



# Layered titanate nanosheets as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II)

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## ABSTRACT

A highly sensitive and selective Hg(II) sensor has been developed by using layered titanate nanosheets (TNs) as an enhanced sensing platform. The TNs with exchangeable sodium cations located in the interlayer are prepared by a facile hydrothermal route. The as-formed sodium titanate nanosheets (Na-TNs) exhibit a porous nanoarchitected network. The surface structure and electrochemical performance were systematically investigated. Such a nanostructured TNs-based platform, as a typical cation-exchange material, is highly efficient to capture Hg<sup>2+</sup>, which dramatically facilitates the enrichment of Hg<sup>2+</sup> onto their surface and realizes the stripping voltammetric detection of mercury ions with a remarkably improved sensitivity and selectivity. The detection limit was found to be as low as 5 ppt (S/N = 3), much below the guideline value from the World Health Organization (WHO). The interference from other heavy metal ions such as Cd<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> ions associated with mercury analysis could be effectively inhibited. Toward the goal for practical applications, the sensor was further evaluated by monitoring Hg(II) in real mushroom samples.

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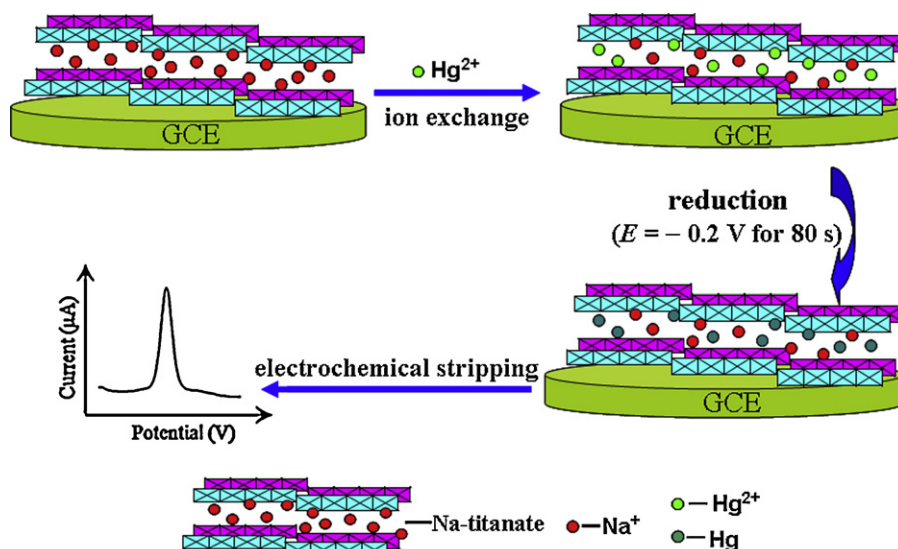
## 1. Introduction

Mercury, a neurotoxicant, is considered to be one of highly toxic heavy metal ions [1–4]. Even a trace amount of mercury intake can induce serious health problems, like kidney and respiratory failure, damage in the gastrointestinal tract and nervous system [5]. Obviously, the development of a rapid determination and reliable quantification of a trace level of mercury has become increasingly important for public security and health protection. Various methods, including gas chromatography–atomic fluorescence spectrometry [6], atomic absorption spectrometry [7–9], atomic fluorescence spectrometry, and isotope dilution cold vapor inductively coupled plasma mass spectrometry [10,11] have been reported for monitoring Hg(II). However, these methods have several disadvantages such as costly instrumentation, complicated sample preparation, and the need for well-trained operators. Therefore, there is a growing need for developing a low-cost and portable sensing system for on-site analysis of trace mercury.

Electrochemical analysis, particularly stripping voltammetry, has attracted significant interests for trace analysis of heavy metals, due to their excellent sensitivity, short analysis time, low power consumption and cheap equipments [12–21]. The stripping

voltammetry (including the preconcentration process of the target first and then followed by stripping step) provides an efficient and reliable way to detect mercury at low concentration. The efficient preconcentration of the targets onto a certain substrate plays a great role for stripping analysis. Many solid electrodes (e.g. gold, gold wire, platinum and chemically modified electrodes) in particular gold electrode, were found to be a superior substrate as a working electrode because of its high affinity for mercury, which could enhance the preconcentration effect [9,22–24]. However, the undesirable formation of gold–amalgam may destroy the surface feature of the electrodes [25]. To achieve reproducibility, complex electrochemical and mechanical pretreatments have to be adopted to refresh the gold electrodes. Recently, nanotechnology-based sensors have become one of the most active areas in environmental analysis [26–28]. Owing to unique capabilities, such as high affinity for mercury, renewable electrode surface, large surface area, and increased mass transport, nanosized Au particles (AuNPs) assembled on various supports as modified electrodes have emerged as a promising alternative for the electroanalysis of Hg(II) [28,14,24]. For instance, Compton et al. loaded AuNPs onto glassy carbon microspheres [14]. Raj and Jena constructed AuNPs-based ensembles onto the silicate-based network by a colloidal chemical approach [24]. Recently, our group successively constructed a bimetallic Au–Pt inorganic–organic hybrid, and monodispersed AuNPs–graphene composite, respectively, as a highly sensing platform for the detection of Hg [18,19]. These studies demonstrated

