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Short communication

Ultrafast synthesis of SiC@graphene nanocomposites by one-step laser induced fragmentation and decomposition

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ABSTRACT

Carbides with high strength and chemically inert have unique optical and electrical properties, but widely used and controllable wet chemical methods are unsuitable for the synthesis of their nanocomposites because of the ultrahigh melting point. In this paper, we demonstrate one novel, simple and ultrafast laser irradiation method to synthesize ultrafine SiC@graphene nanocomposites. Both the fragmentation and spheroidization of bulk SiC flakes and surface covered by 1–3 graphene layers are accomplished in the one-step laser irradiation process.

1. Introduction

The ability to synthesize nanocomposites with well-controlled composition, sizes and microstructure is central to advance the applications in many aspects of modern science and technology [1–4]. Silicon carbide (SiC) is typical wide-bandgap semiconductor with a great potential for applications in high-frequency and high-power electrical devices under extreme conditions due to its high thermal, mechanical and chemical stability [5–7]. Due to the exceptional physical properties and chemical tunability, graphene has shown great potential for different applications. High-purity graphene growth must be carried out under highly isothermal conditions at a high temperature of 1800–2000 °C in an ultrahigh vacuum or a buffer inert gas [6,10,11]. Graphene obtained by sublimation on 4H- and 6H-SiC (C-face graphene) exhibits very high mobility ($\mu > 18{,}000\ cm^2\ V^{-1}\ s^{-1}$) at room temperature [8], which is regarded as an effective method to grow electronic grade two-dimensional carbon material on a semi-insulating substrate without the need of transfer [9]. SiC/graphene nanocomposites are important zero-dimensional nanocomposites in advanced reactor designs and microsupercapacitors [12,13]. However, due to the high melting point of SiC (generally > 2000 °C), synthesizing such nanocomposite remains a significant challenge using existing fabrication methodologies.

Here, we proposed a novel laser-assisted growth strategy for core-shell SiC@G nanocomposites at ambient conditions. The laser beam induces the extreme non-equilibrium condition (> 10^4 K and > 1 GPa) around the laser spot-material interface that can melt SiC nanoparticles and fully meet the growth conditions of epitaxial graphene. Such one-step laser irradiation process includes: (1) the bulk SiC flakes are fragmented to irregular ultrafine nanoparticles (~ 8 nm), (2) irregular nanoparticles are spherified by laser-stimulated surface tension energy release (LSTER), (3) the surface decomposition of SiC nanospheres and subsequently Si atoms evaporation and reconstruction of C atoms to form graphene shells (1–3 layers) are caused by laser induced photothermal decomposition (PTD). This simple and ultrafast synthesis technique presented here could also be used as a common fabrication method for other carbide/graphene nanocomposites.

2. Experimental

The ultrafine SiC@G nanocomposites was fabricated by KrF pulse laser irradiation in ethanol at room temperature. Commercial SiC flakes (99.9%, Macklin) were dispersed in ethanol to form a dispersed suspension solution (10 g L^{-1}). Then a 248 nm laser beam (10 Hz, 25 ns, Coherent, CompexPro 205) was focused on the SiC dispersions through a group of convex lens. Laser irradiation process were performed under a laser fluency of 0.8 J $pulse^{-1}$ cm^{-1} for 5 min. The SiC dispersion was continuously stirred during laser irradiation to prevent gravitational

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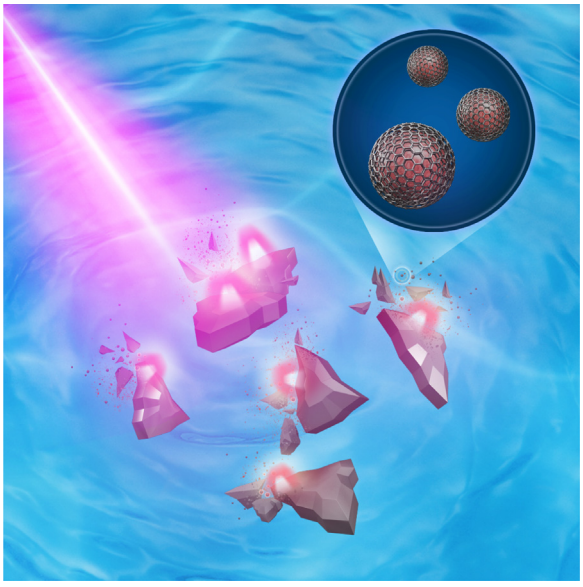

Fig. 1. Schematic illustration of the ultrafast growth process of SiC@G nanocomposites by laser irradiation.

sedimentation. After laser irradiation, the solution was divided by centrifugal screening and washed by mixed acid (5 wt% HF and 5 wt% H_2O_2) several times. Finally, the obtained products were dried at 30 °C to for further characterizations. The material characterization details were presented in Supporting information.

