



# A graphene oxide nanosheet-modified Ti nanocomposite electrode with enhanced electrochemical property and stability for nitrate reduction

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## HIGHLIGHTS

- A graphene oxide nanosheet-modified Ti electrode was prepared by hydrothermal method.
- Graphene oxide in Ti-GO electrodes improved electrochemical activity and stability.
- The electrode performed higher electrochemical activity than typical electrodes.
- The electrode showed higher stability than Cu-Zn electrode in repeated experiments.
- An ionic strength affected electrical-double-layer of GO mechanism was proposed.

## ARTICLE INFO

### Keywords:

Hydrothermal method  
Graphene oxide modified electrode  
Electrochemistry  
Nitrate reduction  
Current efficiency

## ABSTRACT

A convenient and simple hydrothermal method was used to prepare a graphene oxide nanosheet-modified Ti nanocomposite (Ti-GO) electrode with highly stable nitrate reduction activity. The samples' electrochemical activity for nitrate reduction was studied under 120 min electrolysis. The results demonstrated that Ti-GO showed higher nitrate reduction efficiency than Ti and Cu electrodes, and comparable to Cu-Zn electrode due to its surface GO modification. The low current efficiency of the electrode (0.0015) was attributed to its high selectivity of ammonia. The specific addition of NaCl resulted in efficient by-products removal and increased reduction efficiency. Electrochemical test showed that the Ti-GO electrode has stronger electrochemical activity and much higher real surface area than that of Ti electrode. The Ti-GO electrode exhibited excellent durability without apparent variation in the electrolytic property was observed after 5 treatment cycles (10 h in total), while only slight decrease in the reduction efficiency was noted (Standard Deviation = 1.72). In conclusion, the developed Ti-GO electrode showed excellent electroreduction behavior and promising results for electrochemical nitrate reduction.

## 1. Introduction

Electrochemical methods have already succeeded in wastewater treatment because they are cheap, rapid, direct and efficient [18,22,27]. Nitrate as a nutrient has the potential to form nitrosamines [19], and has become a widespread environmental problem in water resources due to the massive use of fertilizers in agriculture, the emission of large amounts of domestic sewage and industrial waste, and inefficiently treated wastewater [34]. In recent decades, electrochemical reduction has shown great potential as a useful and environmentally-friendly approach for nitrate removal [26,31,42]. Cathode materials significantly affect the reduction efficiency of nitrate [29]. High-property, hard-passivation electrodes are needed. Currently,

the most commonly used cathodes are metal materials and alloy materials, such as Fe, Cu, Ti and Cu-Zn [5,30,59]. To improve property, the electrode surface is modified or coated by metal atoms and conducting materials, such as Ni, Cu, Pt, B, Rh, Pb and graphene [15,49,56,63]. While these modification and coating have significantly enhanced property, there is a limited stability for repeated applications.

As a conducting material, graphene has attracted significant interest owing to its excellent material parameters, such as mechanical stiffness, elasticity, strength, and very high thermal and electrical conductivity [20,21,41]. Graphene and graphene-based materials offer a high specific surface area ( $2965 \text{ m}^2 \text{ g}^{-1}$ ) [6,52], the ability to sustain large current densities [40], and unique electrical and optical properties, which mean it is applied widely in photodetectors [41], sensing [35],

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energy conversion [32], photocatalysis [23] and electrochemistry [1,4]. The outstanding heat dissipating ability [3] and electrical tunability of graphene, based on its unusual band structure, optimize its electrical conductivity, which is important for its application in conducting electrodes [2,24]. In addition to the formation of electron and hole “puddles” observed on graphene [38,52,55], the basal planes and edge of graphene play significant roles in the performance of graphene-based electrode materials [52]. Öznülür et al. [42] recently report a graphene-modified Cu cathode with high electrochemical activity by a chemical vapor deposition (CVD) method, but repeated stability was not studied. The data supports the feasibility of a graphene-modified metal electrode for electrochemistry.

An electrical double layer (EDL) is a layer containing solvent molecules and solvated ions, and is typically one to tens of nanometers thick, depending on the solution concentration [51]. With many important processes in electrochemical reactions, such as ion desolvation and charge transfer [51], EDLs play a key role in the understanding of the interfacial structure of charged surfaces in aqueous solutions [64]. The space of EDL affects the ions in it and then affects the reaction activity. The EDL of GO can be compressed under high ionic strength [8]. Oxygen-containing groups (GO, reduced graphene oxide,  $-SO_x$ ,  $-NO_x$  and  $-PO_x$ ) or adjacent defects, with the ability to modify the electronic structure of graphene [11]. The oxygen-containing groups, including hydroxyl and carbonyl, are usually considered as possible active sites in different reaction system [8,11,14]. With graphene placed on the surface of a metal, it is expected that there will be electron transfer between graphene and the metal, which may enhance the adsorption and reactions of molecules on the surface of graphene instead of on the metal [11]. Moreover, graphene with stability for harsh conditions, such as high temperature, strong oxidation, and acid and alkaline conditions [8], can protect the metal substrate in the above conditions [11]. Therefore, when GO was modifying on the surface of metal cathodes, it would not only increase the surface area of cathodes and modify the electronic structure, but also provide more active sites for the adsorption of molecules during reactions.