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**Scheme 1.** Schematic illustration for the principle of electrochemical stripping analysis of Hg(II) ion coupled with the cation exchange using Na-TNs/GCE.

that AuNPs-based ensembles combined with stripping voltammetry could well meet the requirements of determination of trace mercury ions. Despite some outstanding achievements obtained, the complicated procedures and inconvenience in the fabrication of platform have obviously obstructed their sensing applications. To meet the fast-growing demands for on-site environmental monitoring of trace mercury ions, currently, it is still a great challenge to develop a newly alternative and high-performance sensing platform in a simple fashion.

Layered titanates are typical inorganic cation exchange materials, where  $\text{TiO}_6$  octahedral join each other to form layers carrying negative charge and sodium cations located between layers are exchangeable [29–31]. Owing to the preferentially cation-exchangeable property, layered titanates have been demonstrated as desirable intelligent decontamination materials [29,32–35]. In recent years, they have been widely used for the removal of heavy metal ions and radioactive cations in wastewaters by ion-exchange process [32–34]. This feature inspires us to construct layered titanates-based sensing platform for the detection of Hg(II). It is expected that the resulting sensor can dramatically facilitate the enrichment of mercury ions and realize their stripping voltammetric detection. Herein, layered sodium titanates (Na-titanate) nanosheets have been synthesized as the powerful platform. This new electrochemical sensing protocol involves the facile preparation of layered titanates nanosheets modified glassy carbon electrode (labeled as TNs/GCE), subsequent intercalation of Hg(II) by an ion-exchange process, then followed by electrochemical deposition of Hg, and final electrochemical stripping detection of deposited Hg (Scheme 1). Nowadays, titanate-based materials are mainly focused on their decontamination applications. To the best of our knowledge, this is the first report on an ultrasensitive Hg(II) sensor utilizing layered titanates as powerful sensing platform. Encouragingly, the combination of the inorganic layered titanates materials, ion exchange, and stripping voltammetry would open up new opportunities for fast, simple and sensitive analysis of mercury ions.

## 2. Experimental

### 2.1. Apparatus

A conventional three-electrode system comprising a platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE)

as the reference and a modified or unmodified glassy carbon electrode (GCE,  $\varphi = 2$  mm) as the working electrode. Before use, the basal GCE was polished to a mirror finish using 1.0, 0.3 and 0.05  $\mu\text{m}$  alumina slurries. After each polishing, the electrode was sonicated in ethanol and deionized water for 5 min, successively, in order to remove any adsorbed substances on the electrode surface. Finally, it was dried under nitrogen atmosphere ready for use. The general morphology of the products was characterized by the scanning electron microscopy (SEM, JSM-5600). X-ray powder diffraction (XRD) measurements of all the samples were collected with a Rigaku Ultima III X-ray diffractometer with high-intensity  $\text{Cu K}\alpha_1$  irradiation ( $\lambda = 1.5418$  nm).

### 2.2. Reagents

$\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$  (98%) was purchased from Fluka. NaOH and other chemicals were of analytical-reagent grade and used without further purification. Deionized water (18.2  $\text{M}\Omega$  resistance) was used throughout. All experiments were carried out at ambient temperature.

### 2.3. Preparation of titanates nanosheets (TNs) and the modified electrode

Titanate nanosheets in this study were prepared via a hydrothermal reaction between a concentrated NaOH solution and inorganic titanium salt [29,32]. Typically, a solution of 10.7 g  $\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$  in 80 mL of water was mixed with 200 mL of 15 M NaOH solution. The mixture was then autoclaved at 200  $^\circ\text{C}$  for 48 h to yield sodium titanate. The as-prepared Na-titanates were rinsed with water and dried at room temperature for further experiments.

The as-prepared titanate powder (35.0 mg) was dispersed into 1 mL deionized water to form a homogenous dispersion under mild ultrasonication for 2 h. Subsequently, 10  $\mu\text{l}$  of the dispersion was dropped onto the surface of the cleansed GCE and was kept at room temperature until dry (labeled as TNs/GCE).

### 2.4. Measurement procedure

Square wave anodic stripping voltammetry (SWASV) was applied for the successive determination of Hg(II) under optimal conditions. Mercury was deposited at  $-0.2$  V for 80 s in 0.1 M HCl by the reduction of Hg(II) to Hg(0). The anodic stripping

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