Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–11

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

A highly conducting flower like Au nanoparticles interconnected functionalized CNFs and its enhanced electrocatalytic activity towards hydrazine through direct electron transfer

Mani Sakthivel[a], Sukanya Ramaraj[a], Shen-Ming Chen[a,*], Bose Dinesh[b,*], Kuang-Hsiang Chen[a]

[a] Electroanalysis and Bioelectrochemistry Lab, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan
[b] Nano and Bioelectrochemistry Research Laboratory, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology University, Vellore 632014, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 3 October 2017
Revised 4 November 2017
Accepted 6 November 2017
Available online xxx

Keywords:
Carbon nanofiber (CNF)
Au nanoparticle
Electrodeposition
Electrochemical sensor
Hydrazine

ABSTRACT

A numerous number of carbon-based nanomaterials have been developed for various technological applications, nevertheless a degree of accessibility is very less. Notably, carbon nanofibers (CNFs) based materials are insufficiently studied compare to CNT and graphene due to their inaccessibility in aqueous dispersion. Here we have functionalized the CNF by using acid treatment for further modification. Functionalization of CNF was confirmed by different characterization techniques like FT-IR, RAMAN, and XRD. To increase the electrical conductivity of F-CNFs, flower-like Au nanoparticles were electrodeposited onto the F-CNFs. Optimization study for electrodeposition of Au nanoparticles was performed with Au precursor's concentration and deposition cycle number. As the result, the optimal electrochemical active surface area (EASA) of the modified electrode is obtained to be 1.67 cm^2 for 20 cycles which are higher than that of the previously reported Au nanoparticles based literature. The developed material was used as an electrode modifier for the detection of hydrazine. As expected, the amperometric hydrazine sensor shows a very low detection limit of 8 nM with a high sensitivity of 7.5 μA μM^{-1} cm^{-2}. The excellent analytical parameters of the F-CNF@Au/GCE modified electrode over the various related modified electrodes suggest that the electrode can be useful for use in trace level detection of hydrazine in several industrial and pharmaceutical applications.

1. Introduction

Carbon-based nanomaterials, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), ordered mesoporous carbon, graphene, carbon nanospheres, and so on have attracted much interest in the design of electrodes used in electroanalytical chemistry because of their large surface area, high electrical conductivity, unique stability, chemical inertness, and high edge-plane-like defects, high electrocatalytic activity towards variety of electrochemical applications [1–3]. The attractive physical, chemical, electronic, and electrochemical properties of carbonaceous nanomaterials strongly depend on their conformations. Recently, carbon nanofibers (CNFs) have attracted interest in variety of applications including battery [4], supercapacitor [5] fuel cell [6] and solar cell [7,8] etc. due to their high mechanical strength, chemical stability, superior laboriousness, excellent electrical and thermal conductivities, as well as substantial exhaustion, corrosion resistance and larger surface to volume ratio than CNT [9]. Interestingly, the cylindrical nanostructure with stacking arrangement of graphene sheets and more edge plane defects on the outer wall of CNF are offering more and efficient electron transfer [10]. Nevertheless, the electrode preparation using pristine CNF shows some difficulties due to its insolubility in water. In order to improve the solubility of CNF, which is treated in the acid solution (HNO_3/H_2SO_4) for functionalization process [11]. The functionalization process not only improves the solubility and also enhances the electrochemical properties of CNF by introducing the more anchoring sites and surface reactive groups including carboxylic acid, hydroxyl, and carbonyl groups on its open end and side walls. Hence, the functionalized CNF (F-CNF) can believe as more comfortable carbon material to prepare an electrode with better electrochemical properties for aforementioned applications.

Although the reported applications are extensive, to the best of our knowledge, there is no report using Au nanoparticles

* Corresponding author.
E-mail addresses: smchen78@ms15.hinet.net, smchen@ntut.edu.tw (S.-M. Chen), bosedinesh210@gmail.com (B. Dinesh).

https://doi.org/10.1016/j.jtice.2017.11.010
1876-1070/

interconnected F-CNFs as an electrode material for hydrazine detection by electrochemical methods.

The electrochemical properties of CNF can be tailored by making it as a composite with metal nanoparticles, metal oxides, and polymers. Such CNF composites show excellent electrocatalytic behavior owing to the good synergy between conductive CNF and efficient metal/metal oxide particles. For instance, Ni et al., demonstrated the in-situ growth of Co_3O_4 nanoparticles on mesoporous CNFs for nonenzymatic amperometric H_2O_2 sensor [12], Mondal et al., fabricated metal nanoparticle impregnated free standing CNFs non-enzymatic biosensor for triglyceride [13] and Oularbi et al., determined a traces level of lead ions using polypyrrole/CNFs nanocomposite [14]. Thus, the electrochemical properties of CNF can be actually enhanced by finding a suitable support material. Recently, the combination of Au nanoparticle with carbon materials has recommended as an effective route to improve the electron transfer rate as well as enhancing the electrochemical properties of carbon materials [15]. Especially, the metal Au nanoparticles possess high electrical conductivity, excellent catalytic properties, high surface to volume ratio and provide small double layer capacitance which is making them as a suitable active material for fabricating a novel electrode for electrochemical sensor and biosensor applications [16]. In general, the Au nanoparticle and its composites have been prepared by using a variety of techniques including green chemical synthesis [17], microwave-assisted [18], hydrothermal method [19] and electrochemical deposition [20]. Among all, the electrochemical deposition is very straightforward and low-cost method to prepare the uniformly deposited of Au nanoparticle on a small area of the electrode with excellent electrocatalytic activity. Thus, we believed that the electrodeposited Au nanoparticles might enhance the electrochemical performance of functionalized carbon nanofiber towards the sensing of hydrazine.