3. Results and discussion

Fig. 1 outlines the growth process of ultrafine SiC@G nanocomposites by one-step laser irradiation-induced fragmentation and decomposition. When a laser beam irradiates the SiC dispersions, one extreme non-equilibrium condition in nature, like ultrahigh temperature ($> 10^4$ K) and ultrahigh pressure (> 1 GPa), can be produced around the laser spot-material interface instantly due to the absorption of high laser power [14–20]. Under such transient plasma and photothermal effect, big SiC flakes explode to smaller fragments, and then melt into nanospheres by a laser-stimulated surface tension energy release process to attain the lowest specific surface energy (Fig. 1), as reported by our previous work [17,21]. Meanwhile, the decomposition of SiC particles occurs in the liquid. Due to the bigger vapor pressure of silicon than that of carbon, the Si sublimation from the SiC enables carbon enrichment on the SiC surface. Then, graphene can be grown through the reconstruction of the C atoms on SiC particle surface. As a result, SiC@G nanocomposites are synthesized by the ultrafast and simple laser irradiation of SiC dispersions in one step under ambient conditions. This super-fast method totally overcomes the shortcoming of SiC volume growth as submicron scale caused by the laser induced high-temperature melting and merger in our previous work [22], which can obtain elegantly ultrafine nanoparticles (less than 10 nm). In addition, the novel one-step laser irradiation is no need any pretreatment like hydrogen etching and high-temperature annealing in vacuum compared with the traditional vapor method [8,9].

The morphology and microstructure change from raw SiC flakes to laser irradiation-induced SiC@G nanocomposites are investigated by transmission electron microscope (TEM), as shown in Fig. 2. Raw SiC particles are of irregular shape with sharp edges (Fig. 2(a)). When SiC particles were irradiated by pulse laser for 5 min in ethanol, the big flakes were fragmented into small nanospheres (Fig. 2(b)). The high resolution transmission electron microscope (HRTEM) image in Fig. 2(c) shows the small nanosphere has a core-shell structure, e.g. SiC core with 1–3 graphene shells. The size distribution of the laser irradiation-induced nanocomposites are exhibited in Fig. 2(d) showing a mean diameter of ~ 8 nm.

The X-ray diffraction (XRD) spectra of the raw SiC flakes and SiC@G nanocomposites obtained by pulse laser irradiation are shown in Fig. 3(a). The peaks appear at 35.6°, 41.4°, 60.1° and 71.9° correspond to the (111), (200), (220), and (311) planes of 3C-SiC. After laser irradiation, the peaks show left shift of ~ 0.5° and wider full width at half maximum, which indicate the particle size of SiC@G decreases and the corresponding crystallization is lower, respectively. In addition, the weak broad diffraction at ~ 26.5° can be indexed to the (002) peak from disordered stacked graphene layers. Fig. 3(b) compares the corresponding Raman spectra of SiC and SiC@G particles. After laser irradiation, the typical D and G peaks of graphene are observed, which clearly indicates the successful preparation of graphene shell on the SiC particles.

To further understand the SiC@G core-shell particle growth process, X-ray photoelectron spectroscopy (XPS) (Fig. 4) were measured for raw SiC flakes and SiC@G nanocomposites before acid washing. XPS survey spectrum, and core-level spectra of Si 2p and C 1s are shown in Fig. S1 and Fig. 4. For raw SiC flakes, the Si 2p peak (Fig. 4(a)) can be fitted with two components: the two main peaks (101.1 eV and 102.4 eV) are assigned to Si–C bond and the other peak (103.5 eV) should be assigned to Si-O (adsorption oxygen from the air). The Si 2p peak (Fig. 4(c)) from the laser irradiated SiC@G nanocomposites show the characteristic signals of higher binding energies Si–C bond (101.9 eV and 103.2 eV), Si–O bond (104.3 eV) and Si-Si bond (100.4 eV), respectively, indicating the decomposition of SiC. The intensity of C-Si in SiC@G nanocomposites is much lower than the one in raw SiC flakes, as shown in Fig. 4(b) and (d), which is caused by the graphene shells covered on SiC nanosphere surface. Such ultrafine SiC nanospheres (~ 8 nm) decorated by 1–3 graphene layers can effectively improve the electron transport efficiency and further potential applications in photocatalyst and supercapacitor are explored in our lab.

