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One-step synthesis of TiC/multilayer graphene composite by thermal plasma

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ABSTRACT

Graphene hybrid materials have been attracting a great deal of attention due to their superior properties. Nevertheless, problems such as expensive and complicated production processes have limited their application to industrial fields. Here, we introduce a one-step synthesis of titanium carbide (TiC) nanoparticles on multilayer graphene nanosheet (TiC/multilayer graphene) composites using thermal plasma. Although there are three types of titanium alkoxides (titanium ethoxide, titanium isopropoxide and titanium n-butoxide), the TiC/multilayer graphene was synthesized from only titanium isopropoxide. The injection temperature of the precursor was varied to investigate the effects of the precursor concentration in the plasma region. A TiC/multilayer graphene hybrid material with crystalline TiC nanoparticles below 50 nm on graphene nanosheets was observed. The number of graphene nanosheet layers varied from one to over 10 according to the injection temperature. When titanium ethoxide and titanium butoxide were injected, TiC with amorphous carbon and graphite were synthesized. The formation of graphene is considered to be affected by the structure of the carbon chain in the precursors and the concentration in the plasma region.

1. Introduction

Graphene, which is a two-dimensional carbon material reported first in 2004 [1], has superior properties such as a large surface area, high electron mobility, high thermal and electrical conductivity and extreme mechanical strength [2–4]. Graphene hybrid materials have recently been attracting a great deal of attention since the combination of graphene with metals [5–7], ceramics [8–11] and polymers [12–14] was found to enhance its physical and chemical properties.

Titanium carbide (TiC)/carbon composites are of great interest for applications in electrical devices because of their enhanced electrical and mechanical properties [15–18]. Therefore, dispersion of TiC nanoparticles into the carbon matrix improves the mechanical and electrical properties of carbon materials such as high hardness and low friction coefficient. Although a variety of carbon materials including amorphous carbon, mesoporous carbon and carbon nanotubes (CNT) have been applied for TiC/carbon composites, recent interest has focused on TiC/graphene. It has been reported that TiC/graphene composite has superior properties to other types of TiC/carbon composites [19]. However, the dispersion of TiC nanoparticles on graphene and obtaining a high-quality graphene are still challenges.

In our previous study, we described the synthesis of graphene from hydrocarbons using thermal plasma [20]. However, the presence of substrate and the injection of hydrocarbons as precursors limited further research. In view of this point, substrate-free synthesis of graphene from hydrocarbon derivatives such as alcohol, a new technique reported first by Dato et al. is an innovative method that is convenient, inexpensive and uses relatively safe precursors [21]. Most studies introducing this new method have employed microwave plasma, but not thermal plasma [22–24]. Although both microwave plasma and thermal plasma are applied as energy sources for material synthesis, the differences in their temperature and velocity distribution would lead to the distinct results. Nevertheless, the introduction of thermal plasma to this new technique may enable mass production of graphene and graphene-related materials if it is possible since the thermal plasma apparatus is more applicable for industries.

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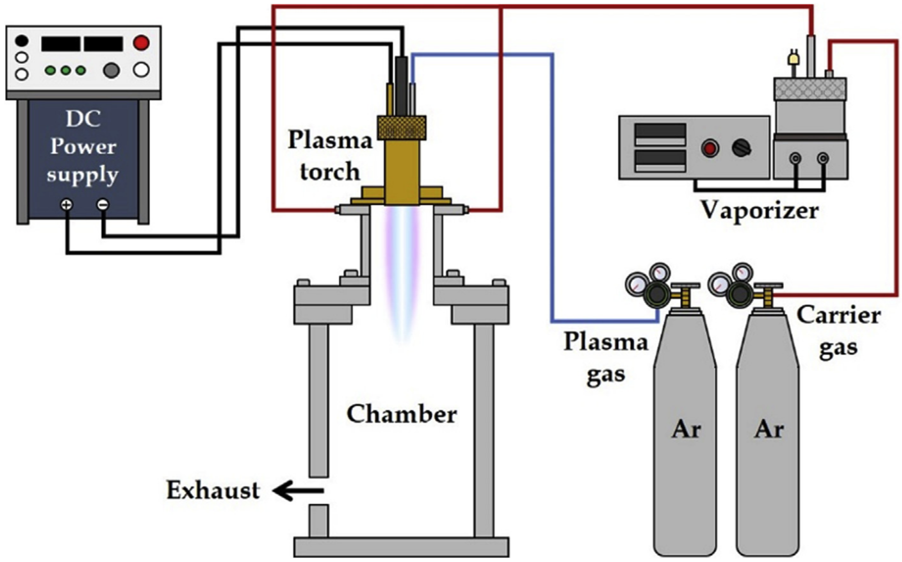

Fig. 1. Experimental apparatus for the synthesis of TiC/multilayer graphene composite.

