INTRODUCTION

Since Fujishima and Honda found that TiO₂ has photocatalytic activity in 1972 (Fujishima & Honda, 1972), the potential applications of photocatalytic materials have gained more attention. A large number of semiconductor materials with a wide band gap (Kang et al., 1999; Zhou et al., 2006) have been studied for their photocatalytic properties. As one of the third generation, silicon carbides have been extensively investigated for their physical and chemical properties (Kang et al., 2007; Kang et al., 2009; Shao et al., 2009; Nacera et al., 2011; Liu et al., 2012), among them the photocatalytic properties have attracted particular attention until recent years (Noboru et al., 2002; Nicolas et al., 2004; Isaias et al., 2013). Nariki et al. (1990) firstly reported the photocatalytic property of SiC synthesized by DC arc plasma method. They used the bulk SiC as raw material to produce SiC nanoparticles under the ambient atmosphere of hydrogen and inert gases with different ratios. It was found that the photocatalytic performance of SiC nanoparticles is comparable to that of Pt/TiO₂ in the produced capacity of hydrogen, in which the productions were exposed to the ultraviolet irradiation in the wavelength range of 210 to 460 nm. The microstructure of SiC composite is beneficial in photocatalytic decomposition of the contaminants, due to the surface graphite layer with better conductivity can quickly deliver the generated photoelectrons away and significantly reduce the electron-hole complex, thus the efficiency of photocatalytic decomposition of pollutants is greatly improved (Anieuddh et al., 2011; Liu et al., 2012; Pan et al., 2012). Up to date, SiC/C composites are mainly fabricated by a heat-treatment in air and their photocatalytic performances were then greatly improved.

Key Words: Arc-discharge, Different carbon sources, SiC/C, Nanocomposite, Photocatalytic

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mal reduction or the vapor deposition method. Zhu et al. (2012) synthesized the graphene packaged SiC by sintering SiC under a low pressure and high temperature; George et al. (2010) prepared the microporous SiC/C composites by carbon thermal reduction of polysilsesquioxanes gel; Kim et al. (2003) reported that the aligned SiC/C coaxial nanocables were synthesized via the direct growth of SiC nanowires from silicon substrates and subsequent carbon deposition by pyrolysis of methane. Nevertheless, the preparation of SiC/C nanocomposites by the arc-discharge plasma and their photocatalytic performances have rarely been investigated.

In this work, a series of SiC/C nanocomposite powders have been synthesized by the arc-discharge plasma (Dong et al., 1999; Lei et al., 2009). The structures, compositions and morphologies of these nanocomposites were analyzed by means of X-ray diffraction (XRD) and scanning electron microscope (SEM). The photocatalytic degradation of methylene blue (MB) by such SiC/C nanocomposite powders were also examined.

**MATERIALS AND METHODS**

The arc-discharge plasma method was used to synthesize SiC/C nanocomposite powders. In any case, the micron-sized Si powders were used as the source of silicon. Firstly, to mix the micro-sized powders of graphite and silicon, then compress the mixture into a block which was then put into a graphite crucible to act as the anode of arc-discharge, while a graphite rod served as the cathode. Secondly, after the chamber was evacuated, a mixture of hydrogen and argon was introduced as the source of hydrogen plasma and the condensation gas, respectively. Finally, to ignite the arc and maintain the current at 90 A. Priority to take the nanopowders out from the chamber, a passivation process was necessary on the nanoparticles for stabilization.

