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Research paper

Nanohybrid sensor based on carboxyl functionalized graphene dispersed palygorskite for voltammetric determination of niclosamide

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ABSTRACT

The stably dispersible palygorskite (Pal) nanorods onto carboxyl functionalized graphene (Gr-COOH) nanosheets were successfully employed for the facile fabrication of a novel nanohybrid sensing platform and the voltammetric determination of niclosamide (NA) in tablet and paddy water samples. A water-processable Gr-COOH can improve the dispersion and stability in water of Pal. The structure and properties of the formed Pal-Gr-COOH nanohybrid were characterized. The electrochemical behavior of NA, analytical conditions and the sensing performance of the prepared sensor were investigated. The sensor displayed the enhanced synergistically electrocatalytic ability toward NA in a linear range from 0.02–0.99 μM with low limit of detection (4.6 nM), good sensitivity, high reproducibility and satisfactory practicability, suggesting Pal-Gr-COOH nanohybrid will provide a promising platform for sensing application and facile preparation and potential application of other nanoclay mineral nanocomposites.

1. Introduction

Niclosamide (2,5-dicloro-4-nitrosalicylanilide, NA), an effective anthelmintic medicine, is widely used in public health, veterinary and aquaculture (Swan, 1999; Datta and Bera, 2000; Abreu et al., 2002). The World Health Organization has put it as the only commercially available molluscicide for the large-scale use in schistosomisasis control programs (World Health Organization, 1993). However, nowadays, many researchers found it has high toxicity to some aquatic snails and organisms (Andrews and Thyssen, 1982; Oliveira-Filho and Paumgartten, 2000). Thus, it is a great challenge to develop a sensitive and selective method for the NA determination. At present, electrochemical methods have received the increasing attention owning to their many excellent advantages such as rapid, easy operation, high sensitivity, online testing and low-cost. Electrochemical sensor based electroanalytical methods have widely used for various fields such as environmental protection, pharmaceutical monitoring, and so on (Janssen and Koene, 2002; Karimi-Maleh et al., 2016, 2017). There were also some reports for the NA determination by electroanalytical methods (Sridevi and Reddy, 1991; Alemu et al., 2002, 2003). However, electrochemical sensors based on nanomaterials modified electrodes were mainstream methods of the NA determination in recent years (Ghalkhani and Shahrokhian, 2010; Dede et al., 2014; Yao et al., 2014a,b). Ghalkhani et al. fabricated carbon nanoparticle/chitosan nanocomposite modified electrode for detecting NA, and it showed high stability, good reproducibility and excellent electro-catalytic activity toward NA (Ghalkhani and Shahrokhian, 2010). Mehretie et al. also investigated poly (3,4-ethylenedioxythiophene) modified glassy carbon electrode (GCE) toward the electrochemical determination of NA with excellent performance (Mehretie et al., 2012). In our previous work, we also built electrochemical sensors based on carbon nanomaterials modified GCE with wonderful properties (Yao et al., 2014a,b). Nevertheless, these nanomaterials were more expensive. Thus, low-cost nanomaterials with excellent properties were necessary to seek for producing novel electrochemical sensors for detecting NA with high effective, cheap and good sensitivity.

Nanoclay minerals are good candidate as modified electrodes for applications in sensors and biosensors due to their exclusive features, such as abundance, high specific surface areas, inexpensive availability, environmental stability, high adsorptive and ion exchange properties (Mousty, 2004; Bergaya and Lagaly, 2013). Palygorskite (Pal), a type of hydrated magnesium aluminum silicate rich in the content of natural nanoclay minerals, which has fibrous crystal structure and chemical structural formula $Si_8O_{20}(Mg, Al, Fe)_5(OH)_2(OH_2)_4.4H_2O$ (Haden and Schwint, 1967; Drits and Sokolova, 1971; Gonzalez et al., 1989). Nowadays, Pal has been widely used in foodstuff, environmental protection and medicine owning to its cheap, large specific surface area, strong

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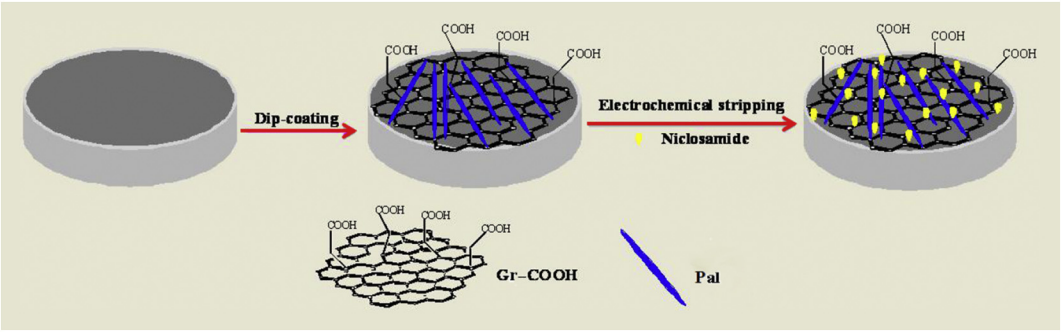
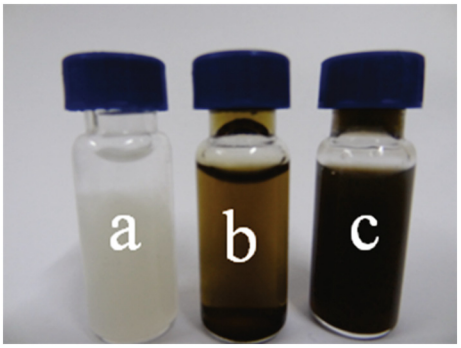