Fig. 5(a) compares the UV–Vis absorption spectrum of raw SiC particles and SiC@G nanocomposites before acid washing in in ethanol. Due to the indirect bandgap of 3C-SiC particles [23,24], the absorption spectra of raw SiC and SiC@G suspensions have no absorption edge. The difference is that SiC@G suspension has a noticeable absorption in the long wavelength range of 700–800 nm, which may be caused by the Si nanoparticles (~ 1.3 eV) produced by PTD, while the whole absorption spectra of raw SiC is basically flat. Yang et al. found an anomalous spectral shift from the beaded SiC nanorings (9–20 nm) fragmented by laser irradiation [17]. In order to verify whether the anomalous phenomenon is induced by laser, Fig. 5(b) also depicts the typical photoluminescence (PL) emission spectra of SiC@G suspensions at different excitation wavelengths. When the excitation wavelength shifts from 310 nm to 390 nm, the emission peak moves monotonically from 409 nm to 482 nm and no anomalous red spectral shift is observed. Such blue spectral shift is ascribed to quantum confinement effects: as the excitation wavelength is decreased, smaller SiC nanoparticles are excited, and emitting shorter wavelengths because of the larger bandgap of SiC [23,25].

4. Conclusions

In summary, we take full advantage of the extreme non-equilibrium conditions induced by laser beam and propose a novel laser-assisted growth strategy for core-shell SiC@G nanocomposites with ultrahigh melting point and hardness at ambient conditions. The one-step laser irradiation process includes the fragmentation of bulk SiC flakes and spheroidization by releasing the surface tension energy, and residual carbon atoms graphitization on the surface of SiC nanospheres to form layer shells. Such nanocomposites can effectively improve their electron transport efficiency and enlarge further potential applications of SiC.