In this paper, three carbon sources, i.e., solid graphite, gaseous methane (CH₄) or liquid ethanol, were employed to synthesize the SiC/C nanocomposite powders. Table 1 shows the preparation conditions of carbon sources and evaporation atmospheres for SiC/C nanopowders. In the case of solid carbon source, the molar ratios of graphite and silicon micropowders were fixed as 1.0:0.1, 1.0:0.9 and 1.0:1.0, accordingly the corresponding nanopowder samples are marked as S1, S2 and S3, respectively. As an auxiliary carbon source, the methane gas has been also applied as the atmosphere for evaporation of the solid mixture of graphite and silicon (the molar ratio of 1.0:0.9) and the produced nanopowders is labelled as SG1. The SiC/C nanopowder samples synthesized by using of unitary methan gas or liquid alcohol are labelled as G1 or L1, respectively. The nanopowders were characterized by means of XRD, SEM and transmission electron microscopy (TEM). The photocatalytic performances of SiC/C nanopowders were also measured according to following steps: to weigh up 0.5 g of nanopowders and put them into the MB solution with concentration of 10 mg/L, then sonicate for 5 minutes and stir for 15 minutes with a magnetic stirrer under black light condition; then place the solution under an ultraviolet lamp (power of 300 W) and continue stirring. To sample 1.5 mL of the solution in an interval of 20 minutes and centrifuge them for 10 minutes with speed of 8,000 r/s. The supernatant fluid was taken to test its absorbance by ultraviolet visible light. Using the calculated concentration, the degradation curve of MB was drawn.

**RESULTS AND DISCUSSION**

**Solid Carbon Source for SiC/C Nanopowders**

Fig. 1 shows XRD patterns of samples S1, S2 and S3, all of these SiC/C nanopowders were prepared by using of solid graphite source, however different in molar ratios of C and Si in the raw materials. As it can be anticipated, the sample S1 (Fig. 1 ‘a’) has a main phase of graphite due to the abundant content of carbon in its raw material, and secondary phase of \( \beta \)-SiC with cubic lattice (JCPDS No. 29-1129). The sample S2 (Fig. 1 ‘b’) consists of almost single phase of \( \beta \)-SiC, nevertheless a small quantity of free graphite and silicon phases exist in sample S2 (Fig. 1 ‘c’). Thus, the optimum composition range could be determined for C and Si elements, that is the content of carbon should be a little higher than the stoichiometry of SiC and then near single

| Silicon source | Carbon sources | Atmospheres (MPa) | Samples marked |
|----------------|----------------|-------------------|---------------|
| Si micropowders | Graphite micropowders | CH₄ (MPa) | Alcohol | H₂ | Ar | |
| Si micropowders | C/Si=1.0/0.1 (molar) | - | - | 0.025 | 0.05 | S1 |
| Si micropowders | C/Si=1.0/0.9 (molar) | - | - | 0.01 | 0.04 | S2 |
| Si micropowders | C/Si=1.0/1.0 (molar) | - | - | - | - | S3 |
| Si micropowders | C/Si=1.0/0.9 (molar) | 0.01 | - | 0.01 | 0.04 | G1 |
| Si micropowders | - | 0.02 | - | - | - | L1 |

Table 1. The raw sources and evaporation atmospheres for SiC/C nanocomposite powders
phase of SiC or carbon-riched SiC/C nanopowders can be obtained. From the width of diffraction peaks of SiC, its grain size can be estimated. For example, the mean size of crystal SiC in sample S2 is ~50 nm, which is calculated by Scherrer formula \( D_{\text{hkl}} = K \lambda / (\beta \cdot \cos \theta) \) and would be much more bigger than that in sample S1.

Fig. 2 display SEM and TEM images of samples S1, and S2 and S3, respectively. It is found that morphologies of SiC/C nanopowders are quite different each others due to their diverse compositions in raw materials. As shown in Fig. 2A, one-dimensional carbon nanostructures (Cai et al., 2012) are observed in S1 which has a rich-carbon content, that means a great deal of carbon can result in an anisotropic growth of nanorods in existence of SiC nanostructures; Sample S2 is nearly single phase of SiC, nonetheless exhibits the complicated nanostructures of nanoparticles and claddings, as shwon in Fig. 2B. The possible formation mechanism is as follows: the solid sources of silicon and graphite are co-evaporated by arc-discharge to be the high-energy atomic states, and react to form SiC. The higher atomic concentration and temperature gradient around the region of arc plasma promote the migration of C and Si atoms or SiC nucleus, subsequently grow into nanostructures with diverse morphologies and shapes. As the amount of graphite in excess of the stoichiometry of SiC, the carbon-coated or -mixed SiC/C nanocomposite could be fabricated. The nanopowders tend to aggregate together owing to its higher surface energy with larger specific surface area, consequently, the SiC/C nanocomposites with various shapes emerge. In sample S3, the little amount of free Si and graphite confirmed by XRD pattern (Fig. 1 ‘c’) can be recognised as the rods or small round-shaped particles as shown in Fig. 2C. The dominant phase of SiC in sample S3 has nanostructures with the irregular shapes or facets.

