Biosensors and Bioelectronics 85 (2016) 618–624

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

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

Three-dimensional graphene-like carbon frameworks as a new electrode material for electrochemical determination of small biomolecules

Wenfang Deng, Xiaoyan Yuan, Yueming Tan*, Ming Ma*, Qingji Xie

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

ARTICLE INFO

Article history:
Received 17 April 2016
Received in revised form
13 May 2016
Accepted 21 May 2016
Available online 24 May 2016

Keywords:
Three-dimensional graphene-like carbon frameworks
Ascorbic acid
Dopamine
Uric acid

ABSTRACT

Three-dimensional (3D) graphene-like carbon frameworks (3DGLCFs) were facilely prepared via copyrolysis of polyaniline and nickel nitrate powder, followed by acid etching. The as-prepared 3DGLCFs possess graphene-like network structure, high specific surface area, and high content nitrogen dopant. Because these features enable large electrochemically active surface area, rapid electron transfer, and fast transport of analytes to electrode surface, the 3DGLCFs modified glassy carbon electrode (GCE) shows current response much higher than commercial graphene (CG) modified GCE towards the oxidation of ascorbic acid (AA), dopamine (DA) and uric acid (UA). The anodic peak separations at 3DGLCFs/GCE are 0.23 V between AA and DA, 0.13 V between DA and UA, and 0.36 V between AA and UA. For the simultaneous electrochemical determination of AA, DA and UA using differential pulse voltammetry, the 3DGLCFs/GCE shows linear response ranges of 1.25×10^{-5}–4×10^{-4} M for AA, 5×10^{-8}–1.0×10^{-5} M for DA, and 5×10^{-8}–1.5×10^{-5} M for UA, with low detection limits of 2×10^{-6} M for AA, 1×10^{-8} M for DA, and 1×10^{-8} M for UA. The 3DGLCFs/GCE was also applied for the measurement of human serum, exhibiting satisfactory recoveries.

1. Introduction

Three-dimensional (3D) carbon architectures have been widely used in electrochemical capacitors (Deng et al., 2015; Fan et al., 2010; Hu et al., 2011; Lee et al., 2010b; Nardecchia et al., 2013; Xu et al., 2013), fuel cells (Yang et al., 2015; Zhang et al., 2014a, 2014b), solar cells (Tang et al., 2013), and lithium-ion batteries (Luo et al., 2013), because 3D carbon architectures can enable fast electron transfer and rapid mass transport in electrochemical applications. 3D carbon architectures have been prepared through the assembly of carbon nanotubes and/or graphene (Fan et al., 2010; Hu et al., 2011; Lee et al., 2010a, 2010b; Nardecchia et al., 2013; Tang et al., 2010; Vickery et al., 2009). However, the electronic conductivities of most these 3D carbon architectures are relatively low resulting from the heterogeneous connections (Wang et al., 2013). 3D carbon architectures with high electronic conductivities have been prepared on porous metal substrates from gaseous carbon precursor by chemical vapor deposition (CVD) approach (Chen et al., 2011; Wang et al., 2014). However, the low-yield production of CVD-prepared 3D carbon architectures still hinders the wide applications because of the use of high-cost porous metal substrates (Wang et al., 2013). Therefore, the development of a new approach to the synthesis of 3D carbon architectures is of great interest and importance.

Ascorbic acid (AA), also called vitamin C, is an essential nutrient in human diets. AA is widely used for the prevention and treatment of mental illness, common cold, cancer, infertility, and AIDS (Arrigoni and Tullio, 2002; Noroozifar et al., 2011). Dopamine (DA) as an important neurotransmitter plays a vital role in the function of cardiovascular, central nervous, hormonal, and renal systems (Damier et al., 1999; Dauer and Przedborski, 2003). Monitoring the concentration of DA in extracellular fluids can be used to monitor neurotransmission process and diagnose Parkinson's disease (Damier et al., 1999; Dauer and Przedborski, 2003; Tsai et al., 2012; Wu et al., 2012; Zhang et al., 2012). Uric acid (UA) is one of the most important analytes in clinical field, because its abnormal level in human body is an important symptom of various diseases including gout, pneumonia, hyperuricemia, and leukemia (Chen et al., 2010; Dutt and Mottola, 1974; Lupu et al., 2002; Noroozifar et al., 2014). Due to their important roles played in human

* Corresponding authors.
E-mail addresses: tanyueming0813@126.com (Y. Tan), mingma@hunnu.edu.cn (M. Ma).

