



## Edge promoted ultrasensitive electrochemical detection of organic biomolecules on epitaxial graphene nanowalls



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### ABSTRACT

We report the simultaneous electrochemical detection of dopamine (DA), uric acid (UA) and ascorbic acid (AA) on three dimensional (3D) unmodified 'as-grown' epitaxial graphene nanowall arrays (EGNWs). The 3D few layer EGNWs, unlike the 2D planar graphene, offers an abundance of vertically oriented nanographitic-edges that exhibit fast electron-transfer kinetics and high electroactive surface area to geometrical area ( $EAA/GA \approx 134\%$ ), as evident from the  $Fe(CN)_6^{3-/4-}$  redox kinetic study. The hexagonal  $sp^2$ -C domains, on the basal plane of the EGNWs, facilitate efficient adsorption via spontaneous  $\pi$ - $\pi$  interaction with the aromatic rings in DA and UA. Such affinity together with the fast electron kinetics enables simultaneous and unambiguous identification of individual AA, DA and UA from their mixture. The unique edge dominant EGNWs result in an unprecedented low limit of detection (experimental) of 0.033 nM and highest sensitivity of 476.2  $\mu A/\mu M/cm^2$ , for UA, which are orders of magnitude higher than comparable existing reports. A reaction kinetics based modeling of the edge-oriented 3D EGNW system is proposed to illustrate the superior electro-activity for bio-sensing applications.

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### 1. Introduction

Graphene (Novoselov et al., 2004) is being considered as one of the most promising materials for next generation nanotechnological applications spanning the field of nanoelectronics (Westerfelt, 2008), energy devices (Gwon et al., 2011) and sensors (Mohanty and Berry, 2008). For sensing applications mainly graphene oxide (GO) (Liu et al., 2010) and reduced GO (Zhou et al., 2009) are the popular choices, with limited use of chemical vapor deposited (CVD) graphene (Huang et al., 2010). Although GO is being used

widely for sensing, its performance should be limited by the presence of abundant oxygen moieties and high defect sites (Ganguly et al., 2011), which would induce high resistance to the charge-transfer from the bio-analytes and hence reduce the efficiency of electrocatalytic behavior. Metal nano particle modified highly sensitive carbon materials have been used successfully for different sensing applications with a very low limit of detection (LoD) (Huang et al., 2008; Oztekin et al., 2012). However, pure carbon based sensors, such as graphene with a hexagonal  $sp^2$  structure, should be a better choice for the detection of organic analytes (Shang et al., 2008; Huang et al., 2011; Ping et al., 2012; Sheng et al., 2012; Niu et al., 2013; Yan et al., 2013; Zhang et al., 2013; Du et al., 2014; Yue et al., 2014), having aromatic or heterocyclic ring structures, that facilitate a strong  $\pi$ - $\pi$  interaction between the two. Intuitively, better graphitic nature should provide improved interaction, at least those with molecular structures promoting the  $\pi$ - $\pi$  interaction, required for bio-sensing applications unless other factors or experimental difficulty presents insurmountable

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thresholds.

One such problem in high quality planar (2D) graphene may be the lack of enough electroactive sites that would present faster electron transfer kinetics. 2D graphene may also have edges at the boundaries or at the inter-grain peripheries rich in dangling bonds and other electronic defects (Hwang et al., 2010). But once stacked (2–10 layers), a large fraction of these edges, and the basal planes, become electrochemically inactive and suppressed leaving only the top surface and the physical boundaries for the adsorption and electroactivity. Although planar graphene is constituted in micrometer-nanometer sized domains with boundaries rich in dangling bonds and other electronic defects (Hwang et al., 2010), those may not present preferred adsorption sites for the oncoming analyte molecules. A 3D graphene structure with oriented edges, accessible for efficient adsorption and electron transfer, may be a better analytical architecture. The 3D edge oriented configuration, on the other hand, offers larger surface area (both basal plane and edge) exposed to the target analyte for adsorption and electron transfer. Each SiC nanowall standing vertically on the surface offers at least two basal plane graphene surface with proportional edges. To verify this design, we have selected to use epitaxial graphene nanowalls (EGNWs), grown on quasi-vertical silicon carbide (SiC) on a suitable substrate (Hu et al., 2011), for electrochemical (EC) detection of dopamine (DA), uric acid (UA) and L-ascorbic acid (AA). This hetero-architecture is formed by growing SiC nanowalls on Si substrates, followed by Si sublimation from the SiC surface and consequent surface graphitization, which leads to well-defined arrays of 2 H-SiC nanowalls sheathed by few-layer epitaxial graphene. This unique three-dimensional (3D) configuration with highly edge-oriented structures could provide an ideal choice of electrode for electro-catalytic as well as sensing applications of the EGNWs. The epitaxially grown graphene shows better graphitic crystallinity compared to GO or reduced GO (Berger et al., 2004; Berger et al., 2006).