For a photocatalytic material, the intrinsic characteristic, structure and morphology have great effects on its photocatalytic performance (Georg & Josef, 2005; Yu et al., 2008; Zhu et al., 2012). In comparison to the nanomaterials with a uniform distribution of particle's size, the SiC/C nanocomposites with a wider distribution in its particle's size may have a broader light absorbance and a better photocatalytic performance (Saber et al., 2010). In this work, sample S2 is chosen to test its photocatalytic property which will be presented in section 3.4 together with the results from other kinds of SiC/C nanopowders synthesized by gaseous methane or liquid ethanol.

**Gaseous Carbon Source for SiC/C Nanopowders**

Gaseous carbon source of methane, meanwhile pure solid Si source, were used to produce the SiC/C nanopowders (sample G1). For comparison, using the same gaseous CH\(_4\) as an atmosphere, however a mixture of graphite and silicon micropowders was used as the solid source to form the SiC/C nanopowders (sample GS1). It means that two kinds of carbon sources (gas and solid) have been adopted here. Fig. 3 show the XRD patterns of samples G1 and GS1, respectively.

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**Fig. 1.** X-ray diffraction patterns of SiC/C nanocomposite powders using solid graphite and silicon sources: (a) sample S1, C:Si=1.0:0.1 in molar ratio; (b) sample S2, C:Si=1.0:0.9 in molar ratio; and (c) sample S3, C:Si=1.0:1.0 in molar ratio.

**Fig. 2.** Scanning electron microscope (A-C) and transmission electron microscopy (inset) images of SiC/C nanocomposite powders. (A) Sample S1. (B) Sample S2. (C, inset) Sample S3.
As shown in Fig. 3 ‘a’, main phase of SiC has created as using of the gaseous carbon source, except for a small amount of silicon and graphite. The sharp and strong diffraction peaks of SiC imply a well-crystallized nanostructure with a bigger grain size. Such SiC/C nanopowders (G1) is similar to sample S3 (using the unitary solid carbon source) in the characters. As shown in Fig. 4A for SEM images of sample G1, it is an assembly of nanoparticles due to their high surface energies. It can be concluded that both of carbon sources regardless in solid or gaseous state are equivalent in formation of SiC/C nanopowders, but the composition and morphology of SiC/C nanopowder could be different, depending on the manner to control or adjust.

For the case of using an extra solid carbon together with CH₄ (gaseous carbon), the resultant SiC/C nanopowders (GS1) is shown in Fig. 3 ‘b’. It is found an excess graphite exists in this product of GS1. It is worth to note that the diffraction peak of graphite at ~45° becomes strong, implying an anisotropic growth of graphite which is further proved by the nanosized flakes shown in SEM and TEM images (Fig. 4C). The flakes

![Fig. 3. X-ray diffraction patterns of SiC/C nanocomposite powders: (a) sample G1 and (b) sample SG1.](image)

![Fig. 4. Scanning electron microscope (A-D) and transmission electron microscopy (insets in Fig. 4C and D) images of SiC/C nanocomposite powders. (A) Sample G1. (B-D, insets in Fig. 4C and D) Sample SG1.](image)

![Fig. 5. X-ray diffraction pattern of SiC/C nanocomposite powders sample L1.](image)
are actually of graphite nanosheets or graphenes, and had been successfully fabricated by arc-discharge method (Guo et al., 2013). Fig. 4B-D and insets in Fig. 4C and D show SEM and TEM images of these SiC/C nanopowders (GS1) by different magnifications. Besides the nano-flakes of graphite, a great amount of nanoparticles, such as SiC, Si or graphite are also found.