Table 1
Detailed plasma operating conditions.

Discharge gas	Ar 15 L/min
Current	300A
Voltage	30V
Power	9.0 kW
Carrier gas	Ar 1 L/min
Pressure	760torr
Feeding time	10min

In this study, we demonstrated the facile synthesis of titanium carbide nanoparticles on graphene nanosheets (TiC/multilayer graphene) using DC thermal plasma. Titanium alkoxides such as titanium ethoxide (TE), titanium isopropoxide (TTIP) and titanium n-butoxide (TTBT) were selected as possible precursors because alkoxy groups in these precursors were expected to play a similar role as alcohol in the aforementioned studies. Moreover, injecting ethanol and isopropanol was attempted to confirm the formation mechanism of multilayer graphene and TiC/multilayer graphene in DC thermal plasma. As a result, TiC/multilayer graphene was synthesized with only TTIP in one-step. The product possessed crystalline TiC nanoparticles at below 50 nm and single-, few- or multi-layer graphene according to the precursor-vaporizing temperature.

2. Experiments

Fig. 1 shows the experimental set-up for the one-step synthesis of TiC/multilayer graphene composite. To generate thermal plasma, a DC non-transferred plasma apparatus consisted of a DC power supply with a maximum power of 30 kW, a plasma torch and a double walled cooling chamber. The plasma torch had a tungsten cathode and copper anode. The three types of precursors in this study (titanium ethoxide ($C_{32}H_{80}O_{16}Ti_4$, TE), titanium isopropoxide ($C_{12}H_{28}O_4Ti$, TTIP) and titanium butoxide ($C_{16}H_{36}O_4Ti$, TTBT)), which are liquid at room temperature, were poured into a vaporizer. A stainless-steel tube connecting the vaporizer and the plasma reactor was heated with a band heater to prevent condensation of the vaporized precursors during injection. Once the plasma was generated, the vapor of the precursor generated by heating the vaporizer was injected in to the plasma jet with 1 L/min argon as carrier gas.

Table 2
List of the samples and precursor injection conditions.

Preucrsor	Sample name	Injecting temperature(K)	Injection rate (g/min)
Titanium isopropoxide	TTIP441	441	0.64
	TTIP473	473	0.96
	TTIP505	505	2.50
Titanium ethoxide	TE425	425	0.38
Titanium n-butoxide	TTBT504	504	0.95

Table 1 shows the detailed plasma operating conditions for synthesis of TiC/multilayer graphene composite. As operating variables, the vaporizing temperature of each precursor was controlled. At first, the boiling temperatures of each precursor were selected as the vaporizing temperature; 425 K for TE, 505 K for TTIP and 585 K for TTBT. These experiments were conducted to investigate the effects of the type of the precursor on the synthesis of TiC/multilayer graphene. However, it should be noted that the experiment in which TTBT was injected at 585 K was not successful because TTBT decomposed simultaneously during when it was vaporized (Fig. S1). As a result, this experiment was repeated at 504 K.

Next, TTIP was injected at 441 K and 473 K, which are below its boiling point, leading to a lower injection rate of TTIP. These experiments were conducted to investigate the effects of the precursor concentration in the plasma region. The experiments according to the precursor injection conditions are listed in Table 2. During each experiment, the plasma was discharged for 10 min. After the plasma was turned off, the black powders were collected from the wall of the reactor.

The as-synthesized powders from each operating condition were analyzed by X-ray diffractometry (XRD, DMAX 2500, Rigaku Co.), field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi Co.), field emission transmission electron microscopy (FE-TEM, JEM-2100F, Jeol Co.), Raman spectrometry (Lab Ram ARAMIS, Horiba) and using a physisorption analyzer (ASAP2020, Micromeritics). The phase composition of the as-synthesized powders was confirmed by XRD. The morphologies of the as-synthesized powders were observed by FE-SEM and FE-TEM. A Raman

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