Applied Surface Science 356 (2015) 399–407

Contents lists available at ScienceDirect

Applied Surface Science

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

# Effect of titanium nitride coating on physical properties of three-dimensional graphene

Fatemeh Dabir[a], Rasoul Sarraf-Mamoory[a,*], Manuela Loeblein[b,c], Siu Hon Tsang[c], Edwin Hang Tong Teo[b]

[a] Materials Eng. Department, Tarbiat Modares University, 1411713116, Tehran, Iran
[b] School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore
[c] CINTRA CNRS/NTU/THALES, UMI 3288, Research Techno Plaza, 50 Nanyang Drive, 637553, Singapore

ARTICLE INFO

*Article history:*
Received 10 May 2015
Received in revised form 15 July 2015
Accepted 11 August 2015
Available online 13 August 2015

*Keywords:*
Three-dimensional graphene
Titanium nitride
Ammonia
Physical properties

ABSTRACT

In this paper, titanium nitride (TiN) was applied on the surface and into the porous structure of three-dimensional graphene (3DG) by chemical method. This method consists of immersing 3DG into a solution containing Ti ions and annealing under ammonia atmosphere at 850 °C. The effects of TiN coating and high temperature annealing under $NH_3$ on the physical properties of 3DG were investigated. For this purpose, the 3DG samples, with and without TiN coating, were characterized via XRD, SEM, XPS, and Raman spectroscopy. Then, the electrical resistivity, work function, and wettability of samples were determined by Van der Pauw method, contact angle meter, and UV photoelectron spectroscopy (UPS), respectively. The results showed that an almost pure and very crystalline TiN phase with titanium/nitrogen atomic ratio of 1.09 was formed on the 3DG network. Annealing of 3DG under $NH_3$ resulted in locally doping of graphene with nitrogen and generation of defects in its structure. After TiN coating, the work function value of 3DG (5 eV) was reduced to 4.68 eV, while its initial water contact angle decreased from 127° to 83°.



## 1. Introduction

Graphene (G), two-dimensional hexagonal arrangements of carbon atoms, is at the forefront of materials research due to its unique physical, chemical, and mechanical properties [1]. The outstanding properties of graphene provide a wide range of potential applications for graphene-based functional materials [2]. However, it is worth pointing out that the performance of these functional materials is still lower than the expected data because of the restacking or aggregation of 2D graphene sheets owing to the strong van der Waals interactions between them [3].

Recently, a three-dimensional form of graphene (3DG) has been introduced as an ultra-light, very porous, conductive, and flexible interconnected network [4]. This unique structure of 3DG, while maintaining outstanding properties of two-dimensional graphene, has opened many applications for it such as in sensors [5], fuel cells [6], Li-batteries [7], and supercapacitors [8]. Moreover, the 3DG can be utilized as a scaffold for the growth of various nanomaterials in order to improve its own surface properties and expand the range of applications. There are some reports about the growth of different nanomaterials on 3DG, such as metal oxides [9,10], hydroxides [11], sulfides [12], noble metals [13], and polymers [14]. Nevertheless, to the best of our knowledge, there are too few studies on decoration of 3DG with transition metal nitrides. Transition metal nitrides, such as TiN, are important functional materials in research and industrial fields because of their superior electrical conductivity and high chemical stability [15]. In reports on TiN/graphene composites, so far the two-dimensional form of graphene has been used [16–19]. However, to this date, there is no study focused on the growth of TiN on the CVD-grown three-dimensional graphene networks.

We expect that the TiN will increase the surface wettability of 3DG, while retaining its high electrical conductivity and chemical stability. Additionally, we also predict TiN to reduce the work function of 3DG which affects the charge transport processes. Therefore, it is expected that the TiN/3DG composite creates new applications in graphene field, because it combines superior properties of both 3DG and TiN. As a result, it is highly beneficial to evolve an

* Corresponding author. Tel.: +98 9121334979; fax: +98 2182884390.
*E-mail addresses:* f.dabir@modares.ac.ir (F. Dabir), rsarrafm@modares.ac.ir (R. Sarraf-Mamoory), manuela001@e.ntu.edu.sg (M. Loeblein), shtsang@ntu.edu.sg (S.H. Tsang), htteo@ntu.edu.sg (E.H.T. Teo).

http://dx.doi.org/10.1016/j.apsusc.2015.08.086
0169-4332/

efficient method for integrating 3DG with TiN into three-dimensional networks and also to discover their functional properties and possible applications.

One of the most common and cost-effective routes for 3DG synthesis is chemical vapor deposition (CVD) using a porous transition metal foam as a template with subsequent removal of metal by chemical etching [4].

In this study, the 3DG foam was synthesized via thermal CVD process using Ni template. Then, the TiN was coated on porous CVD-grown three-dimensional graphene using a chemical method, followed by annealing under $NH_3$ atmosphere. Finally, the effects of TiN coating and high temperature annealing under $NH_3$ atmosphere on physical properties of 3DG were investigated by comparing the 3DG properties before and after applying TiN.

## 2. Materials and methods

### 2.1. Preparation of 3DG on quartz glass

The nickel foam (Latech Scientific Supply Pte. Ltd.) with thickness of 0.5 mm was used as a template and heated under Ar and $H_2$ flow (200:50 sccm). Graphene was grown on Ni foam using an ethanol bubbler at 1000 °C for 10 min. After growth, the 3DG-coated Ni foam was dip-coated with poly(methyl methacrylate) (PMMA) (950A4) to protect the structure and then immersed into diluted HCl with temperature of 80 °C for 3 h to remove the Ni template. After rinsing with DI water, the PMMA-covered 3DG was transferred on quartz slide and annealed under Ar and $H_2$ flow at 700 °C for 1 h.