Hydrazine and its derivatives are highly relevant compounds owing to their industrial and pharmaceutical applications including fuel cells, herbicides, catalysts, corrosion inhibitor, plant growth regulator and rocket propellant [21, 48]. Moreover, they are highly toxic, and their exposure to the body produces severe carcinogenic and mutagenic effects. Therefore, the sensitive determination of hydrazine is great significance. Even though numerous methods have been available for the hydrazine determination such as titrimetric [22], potentiometric [23], flow injection chemiluminescence [24] and spectrophotometric methods [25], most of them are time-consuming and cost-effective. On the other hand, the electrochemical techniques offer high selectivity, sensitivity, low cost and simplicity [26]. Because of large overpotential associated with bare electrodes, which has been modified and employed for the enhanced electrochemical determination of hydrazine [27]. Though, various chemically modified electrodes were applied in the past. Still, thirst to explore a better-modified electrode is encouraged aiming towards a sensitive and selective electrochemical determination of hydrazine. Recently, the delicate and careful determination of hydrazine was achieved using Au nanoparticle supported carbon nanocomposite modified electrodes. For instance, Madhu et al., reported a new gold nanosphere incorporated activated carbon nanocomposite for sensitive and selective detection of toxic hydrazine [28] and Lu et al., explains that the Au nanoparticle-decorated graphene oxide modified electrodes for nanomolar detection of hydrazine [29]. As mentioned, the excellent electrochemical activity of Au nanoparticle offers a chance to use it for electrochemical sensing of hydrazine.

This study aims to fabricate a novel electrode using F-CNF with Au nanoparticles by using simple electrodeposition technique. We have successfully confirmed the functionalization of CNF and the formation of Au nanoparticle inner core and the outer surface of F-CNF through the subsequent electrodeposition. The prepared Au nanoparticle encapsulated F-CNF (F-CNF@Au) nanocomposite has used for detection of hydrazine in various water samples. The numerous electrochemical techniques such as CV, LSV, and amperometric i-t have been followed to study the electrooxidation of hydrazine at F-CNF@Au nanocomposite modified glassy carbon electrode (F-CNF@Au/GCE). As expected, F-CNF@/GCE shows excellent sensitivity and low detection limit of hydrazine, which is comparatively higher than other electrodes including Au/GCE, F-CNF/GCE, and bare GCE. In addition, the practicability of F-CNF@Au/GCE towards the hydrazine detection also studied in various water samples.

2. Experimental section

2.1. Materials and methods

$HAuCl_4 \cdot 3H_2O$ and CNF were purchased from Sigma Aldrich. Hydrazine hydrate was purchased from Acros Organics. The supporting 0.1 M PBS (pH 7) electrolyte solution was prepared by using 0.05 M Na_2HPO_4, and NaH_2PO_4 and the pH of electrolytes solution were adjusted by addition of $NaOH/H_2SO_4$. All chemicals reagents were of analytical grade and were used without further purification.

The surface morphology and crystalline properties of F-CNF@Au were characterized by using various analytical techniques. Fourier transform infrared spectroscopy (FT-IR) measurement was recorded using JASCO FT/IR-6600. XRD characterization was carried out using XPERT-3 diffractometer with Cu Kα radiation ($K = 1.54$ Å). Raman spectroscopy was a recorded using WITech CRM200 confocal microscopy Raman system with a 488 NM laser. TEM was used to investigate the morphology and microstructure of F-CNF@Au. The Cyclic Voltammetry (CV), amperometric studies were performed using CHI611A electrochemical analyzer. The conventional three-electrode system was utilized in these following all electrochemical studies where glassy carbon electrode (GCE, geometric surface area: 0.07 cm^2) was used as a working electrode, a saturated Ag/AgCl electrode as a reference electrode and a platinum electrode as the auxiliary electrode. All measurements were carried out at room temperature.

2.2. Fabrication of Au decorated CNF modified glassy carbon electrode

The fabrication of F-CNF@Au/GCE was prepared by following the stepwise synthesis processes. In the first step, CNF was exposed to acid treatment to enrich its electrical conductivity and solubility by introducing the oxygen functional groups. In a typical experiment, 1 g of CNF was added into the 40 ml of HNO_3/H_2SO_4 (1:3) acid mixture at 50 °C for continuous magnetic stirring up to 8 h. Then, the resultant CNF solution was centrifuged and washed by using water until the pH value reaches around 7. Finally, the resultant product was dried in vacuum oven for a whole night. In the second step, GCE was freshly polished using alumina slurry followed by washing with ethanol and DD water. The as-prepared F-CNF was dispersed in 1 ml of water solvent and sonicated for 15 min. Then, the 6 µL of resultant solution was drop cast on well-polished GCE and dried in oven at 45 °C. To carry on the electrodeposition of Au nanoparticle, the prepared F-CNF modified electrode GCE was immersed into the electrochemical cell containing 0.5 M of H_2SO_4 and $HAuCl_4 \cdot 3H_2O$ (3.5 mM, 5 mM, 6.5 mM, 8 mM and 10 mM). The Au nanoparticle was electrodeposited on F-CNF/GCE in CV technique by fixing the set of potential range from −0.2 to 1.5 V by varying the number of deposition cycles (5, 10, 15 and 20 cycles) at the scan rate of 50 mV s^{-1} as shown in Fig. S1. The deposition of Au NPs was confirmed from this CV curve, herein the formation of Au oxides is observed at the potential of 1.08 V and it is consequently reduced to metallic AuNPs at the potential of

Please cite this article as: M. Sakthivel et al., A highly conducting flower like Au nanoparticles interconnected functionalized CNFs and its enhanced electrocatalytic activity towards hydrazine through direct electron transfer, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.11.010