



# Fabrication of graphene/titanium carbide nanorod arrays for chemical sensor application



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## ABSTRACT

Vertically stacked graphene nanosheet/titanium carbide nanorod array/titanium (graphene/TiC nanorod array) wires were fabricated using a direct current arc plasma jet chemical vapor deposition (DC arc plasma jet CVD) method. The graphene/TiC nanorod arrays were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction spectroscopy. The TiO<sub>2</sub> nanotube array was reduced to the TiC nanorod array, and using those TiC nanorods as nucleation sites, the vertical graphene layer was formed on the TiC nanorod surface. The multi-target response mechanisms of the graphene/TiC nanorod array were investigated for ascorbic acid (AA), dopamine (DA), uric acid (UA), and hydrochlorothiazide (HCTZ). The vertically stacked graphene sheets facilitated the electron transfer and reactant transport with a unique porous surface, high surface area, and high electron transport network of CVD graphene sheets. The TiC nanorod array facilitated the electron transfer and firmly held the graphene layer. Thus, the graphene/TiC nanorod arrays could simultaneously respond to trace biomarkers and antihypertensive drugs.

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## 1. Introduction

Graphene, with a high surface area and high mechanical and outstanding electronic properties [1–3], consists of a sp<sup>2</sup> carbon atom layer with a six-membered benzene ring framework [4–9]. Since many compounds composed of C, H, N, and O atoms have a good electrochemical response, there is wide potential for application in the electrochemical devices [10,11]. Graphene has applied in sensors, water treatment, and energy storage devices, most of which are prepared by a liquid-phase oxidation method [12–14]. In this preparation process of graphene, the graphene structure is largely destroyed causing the loss of its good electrical properties. The quality of graphene must be improved to further increase the specific surface area and improve the electrical properties in order to form an electrical response to trace species.

Chemical vapor deposition (CVD) graphene has regularly arranged carbon atom layers, high electron mobility, and stable performance, which can provide direct and stable pathways for rapid electron transport [15–17]. At present, most CVD graphene products are attached to the substrate surface because of the lateral growth and this obviously reduces the effective surface area [18–20]. Vertically oriented graphene sheets provide a highly conductive network without the formation of junction resistance [21,22]. In addition, vertically oriented graphene layers possess high porosity, which is ideal for use as an electrode

material. The surface step and edge defects of few-layer graphene sheets are considered active sites with high catalytic efficiency, biocompatibility, and adsorption capacity in physiological environments [23]. There are a number of key scientific issues that need to be studied, including how the vertical growth of graphene by CVD method can be used to obtain both a large surface area and faster electronic transmission channel. Recently, vertically oriented graphene consisting of a continuous three-dimensional (3D) structure with a large surface area was used for capacitor electrode applications [1,24,25].

Various metals, such as Ni, Cu, Pt, and Ir, have been proven to be catalytic to the growth of graphene [26–29]. Different metals each have their own unique mechanism for growing graphene [30–32]. Theoretically, graphene has a strong interaction with the Ti surface, and graphene can be grown from bulk carbide [27]. To the best of our knowledge, there are no reports on using Ti as the substrate and the catalyst for the growth of graphene.

We suggested that the carbonized TiO<sub>2</sub> nanotube arrays can not only be reduced into TiC nanorod arrays, but can also be used as a base to achieve the vertical growth of graphene. In addition, it can be used in the principle analysis of electrochemical responses for various compounds. For example, it is used to detect ascorbic acid (AA), dopamine (DA), uric acid (UA), and hydrochlorothiazide (HCTZ). This study is very important for diagnostic applications, especially because hypertension is a major risk factor associated with cardiovascular morbidity and end-stage renal failure [33]. HCTZ has been used as an antihypertensive therapy because it reduces the active sodium reabsorption and peripheral vascular resistance [34,35]; however, HCTZ increases the

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concentration of serum UA [36], which has been implicated in the pathogenesis of hypertension [37–39]. In addition, DA is an important neurotransmitter [40–42], but DA causes hypertension and AA can soften blood vessels [43], and its concentration in serum can affect blood pressure.

In this paper, we prepared vertically oriented graphene on TiC nanorod arrays with Ti wire as the substrate (graphene/TiC nanorod array) by a direct current (DC) arc plasma jet CVD method. The vertical growth mechanism of graphene and the sensing mechanism for trace AA, DA, UA, and HCTZ on the graphene/TiC nanorod array were discussed.

## 2. Experimental

### 2.1. Preparation of the graphene/TiC nanorod arrays

The growth process for vertically stacked graphene/TiC nanorod arrays on Ti wire is shown in Fig. 1. TiO<sub>2</sub> nanotube array/Ti wires were prepared by anodic oxidation as described in earlier studies [44]. TiO<sub>2</sub> nanotube array/Ti wires were then placed in the chamber of DC arc plasma jet CVD. The 1.2 L min<sup>-1</sup> Ar, 1.8 L min<sup>-1</sup> H<sub>2</sub>, and 0.15 L min<sup>-1</sup> CH<sub>4</sub> gases were delivered into the chamber where the pressure was maintained at 3.5 kPa, and an arc power of 8 kW was applied to generate a plasma. The TiO<sub>2</sub> gradually transformed into TiC; the corresponding chemical reactions are  $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$  and  $\text{TiO}_2 + \text{C} + \text{H}_2 \rightarrow \text{TiC} + 2\text{H}_2\text{O}$  (see Fig. 1a). The TiO<sub>2</sub> nanotube array changed the pore structure. With an increase of growth time, the TiO<sub>2</sub> had completely changed to TiC crystals, and their morphology altered from the pore structure to the square hollow structure to the TiC nanorod array, as shown in Fig. 1b. In the process of TiO<sub>2</sub> nanotube array transformation to TiC nanorod array, graphene also grew vertically in addition to on the surface. When the solubility of C in the Ti reached saturation, C atoms began to segregate and deposit on the TiC surface, which formed graphene nucleation sites, and ultimately, the graphene domains. The growth of graphene domains continued along with secondary nucleation of graphene nuclei on the surface of graphene sheets with defective spots. Vertically stacked graphene sheets were proposed to have been formed by stacking numerous overlapping graphene domains, as shown in Fig. 1c. The vertical graphene/TiC nanorod arrays were prepared at 900 °C for 15 min.