### 2.2. Coating the TiN film on 3DG

At the first, a solution containing Ti ions was prepared. For this purpose, 0.5 ml of titanium tetra isopropoxide (TTIP, Aldrich), serving as the titanium source, was dissolved in 5 ml of absolute ethanol (Merck). Then, 3DG-coated quartz glass was immersed in the prepared solution with temperature of 50 °C for 2 h to adsorb effectively the titanium complexes. Finally, the samples were annealed at 850 °C for 3 h under $NH_3$ flow (50 sccm) in a tube furnace.

### 2.3. Characterization

Phase analysis of pristine 3DG and TiN/3DG was performed using low angle XRD (Panalytical) with Cu-K$_\alpha$ radiation ($\lambda$ = 0.154056 nm). Surface morphology of samples was evaluated by SEM analysis (LEO 1550 Gemini). The TEM analysis (JEOL 2100) was used for investigation of 3DG cross section. The chemical composition of pristine 3DG and TiN/3DG was characterized via XPS (ESCALab 250i-XL & Thetaprobe A1333). The details of 3DG structure before and after TiN coating were identified by Raman spectroscopy (WITec CRM200 Raman) using an Ar ion laser ($\lambda$ = 532 nm). The work function of pristine 3DG and TiN/3DG was determined by UPS using a helium lamp radiation at 21.2 eV. The wettability of 3DG before and after applying TiN was measured by contact angle meter (VCA Optima-AST products, Billerica, MA) through dropping DI water on their surfaces under ambient environment. The contact angle data for three different places of each sample were averaged for more accuracy.

## 3. Results and discussion

### 3.1. Structure and phase analysis

Fig. 1 represents the low angle XRD patterns of pristine 3DG and TiN/3DG. In both patterns, the peaks placed at about 26°, 44.4°, and 54.5° are related to the (0 0 2), (1 0 1), and (4 0 0) planes of graphene, respectively (JCPDS 41-1487). In Fig. 1b, the other four peaks at about 36.8°, 43°, 62°, and 74.5° belong to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of rock-salt structure of TiN, respectively (JCPDS 87-0633). These results are indicative of formation of crystalline TiN on 3DG. There are no other peaks in the diffraction patterns of TiN/3DG, representating that an almost pure TiN phase has been grown on the graphene surface. This result has been induced from XRD analysis and should be clarified by another analytical technique such as XPS.

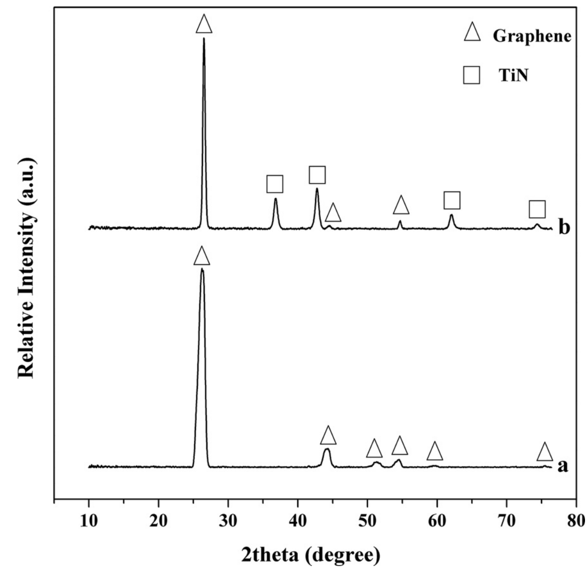


**Fig. 1.** XRD patterns of (a) pristine 3DG and (b) TiN/3DG.

Additional information such as number of stacked layers of 3DG samples with and without TiN coating was extracted from XRD data. The average number of the stacked graphene layers ($n$) can be obtained using the Scherrer equation (Eq. (1)) and by fitting the (0 0 2) peak of graphene [20].

$$L_{002} = \frac{K\lambda}{\beta_{002}\cos\theta_{002}} \tag{1}$$

where, $L_{002}$ is the crystallite size perpendicular to the (0 0 2) plane, $K$ is the shape factor (0.89), $\lambda$ is the X-ray wavelength (0.154056 nm), $\beta$ is the full width at half maximum (FWHM), and $\theta$ is the peak position.

Fig. 2 shows the Lorentzian fits for (0 0 2) reflection of graphene in 3DG with and without TiN coating. The average number of graphene layers ($n$) was estimated from Eq. (2) after calculation of $L_{002}$ using Eq. (1).

$$n = \frac{(L_{002} + d_{002})}{d_{002}} \tag{2}$$

where, $d_{002}$ is the interlayer space [21].

Table 1 shows the extracted data from (0 0 2) reflection of graphene for both pristine 3DG and TiN/3DG.

The (0 0 2) reflection of pristine 3DG (Fig. 2a) shows an asymmetry in line shape and can be fitted with three different peaks which means that there is an inhomogeneity in structure of synthesized 3DG. 71% of 3DG structure has a number of graphene layers of 31. 21% of 3DG is comprised by 54 layers and the rest, which is 8%, has 47 layers. Therefore, the average number of stacked graphene layers in pristine 3DG is about 37 layers.

It is clear from Table 1 that the decoration of 3DG with TiN and annealing under $NH_3$ have led to a change in the number of graphene layers. Moreover, the (0 0 2) reflection of graphene for TiN/3DG (Fig. 2b) is symmetric and can be fitted with one peak.