Article ID:1000-5773(2013)06-0847-09

Synthesis of Graphite-Encapsulated Copper Nanoparticles Using the Sol-Gel Explosive Precursors*

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Abstract: Graphite-encapsulated copper nanoparticles(GECNPs) were synthesized using the sol-gel explosive precursors by a detonation method. The sol-gel explosive precursors were prepared using copper nitrate, citric acid, ethylene glycol and trinitro-1-3-5-triazine. The morphology and nature properties of the composites were investigated by X-ray powder diffraction(XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy(EDX), transmission electron microscopy(TEM), X-ray fluorescence(XRF) and Raman spectrometry(RS). As a result, the GECNPs were successfully synthesized by detonation decomposition of the sol-gel explosive precursors. Results show that the as-obtained composites were with a core-shell spherical structure and the diameters of these composites were in the ranging of 10-40 nm. The different sizes and composition of the composites and the thickness of the carbon coating can be prepared by adjusting the component materials of the sol-gel explosive precursors.

Key words: graphite-encapsulated copper nanoparticles; sol-gel explosive precursors; detonation method; microstructure

CLC number: O381; TB34 **Document code**: A

1 Introduction

Carbon nanostructure materials[1] (including zero-dimensional, one-dimensional, two-dimensional carbon nanomaterials and porous carbon nanomaterials) have potential applications in fields of heterogeneous catalysis, such as selective hydrogenation, oxidative dehydrogenation, ammonia synthesis, decomposition and electro-catalysis in fuel cell and so on. Graphite-encapsulated metal nanocrystal is a new composite structure material, with an inner metal core and several layers of outer graphitic/amorphous structure shells. Graphite-encapsulated nanotechnology is a kind of metal particles coated relatively stable carbon

* **Received date**: 2012-01-31; **Revised date**: 2012-06-26

Foundation Item: Natural Science Foundation of China(11272081); CUMT Sail Project, Introduction of Talent Project; State Key Laboratory of Explosion Science and Technology Open Project (KFJJ13-5M)

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surface[2]. The carbon coating can preserve its metal crystal properties and not influence by physical and chemical changes occur, such as oxidizing reaction and hydrolysis reaction. The coating can not only improve the kernel particle surface resistivity and surface activity, but also effectively prevent metal nanocrystal from growing up together. So that the synthesis of carbon clusters in spherical or tubular form and the encapsulation of foreign materials into them have attracted much attention for their obvious technological promise.

Since Saito *et al*.[3-4] demonstrated the encapsulation of foreign materials with in a hollow graphitic carbon cage for rare-earth and iron-cluster, however, the addition of some metal such as copper to the disadvantage of forming graphite-encapsulated materials. In other ways, Dai *et al*.[5] reported the synthesizing of pure copper or germanium filled carbon nanotubes using polycyclic aromatic hydrocarbon precursors by a helium arc method. Cao *et al*.[6] showed that graphite encapsulated metallic copper nanoparticles were prepared by reduction of $CuCl_2$-graphite intercalation compounds using metallic potassium borohydride/ethylenediamine matrix as reducing reagents. Also Qian *et al*.[7] demonstrated the synthesis of Cu@C spherical core-shell structures by thermal treatment at 600 ℃ under an argon atmosphere.

Nonmagnetic copper nanocrystal particles are expected to have widespread application such as nanofluid, electro-catalytic properties, thermal conductive nano-fluid, nano-lubricants additives, nano coating materials[8-11] and so on. However, the yields of the GECNPs is generally very lower about several gram one time from above synthesis methods. Since the middle of the 20th century the development of detonation synthesis of nanodiamond, detonation technique has the advantage of high efficiency, simple and lower energy consumption, which have attracted many scholars' attention. So that the nanodiamond, metal oxides, nitrides and magnetic composite materials[12-16] have been prepared by a detonation method. With the advantage of the simple equipment/process, low cost and easier operation, detonation technique has gradually achieved some applications and got the rapid development. In this paper, the GECNPs were prepared for the first time using sol-gel explosive precursors by a detonation method. And then the XRD, SEM, EDX, TEM, XRF and RS tests were used to characterize the composites, and the possible forming mechanism were discussed briefly.

2 Expriment

2.1 Preparation of Sol-Gel Explosive Precursors

Firstly, citric acid and copper nitrate were selected according to the certain chemical proportion (2∶3, 1∶1) as metal source materials. Until melted, a certain percentage of ethylene glycol was added into them with a stirrer on heating up. For the preparation of sol-gel explosive precursors, it is important to realize that the pH value of sol-gel solution must be adjusted to alkalescence in the range of 7-9. Meanwhile the solution was heated up at 70-100 ℃ and then put trinitro-1-3-5-triazine powder into the grass green solution until the moisture volatilizes completely. And then cooling to room temperature, the sol-gel explosive precursors were prepared. All the chemical reagents used in this study are analytical grade.