### 2.2. Characterization

Scanning electron microscopy (SEM) (MERLIN Compact, Carl Zeiss, Germany), transmission electron microscopy (TEM) (JEM-2100, 200 kV, JEOL, Japan), X-ray diffraction (XRD) (Ultima IV, Cu K $\alpha$ ,  $\lambda =$

1.5406 Å, Rigaku, Japan), Raman spectroscopy (Raman) (DXR, YAG laser,  $\lambda = 532$  nm, Thermo Scientific, MA, USA), and X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Fisher) were used to determine the morphologies of graphene/TiC arrays.

The electrochemical properties were characterized using a conventional three-electrode system on a CHI 760 E Electrochemical Workstation (Shanghai CH Instruments Co. Ltd., China). Graphene/TiC/Ti wire was used as the working electrode, a Pt sheet as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The Britton–Robinson (B–R) buffer solutions with various pH values were prepared using the stock solution of 0.2 mM NaOH, 0.04 mM mixed acid of boric acid, phosphoric acid, and acetic acid.

## 3. Results and discussion

Fig. 2 shows a series of top view SEM images of the samples. Ti wire surface with the TiO<sub>2</sub> nanotube array, which is a transition layer and template for the formation of TiC nanorods, is shown in Fig. 2a. The surface morphology changed from a nanotube array to a porous surface, and the graphene layer was also formed (Fig. 2b). Oxygen atoms disappeared and aggregated grains into the framework because of surface energy minimization upon heating, which facilitated the formation of TiC square hole morphology [24], as shown in Fig. 2b. In this case, the number of graphene nanosheets, which uniformly covered the surface of the porous structure, increased and began to form into vertically-oriented graphene sheets (Fig. 2d). Obviously, a highly porous structure provides a larger surface area for the growth of graphene compared to a planar substrate. The vertical graphene stems from the mismatches and curved areas of the graphene domain on the TiC frame [21]. With an increase in the deposition time, the graphene layer became thicker and denser, the graphene sheets seemed thin and translucent, and the edges of the graphene sheets were curled, so the sample had a high quality (Fig. 2e and f).

Fig. 3a and b show the cross-section view of SEM images of graphene sheets on the TiC layer at different magnifications. The thicknesses of the graphene layer and transition layer were about 10  $\mu\text{m}$  and 1  $\mu\text{m}$ , respectively. The cross-section SEM images demonstrate that graphene sheets had grown vertically to and tightly adhered with the transition layer. Each graphene sheet is transparent and curling, which means that the graphene nanosheet is very thin. Fig. 3c and d shows the cross-section view of SEM images of the transition layer on the Ti layer at different magnifications. The formation of nanorod array on the Ti wire surface can be clearly seen. In addition, EDS analysis showed that the transition layers were mainly composed of C and Ti, and both of the ratios from the inside to the outside were 41.84/58.16, 47.43/52.57,

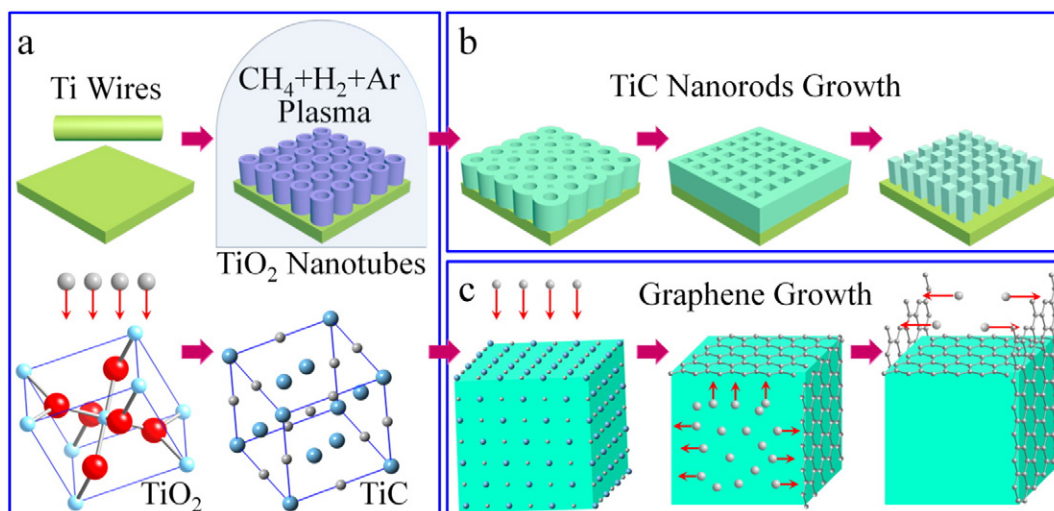


Fig. 1. Fabrication processes of the graphene/TiC/Ti wire electrode.

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