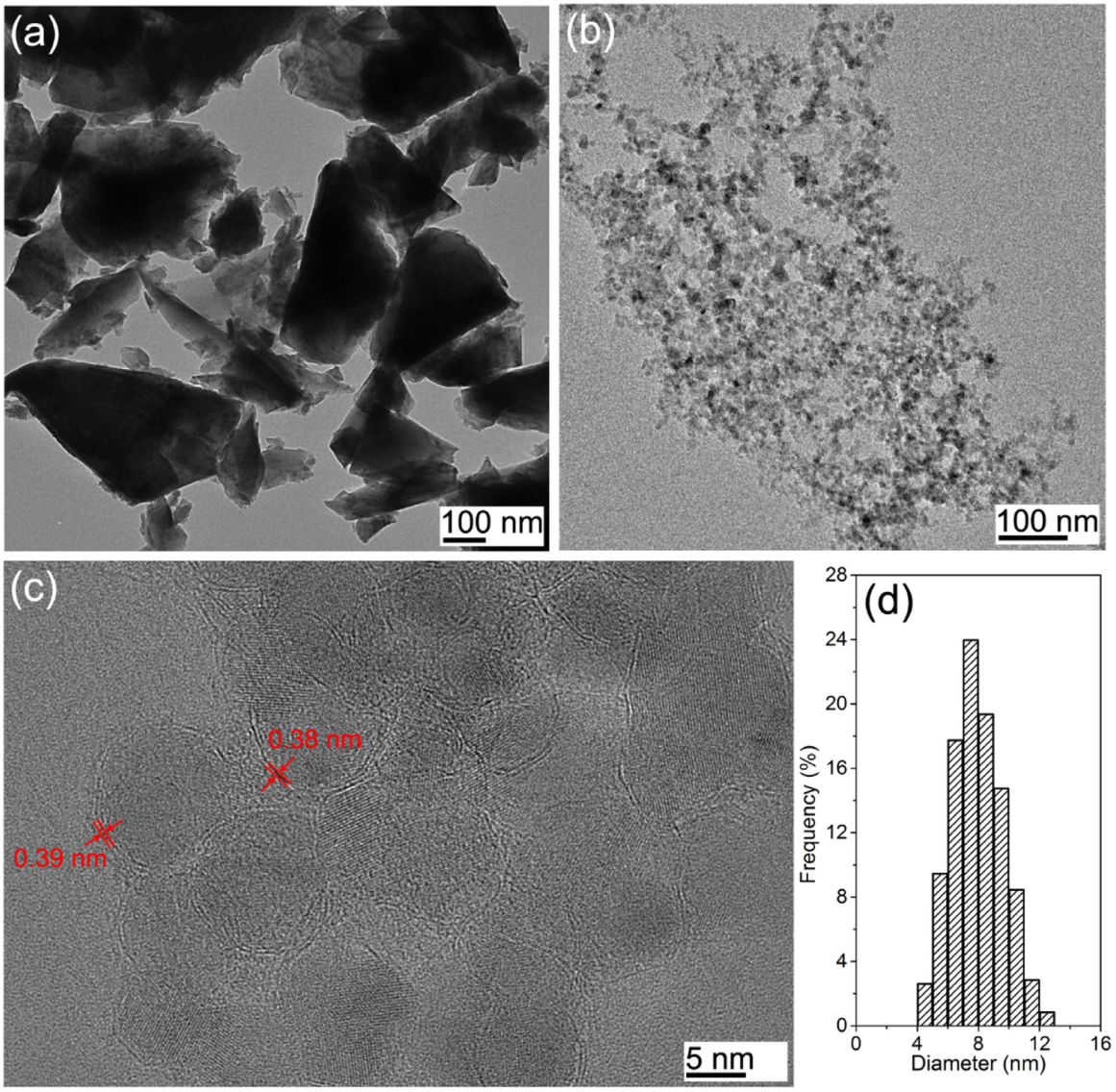

Fig. 2. TEM images of (a) raw SiC flakes and (b) laser irradiation-induced SiC@G nanocomposites. The corresponding HRTEM image (c) and size distribution histogram (d) of SiC@G nanocomposites.

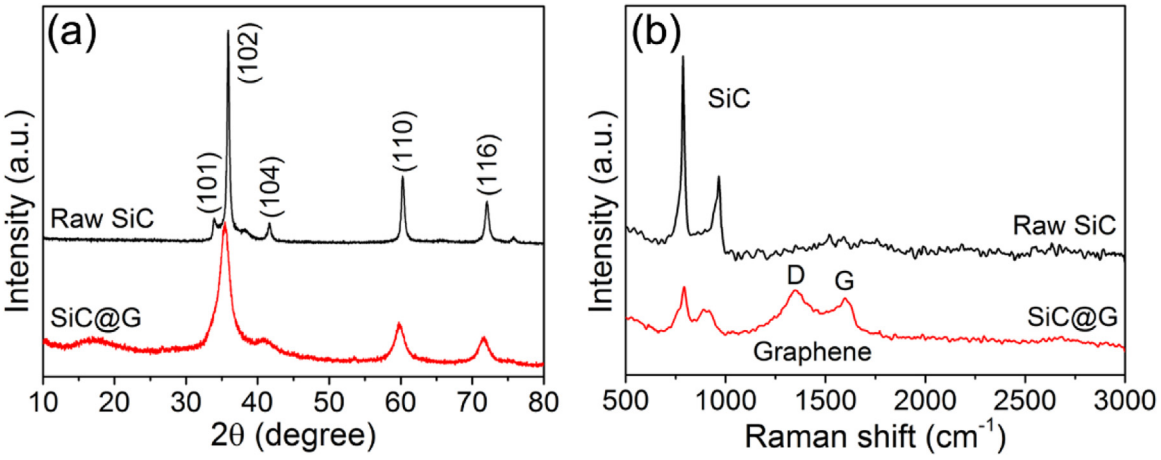

Fig. 3. (a) X-ray diffraction spectra and (b) Raman spectra of raw SiC flakes and SiC@G nanocomposites.