http://dx.doi.org/10.1016/j.bios.2016.05.065
0956-5663/

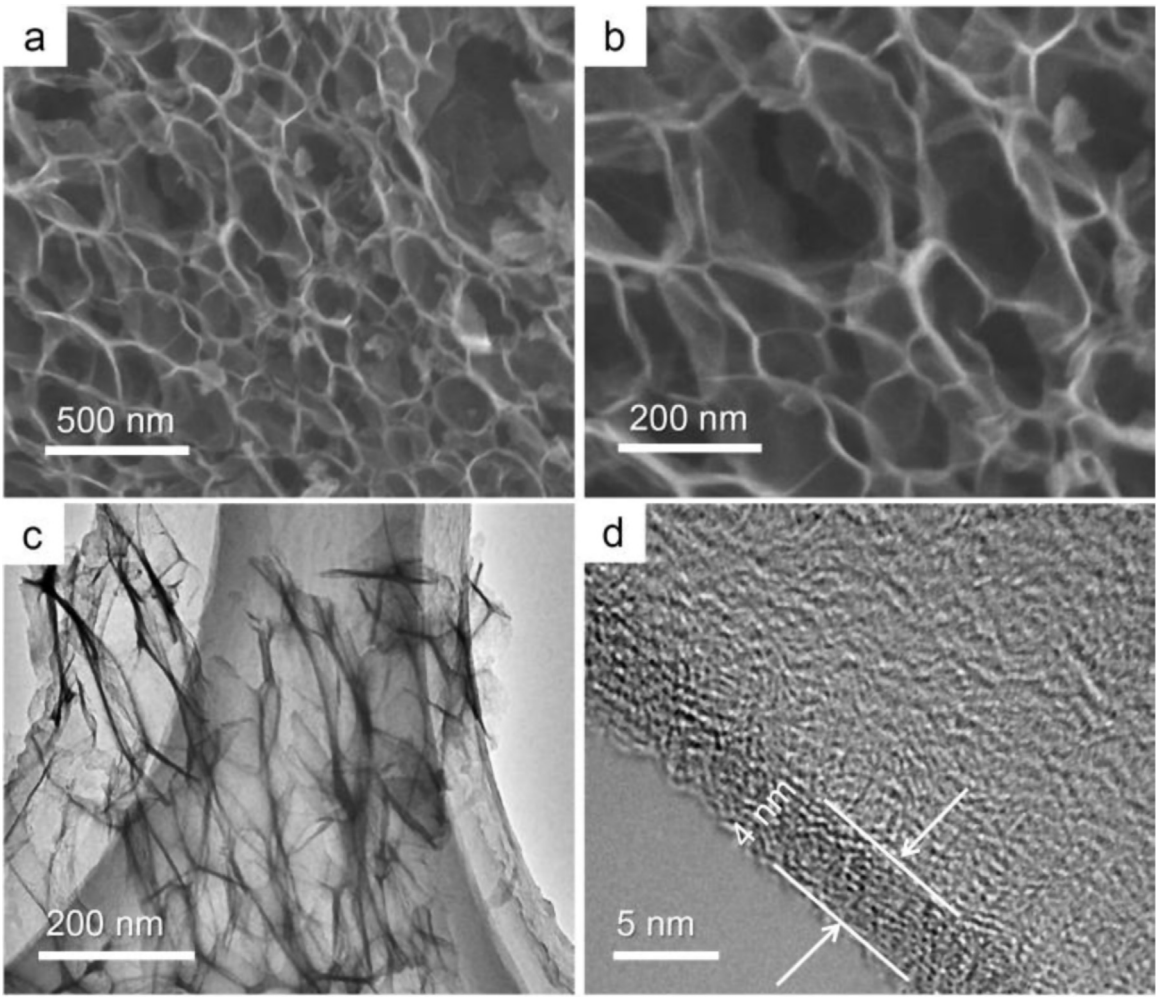

Fig. 1. SEM (a and b) and TEM (c and d) images of 3DGLCFs.

metabolic processes, the determination of these three biomolecules in biological fluids is important. Moreover, AA, DA, and UA usually coexist in biological fluids, so simultaneous detection of these three biomolecules is necessary. Due to the excellent electrochemical activities of AA, DA, and UA, electrochemical determination of these three biomolecules becomes feasible. Unfortunately, the oxidation potentials of these three biomolecules at common solid electrodes are close to each other, resulting in an overlap of their oxidation peaks (Ma et al., 2013; Sekli-Belaidi and Temple-Boyer, 2010; Yuan et al., 2015). Many nanomaterials, especially carbon-based materials, have been extensively applied for the simultaneous electrochemical detection of these three biomolecules, showing enhanced sensitivity and selectivity (Du et al., 2014; Gai et al., 2013; Kim et al., 2010; Li et al., 2010, 2012; Lian et al., 2014; Mao et al., 2011; Sheng et al., 2012; Veeramani et al., 2015; Wang et al., 2009; Yue et al., 2012). 3D carbon architectures are expected to show high performance when serving as electrode material for the electrochemical detection of small biomolecules, due to the improved electron transfer and mass transport.

We report here that 3D graphene-like carbon frameworks (3DGLCFs) can be facilely synthesized and used for simultaneous electrochemical determination of AA, DA and UA. The 3DGLCFs were facilely prepared via copyrolysis of polyaniline and nickel nitrate powder, followed by acid etching. The 3DGLCFs possess graphene-like network structure, high specific surface area, and high content nitrogen dopant. As a result, the 3DGLCFs modified glassy carbon electrode (GCE) shows current response towards the electro-oxidation of AA, DA and UA superior to commercial graphene (CG) modified GCE. The N-3DGLCFs was used for simultaneous electrochemical determination of AA, DA and UA using differential pulse voltammetry, showing ultra-low detection limits and high sensitivities. The 3DGLCFs/GCE was also applied for the detection of real sample with satisfactory recoveries, indicating a promising electrode material in practical applications.

2. Experimental

2.1. Instrumentation and chemicals

Electrochemical experiments were conducted on a CHI760E electrochemical workstation (CH Instrument Co., Inc.) using a three-electrode system. A glassy carbon electrode (GCE), a Pt counter electrode, and a KCl-saturated calomel electrode (SCE) served as the working electrode, the counter electrode, and the reference electrode, respectively. A Hitachi S4800 scanning electron microscope and a TECNAI F-30 high-resolution transmission electron microscope were used in the scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) studies, respectively. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were performed on a PANalytical X'pert Pro X-ray diffractometer and a PHI QUANTUM 2000 X-ray photoelectron spectroscopic instrument, respectively.