Liquid Carbon Source for SiC/C Nanopowders
As presented in above sections, both of solid and gaseous carbon sources can be available to synthesize SiC/C nanopowders. Liquid ethanol has also been tested for the possibility to be a carbon source, and the product sample is marked as L1. As shown in Fig. 5, the XRD profile of sample L1 indicate that a main phase of $\beta$-SiC and a minor phase of 6H-SiC (JCPDS No. 01-070-2550) which has hexagonal lattice and space group of P63mc. The morphologies of sample L1 are

Fig. 6. (A, B) Scanning electron microscope images of SiC/C nanocomposite powders sample L1.

Fig. 7. Photodegradation of methylene blue by SiC/C nanocomposite powders: as-prepared (A), heat-treated at 500°C (B), and heat-treated at 800°C (C). The curves sample S2 (a); sample G1 (b); sample SG1 (c); and sample L1 (d).
tightly coalescent assemblies of fine particles with a petal-like shape in several tens of nanometers of its diameter (Fig. 6), it is quiet different from those in samples S1~3 and G1 (Fig. 2 and 4).

**Photocatalytic Performances of SiC/C Nanopowders**

The graphite layers or particles mixed in SiC/C nanocomposite nanopowders can be altered or removed by a heat-treatment in air. Thus the photocatalytic performances of SiC/C nanocomposites can be controlled and improved. Four kinds of SiC/C nanocomposite nanopowders, i.e., as-prepared samples S2, G1, SG1 and L1, and their heat-treated ones were chosen to measure the photodegradation abilities on MB. As shown in Fig. 7, all the samples have the abilities to photodegrade MB, moreover among them the sample G1 (by methane source) exhibits the best performance in its as-prepared and 500°C-treated ones; the sample L1 (by liquid alcohol source) is best in its 800°C-treated one. The photocatalytic performances of samples S2 (by solid graphite source) and SG1 (by integration of solid and gaseous source), on the contrary, behave a significantly decrease after heat-treatment at 800°C.

The highest photodegradation rates for MB reach 74.9% (S1: 500°C-treated), 76.3% (G1: 800°C-treated), 76.5% (SG1: 500°C-treated) and 85.6% (L1: 500°C-treated), respectively. It is indicated that a themal-treatment in air is significant in the structural modification on SiC/C nanocomposites and the improved photocatalytic performances. The reasons may be from two viewpoints: Firstly, on the one hand, the thickness of graphite in SiC/C nanopowders become thinner by the heat-treatment, so more light incident on the junction regions favor to creat photoelectrons and holes. On the other hand, the time for photochemical reactions between the photogenerated carriers and pollutant molecules become shorter and greatly reduce the recombination probability for the electrons and holes. Secondly, by the heat-treatment, a certain quantity of SiO₂ would appear on the surface of SiC. The combined oxygen in SiO₂ may react with H₂O to form a strong hydroxy group ·OH which can promote the photocatalytic decomposition of MB (Kang et al., 2007).

**CONCLUSIONS**

Three carbon sources, i.e., solid graphite, gaseous CH₄ and liquid ethanol, have been successfully employed to synthesize SiC/C nanocomposite powders by the arc-discharge plasma. In the case of solid sources, the optimum composition of raw material is that the content of carbon should be a little higher than the stoichiometry of SiC and then near single phase of SiC or carbon-riched SiC/C nanopowders can be obtained. The gaseous carbon source is equivalent to the solid one in formation of SiC/C nanocomposites, and favor to control the composition and morphology of SiC/C nanopowders. Liquid ethanol is also an alternative carbon source to synthesize SiC/C nanocomposite powders. It is consisted of a dominant cubic β-SiC and a minor hexagonal 6H-SiC phase, and the morphology is tightly coalescent assembly of fine particles in petal-like shape with several tens of nanometers in diameter. Heat-treatment on the as-prepared SiC/C nanocomposite powders in air is significant in the structural modification and the improved photocatalytic performances of SiC/C nanopowders. The highest photodegradation rates for MB reach 74.9% (S1: 500°C-treated), 76.3% (G1: 800°C-treated), 76.5% (SG1: 500°C-treated) and 85.6% (L1: 500°C-treated), for various kinds of SiC/C nanopowders.

**CONFLICT OF INTEREST**

No potential conflict of interest relevant to this article was reported.

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