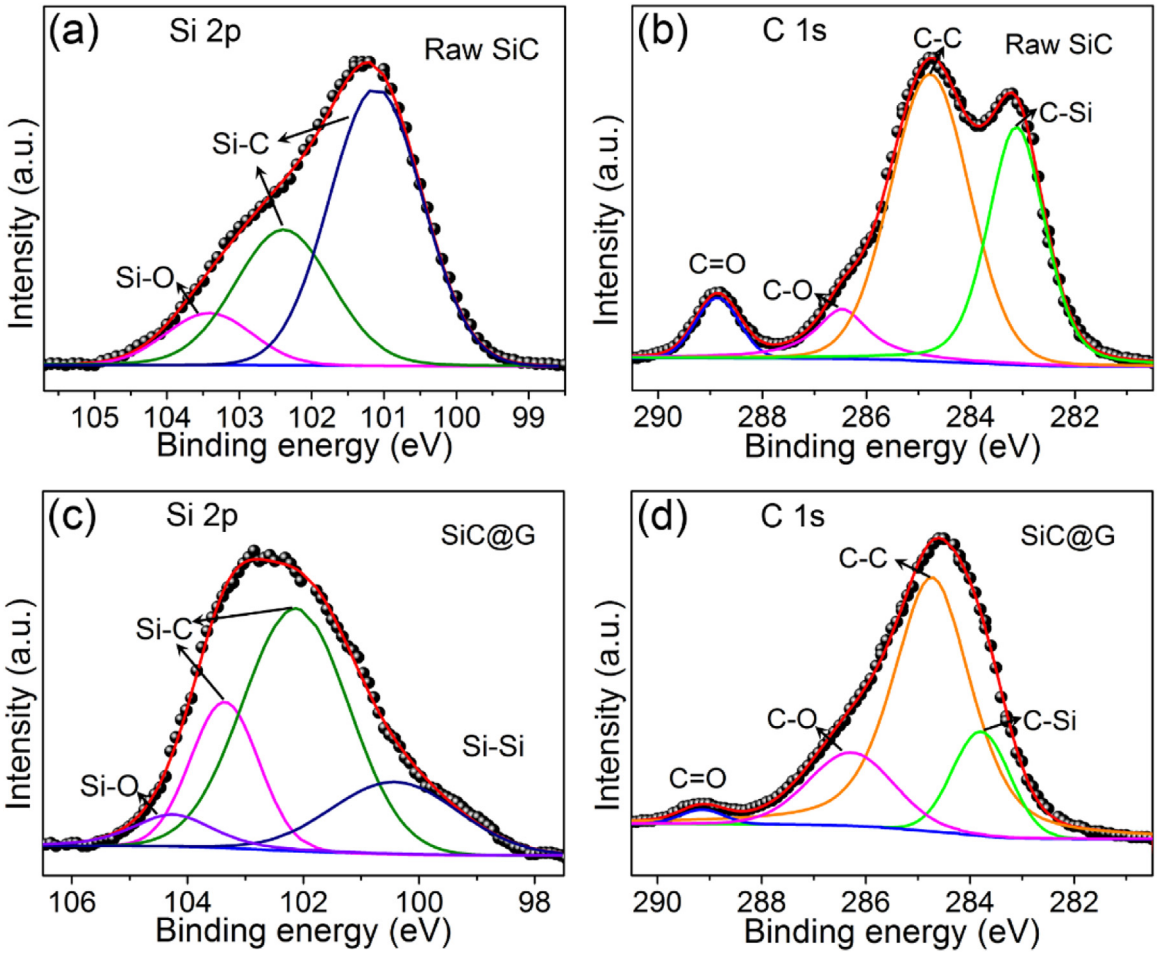

Fig. 4. Si 2p core-level spectra and C 1s core-level spectra of raw SiC particles (a-b) and SiC@G nanocomposites (c-d).

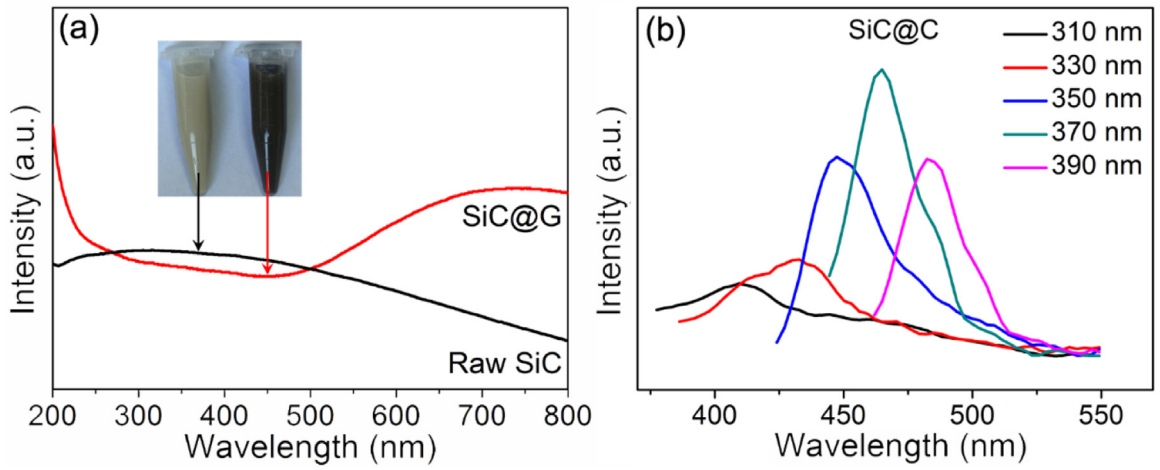

Fig. 5. (a) UV–Vis absorption spectra of raw SiC particles and SiC@G nanocomposites. (b) Photoluminescence (PL) spectra of SiC@G nanocomposites under different excitation wavelengths.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ceramint.2018.07.046.

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