The reasons for choosing DA, UA, and AA are two-fold. First, these molecules express ring or heterocyclic structures with demonstrated  $\pi$ - $\pi$  interaction with graphene, and secondly, all three of these have important roles in human metabolism. DA is an important neurotransmitter in the central nervous system: low levels of which results in neurological disorders, such as Parkinson's disease and schizophrenia (Damier et al., 1999). UA is the final oxidation product of urine metabolism excreted in urine: abnormal UA levels may cause diseases such as hyperuricemia, and gout (Lakshmi et al., 2011). AA is essential in several biological processes such as free-radical scavenging, cancer prevention and immunity improvement (Kalimuthu and John, 2009). Hence, simultaneous determination of these three species is of immense significance not only in biomedical chemistry and neurochemistry but also for diagnostic and pathological research. The physiological concentrations of DA are very low (0.01–1  $\mu$ M in healthy people) compared to its two main interfering substances AA (0.1–0.6 mM), and UA (0.4 mM) (Celebanska et al., 2011; De Oliveira and Burini, 2012). Several methods have been developed for the determination of DA, UA and AA, for instance chemiluminescence (Chen et al., 2010), high-performance liquid chromatography, capillary electrophoresis, electrochemical method (Ali et al., 2008), and ultraviolet-visible spectroscopy (Fraisse et al., 2002). Amongst these methods, the EC approach has been regarded as a promising technique due to its high sensitivity, low-cost, and ease-of-operation advantages. For the traditional electrodes, all these molecules exhibit EC oxidation at nearly the same potential leading to overlapping of voltammetric responses, and hence difficulty in individual identification (Ensafi et al., 2009). Clinical determination of DA, UA, and AA in human blood serum, have always been a challenge due to the presence of different interfering factors such as, glucose, lactose, citric acid, pyruvic and lactic acid (Chao et al.,

2012). To overcome these problems, various chemically modified electrodes using selective membranes (Zen and Chen, 1997), conducting polymers (Kumar et al., 2010), and nanomaterials (Huang et al., 2008), have been developed for the simultaneous determination of DA, UA and AA. Although these modified electrodes have shown improved sensitivity and selectivity, compared with the traditional electrodes, they suffer from several drawbacks such as long time-consumption, ill-defined modification steps, and stability problem of the modifiers (Ping et al., 2012). Therefore, there still remains a quest for a novel electrode-material that can be used as-grown for the simultaneous determination of DA, UA and AA.

Concurrent detection of these three analytes may not be needed for clinical purposes. However, unambiguous and non-overlapping signals, free of interference, are necessary for quantification and selectivity of the sensing process. In this report, we demonstrate that the pristine EGNWs, without any need of surface treatment or any complicated device fabrication process, could be used for the simultaneous EC detection of DA, UA and AA with excellent sensitivity and impressive detection limit.

## 2. Experimental

### 2.1. Preparation of graphene nanowalls

The growth of graphene-sheathed SiC nanowalls was carried out by microwave plasma enhanced chemical vapor deposition (MPECVD) in an AsTex 5 kW microwave chamber, as reported earlier (Hu et al., 2011). In summary, the SiC nanowalls growth was performed on Si(111) substrates at around 1100 °C in a gas mixture of H<sub>2</sub>, CH<sub>4</sub> and SiH<sub>4</sub> at a chamber pressure of few tens of Torr with a microwave power of 1500–2000 W. The final EGNWs nanostructure was obtained with H<sub>2</sub> plasma etching on the surface of SiC nanowalls to form graphene layers for a few minutes. The as-synthesized EGNWs sample was directly employed as a “working electrode”, using metal (Au) wire connected at the front (EGNWs-side) surface of the samples, for electrochemical characterizations and sensing.

### 2.2. Instruments and materials

The surface morphological and structural characterizations were performed by using field-emission scanning electron microscopy (FESEM, 6700F, Jeol, Japan), high-resolution transmission electron microscopy (HRTEM, Tecnai-G<sup>2</sup>-F20, FEI) and Raman spectroscopy (Jobin Yvon HR800, 532 nm laser). The EC characterizations and sensing measurements were carried out using cyclic voltammetry (CV) (scan rate 100 mv/s) and differential pulse voltammetry (DPV) (scan rate 10 mv/s, Modulation time: 0.009 s, Time interval: 1 s, Step potential: 0.01 V, Modulation amplitude: 0.05 V) at room temperature, using a three-electrode Autolab electrochemical workstation (PGSTAT 302N). Pristine EGNWs, Pt wire, and Ag/AgCl (saturated KCl) electrodes served as the working, counter and reference electrodes, respectively. All the voltammetric scans were repeated for several cycles until the EC response stabilized. For comparison purpose, a commercial glassy carbon electrode (GCE, CH instrument, 3 mm diameter) was employed. Before every use, the GCE was polished with 0.25 mm Al<sub>2</sub>O<sub>3</sub> slurry and then ultrasonically cleaned with ethanol and de-ionized water. The electron-transfer (ET) properties were systematically investigated by CV using a standard redox system of Fe(CN)<sub>6</sub><sup>3-/4-</sup>. The K<sub>3</sub>Fe(CN)<sub>6</sub> (Acros Organics) solution of 5 mM concentration was prepared in 1X phosphate buffer saline (PBS, Sigma, pH 7.4). Analytical reagent grade chemicals (99%+pure) DA, UA and AA, were purchased from Acros Organics, and made

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