Scheme 1. The preparation process of Pal-Gr-COOH/GCE.

absorptive capacity and so on, but there were few reports on Pal and its nanocomposites as modified electrodes for applications in sensors and biosensors relatively to other nanoclay minerals like montmorillonite, kaolinite and halloysite (Zen and Kumar, 2004). Therefore, it is well select to fabricate novel sensors for the electrochemical determination of analytes based on Pal nanocomposites combined with merits of other nanomaterials.

Graphene (Gr), one of two-dimensional carbon nanomaterials, has given rise to great interest among physical, chemical and material fields since produced in 2004 (Novoselov et al., 2004). Gr possesses ideal geometric construction and unique optic, thermotic, electric and mechanic properties. Thus, potential applications and fundamental research of Gr have appeared the exponential growth in many fields such as supercapacitors, solar cells, nanometer electrode transistors, electrochemical sensors and composite materials (Stankovich et al., 2006; Geim and Novoselov, 2007; Pumera et al., 2010; Brownson et al., 2012; Zhao et al., 2016). In addition, Gr has highly-focused in sensing analysis due to its stable chemical structure, good conductivity, large specific surface area and excellent electrocatalytic properties. However, the stacking interactions between sheet layers and bad solution-processability of Gr limit its ranges of applications. So far, researchers tried to overcome Gr defects mainly through specific functional groups modified on its surface (Si and Samulski, 2008; Ribeiro et al., 2011; Nie et al., 2012). Consequently, carboxyl group functionalized graphene (Gr-COOH), one of Gr derivatives with hydrophilic groups, was produced. It not only retained the excellent performance of Gr, but also enhanced its water dispersibility, which also made the excellent performance of Gr-COOH composite materials easy to prepare via strong interaction with other materials.

In this paper, a low-cost, simple, sensitive, and selective Pal-Gr-COOH modified GCE was fabricated for the voltammetric determination of NA in tablet and paddy water samples. The Pal-Gr-COOH nanohybrid was prepared by introducing Pal into Gr-COOH dispersion. The structure and properties of Pal-Gr-COOH were characterized, and the nanohybrid sensor based on Pal-Gr-COOH/GCE was fabricated and applied.



Scheme 2. The preparation of Pal (a), Gr-COOH (b) and Pal-Gr-COOH (c).

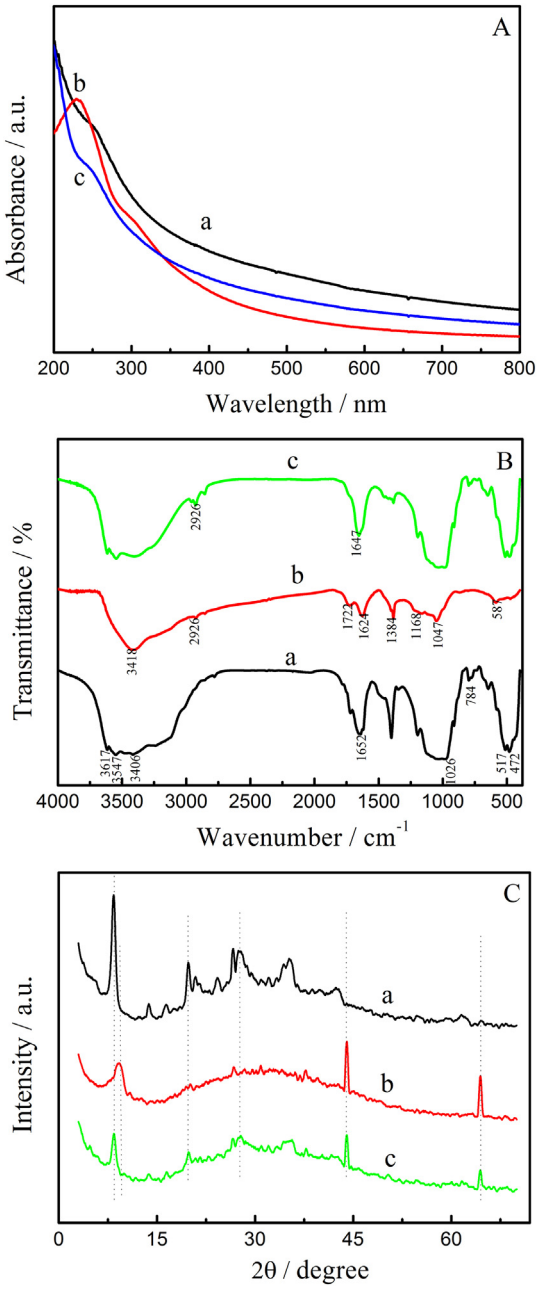


Fig. 1. UV–vis spectra (A), FT-IR spectra (B), XRD patterns (C) of modified electrodes materials Pal (a), Gr-COOH (b) and Pal-Gr-COOH (c).