The synthesis methods of graphene-modified plate-electrodes mainly include electrodeposition and chemical vapor deposition (CVD) [42,61,62]. However, special instruments and rigorous conditions are often required in CVD, such as a experimental temperature higher than 500 °C, the atmosphere of  $N_2$  or  $H_2$  or Ar, and a big experimental area for the quartz chamber and gas cylinder [33,42]. In an electrodeposition process, the typical substrate material, such as glassy carbon electrodes and Cu foils, can limit the practical application of that method to some degree, resulting from their small scale [36,62,63]. Hydrothermal method is a commonly used technique in powder and granular materials synthesis [17,39]. It can be performed under mild conditions with temperature below 200 °C in an oven, which is a necessary equipment in laboratories. Therefore, a new synthesis method use hydrothermal technique for plate-materials not only provide a simple and convenient preparation approach, but also gain a potential pathway for the synthesis of plate-electrodes with large scale in which enhance their practical application potential.

This study aimed to design and synthesize a graphene-modified plate-substrate electrodes with large scale, high electrochemical activity and long time stability under mild conditions. On the basis of study on nitrate reduction by the Ti-GO electrode and by-products oxidation under present of NaCl, the nitrate reduction behaviors of the electrode were discussed to explain how the GO affected the property of the Ti-GO electrode. Field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) were investigated to provide explanation of GO modification clearly. Cyclic voltammetry (CV) and chronoamperometry (CA) were measured to gain explore of the activity and stability of electrodes. The property of the electrode was assessed by the comparison of commonly used cathodes. To the best of our knowledge, this study is the first report on the hydrothermal synthesis of graphene oxide nanosheet-modified Ti plate-nanoelectrode

possessing a high percentage of oxygen-containing groups and defects, and showing an enhanced electrochemical nitrate reduction activity and stability.

## 2. Experimental

### 2.1. Synthesis of the Ti-GO electrode

Titanium substrates (100 mm × 25 mm) were polished using sandpaper (150 mesh) and washed with deionized (DI) water, then dried naturally. Graphene oxide (GO) was prepared from flake graphite (Sigma-Aldrich) using the modified Hummer's method [53]. To prepare Ti-GO electrodes, GO nano-powder was first dispersed in 150 mL of DI water by ultrasonication. Followed by the addition of 0.5 mg mL<sup>-1</sup> sodium dodecylbenzene sulfonate (SDBS) as the surfactant and then poured into the polytetrafluoroethylene. Ti-GO electrodes were then fabricated by a simple hydrothermal method: preprocessed Ti substrates were dipped into the GO dispersion, heated at ~100 °C for approximately 2 h, and then dried naturally. The available area of electrodes used in this study were 80 mm × 25 mm (20 cm<sup>2</sup>).

### 2.2. Characterizations and electrochemical tests of the Ti-GO electrode

The morphology of the as-synthesized Ti-GO electrode was characterized by field emission scanning electron microscopy (FESEM, Merlin, Germany). The surface distribution of elements Ti, C and O on the Ti-GO electrode was studied using energy dispersive spectroscopy (EDS). The surface property of the electrodes was characterized using X-ray photoelectron spectroscopy (XPS, Thermofisher 250Xi, America). Cyclic voltammetry (CV) and chronoamperometry (CA) tests were performed with a CHI660D electrochemical workstation (CHI, Shanghai) at room temperature. In the individual 10 mL reaction volume consisted of 100 mg L<sup>-1</sup>  $NO_3^-$ -N and 0.5 g L<sup>-1</sup>  $Na_2SO_4$ . Ti-GO, Pt and Ag/AgCl electrodes were used as working electrode, counter electrode and reference electrode, respectively. The CV of the Ti-GO electrode was measured at a scan rate of 10 mV s<sup>-1</sup>. The real surface area and stabilities of a Ti electrode and the Ti-GO electrode for nitrate reduction were measured with potential from 0 V to -0.7 V.

### 2.3. Electroreduction experiments

Electrochemical property of the Ti-GO electrode in nitrate contaminated water was investigated in a 100 mL cylindrical undivided electrolytic cell as shown in Fig. S1. Electrochemical experiments were performed using a DC power supply (GD1795-5S, China) and detailed experimental parameters were provided in Table S1. To compare the nitrate reduction efficiency of typical cathodes, Ti, Cu and Cu-Zn plates were also used as cathodes. Electrochemical profiles of the electrodes as a function of electroreduction time were determined in terms of nitrate concentration variation of the electrolyte. In each experiment,  $Na_2SO_4$  was used as the supporting electrolyte. At predetermined time intervals, 1.5 mL sample was collected for the analysis of nitrate-N ( $NO_3^-$ -N), nitrite-N ( $NO_2^-$ -N) and ammonia-N ( $NH_4^+$ -N) using a spectrophotometer (DR 6000, USA). As the little production of other by-products, such as hydroxylamine and hydrazine [10,25], the total nitrogen (TN) concentration in electrolyte was assumed as the summation of nitrate-N, nitrite-N and ammonia-N. The potential was recorded at beginning and ending of every electrolysis.

To determine the electrochemical activity, electrochemical reduction efficiency (ERE, %) of nitrate for different cathodes was calculated by Eq. (1) [44]. Furthermore, average current efficiency ( $E_A$ ) of TN in the electrochemical system, quantifying the current efficiency of nitrogen production, was calculated according to Eqs. (2) and (3) [16]. The selectivity of product X ( $S_x$ ) was evaluated by Eq. (4).

$$ERE (\%) = c_{NO_3^- - N, (r-i)} / c_{NO_3^- - N, 0} \times 100\% \quad (1)$$

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