemiresistors, field effect transistors, potential integration with low-power microelectronics to form complete systems with microprocessor and wireless communication units [21].

Recently, the redox chemistry of dinitramide for the aqueous solutions of potassium dinitramide and dinitramidic was reported by Santhosh et al. [22]. In this work, for the first time, the electrochemical behavior of the ADN was investigated by using cyclic voltammetry and chronoamperometric technique at surface of GMGCE. Finally, the analytical performance of this sensor for determination of ADN in water samples is evaluated by differential pulse voltammetry.

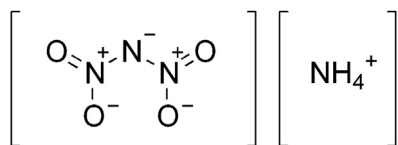
## 2. Experimental

### 2.1. Chemicals and reagents

Graphite flake was purchased from Sigma-Aldrich. All other chemicals were analytical grade and purchased from Sigma or Merck. ADN was synthesized and characterized by spectroscopic methods and elemental analysis, as reported elsewhere [23]. Deionized water was used to prepare all aqueous electrolyte solutions.

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**Scheme 1.** Structure of ammonium dinitramide.

## 2.2. Synthesis of graphene oxide

Graphene oxide was prepared from the graphite powders by an improved hummers method described by Marcano et al. [24]. Briefly, a 9:1 mixture of concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  (360:40 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt equiv) and  $\text{KMnO}_4$  (18.0 g, 6 wt equiv), producing a slight exotherm to 35–40 °C. The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (~400 mL) with 30%  $\text{H}_2\text{O}_2$  (3 mL). The mixture was centrifuged and the supernatant was decanted away. The remaining solid material was washed with de-ionized water and centrifuged repeatedly until the supernatant became neutral to remove remaining impurities. The material remaining after this extended, multiple-wash process was filtered. The dry form of graphite oxide was obtained by drying the finally obtained cake at 45 °C for 24 h.

## 2.3. Electrodeposition of graphene from graphene oxide

The electrodeposition of graphene from graphene oxide was achieved by methods similar to those reported by Guo et al. [25]. In our method, the applied potential was cycled between 0 and –1.4 V vs Ag/AgCl (3 M NaCl) to reduce graphene oxide using a scan rate of  $0.05 \text{ V s}^{-1}$  in an aqueous solution containing  $1 \text{ mg mL}^{-1}$  of graphene oxide and  $0.05 \text{ M Na}_2\text{HPO}_4$ . The electrogenerated graphene deposits onto the glassy carbon electrode (GCE) surface. The contents of the electrochemical cell were stirred using a magnetic stirrer during the experiment.

The effective area of the electrode modified with graphene was obtained by cyclic voltammetry using  $5 \text{ mmol L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$  as a probe at different scan rates. For a reversible process, the following equation exists [26]:

$$I_{pc} = 2.69 \times 10^5 n^{3/2} AD^{1/2} C v^{1/2} \quad (1)$$

where  $I_{pc}$  refers to the cathodic peak current,  $n$  is the total number of electron transfer,  $A$  is the surface area of the electrode,  $D$  is the diffusion coefficient,  $C$  is the concentration of  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $v$  is the scan rate. For  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $n = 1$ ,  $D = 7.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  [27], the effective area can be calculated from the slope of the  $I_{pc} \sim v^{1/2}$  relation. The GMGCE surface was found  $0.159 \text{ cm}^2$ .

## 2.4. Apparatus

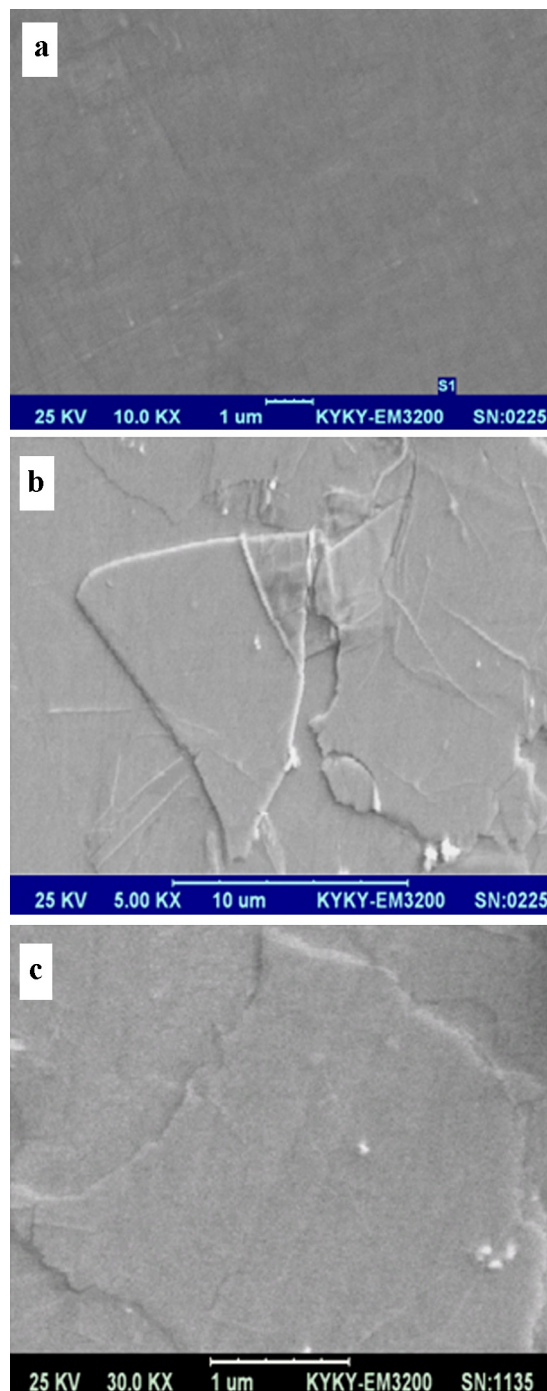
Electrochemical measurements were carried out with a  $\mu\text{Autolab Type III/FRA2}$  computer-controlled potentiostat and run with the General Purpose Electrochemical System (GPES) software. A three-electrode system, including graphene modified working electrode and an Ag/AgCl reference electrode and platinum counter electrode was employed. A glassy carbon disk electrode (Metrohm) with a geometrical area of  $0.0314 \text{ cm}^2$ , bare or modified, was used as working electrode. The bare working electrode was polished, cleaned, sonicated, rinsed with water, and then dried under nitrogen. All the experiments were carried out with the electrochemical cell immersed in a thermostat at  $25 \pm 1 \text{ }^\circ\text{C}$ . All solutions used in voltammetric experiments were purged with nitrogen for at least 10 min before measurements commenced, and then the electrochemical cell was kept under a positive pressure of nitrogen at all times. Background currents for each supporting electrolyte

solutions were recorded and later corrected with the current values obtained with analytes. The scanning electron micrographs were obtained using a field emission SEM (FEI Sirion).

## 3. Results and Discussion

### 3.1. Properties of the GMGCE

For initial studies, a GMGCE was prepared by cycling the potential between 0 and –1.4 V (vs Ag/AgCl) for 10 cycles to ensure a full coverage of graphene using the procedure described in the experimental section. Fig. 1a, b and c show scanning electron micrographs of bare GCE and GMGCE. As shown in Fig. 1b and c graphene



**Fig. 1.** SEM micrographs of electrode surfaces (a) bare GCE, (b,c) GMGCE.

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