The detonation synthesis of the composite nanoparticles were performed in a closed explosion vessel as described in the previous work[17-19]. The as-prepared sol-gel explosive precursors were placed into the closed explosion vessel about 0.4 m^3 capacity filling with argon gas. After the detonation reaction, the as-obtained detonation products were collected from the inner wall of the explosive vessel. The black powders were washed with absolute ethyl alcohol and then dried. The composite particles were prepared with the yield about 15%-25% (more than 150 g) one time. Finally, the

as-obtained composites were characterized by the variety of analysis methods. The related technical parameters of sol-gel explosive precursors were presented in Table 1.

Table 1 Mole ratios, densities, OBs of the elements of explosive precursors for GECNPs

Sample No.	Element composition/(mol)					Oxygen balance(OB)	Density /(g/cm^3)
	C	H	O	N	Cu		
1	3.91	4.42	1.60	1.21	0.1	−1.424	1.62
2	4.38	4.71	1.57	1.20	0.1	−1.521	1.58

2.2 Analysis Methods

The XRD patterns of the products were recorded using a Rigaku D/MAX2400, operated at a step size of 0.02° in the range of 20°-100° and with Cu/K_α radiation (λ=0.15406 nm, 40 kV voltage, 30 mA current). The SEM was performed on JEOL-JSM-5600LV field-emitting scanning electron microscope, and the chemical composition of detonation products were analyzed with the equipped energy dispersive X-ray spectrometer. The TEM was performed on an FEI Tecnai G220 S-twin transmission electron microscope with an accelerating voltage of 200 kV. The XRF(series-1800X) and RS(Renishaw micro-Raman2000, 632.8 nm He-Ne laser excitation) were used to identify some basic components of detonation products concerning the elemental distributions based on the qualitative analysis.

3 Results and Discussions

3.1 Phase Analysis

The crystallization of the composite particles was apparent by XRD (shown in Fig. 1). The main peaks appearing at 2θ=43.4°, 50.4°, 74.0°, 89.9° can be ascribed to the diffraction of the (110), (200), (220) and (310) planes of face centered cubic (fcc-) copper nanocrystal (JCPDS No. 04-0836) from the three samples and the intensity of diffraction peak of copper are gradually increasing with the increase of the content of copper (metal source material containing precursors). The diameter of copper nanocrystal particles is gradually decreasing with the decrease of OBs and density of the explosive precursors. The diffraction peaks of copper oxide does not present in these examples. The average grain diameter of the composites using the scherrer equation[20-21] and the full width at half maximum (FWHM) are shown in Table 2.

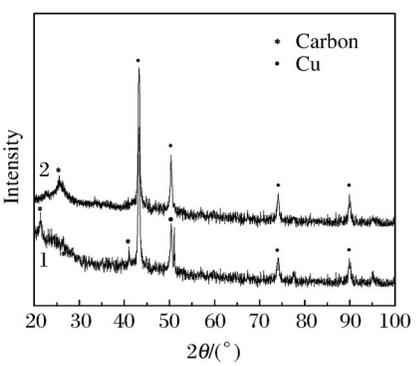


Fig. 1 XRD spectrum of GECNPs

Table 2 Characteristic of the detonation products XRD profiles

Samples No.	Phase composition	2θ/(°)				FWHM	D/(nm)
1	Fcc-Cu	43.44	50.40	74.09	89.90	0.382	22
2	Fcc-Cu	43.47	50.36	74.15	89.98	0.429	18

As shown in Fig. 1, an obvious diffraction peak can be also seen at about 26.40°, this peak is assigned to the (002) reflection of the hexagonal graphite structure in product sample No. 2. And the other two samples, the diffraction peak of graphite carbon are not always so obvious, nevertheless,

there are some weak correlation about amorphous carbon in the range of 20°-43°.

3.2 Morphology Analysis

In order to more comprehensively understand the structure characteristics, the graphite-encapsulated composite nanoparticles were respectively investigated by SEM with EDX and TEM. Of these product samples, the representative sample No. 2 was investigated by SEM with EDX. The SEM images reveal the surface morphology of product sample No. 2, indicating that the particle size of the composite powders (Fig. 2(a), × 20 000, and Fig. 3B, × 100 000) is a fine powder state and well-distributed uniformly. The bright areas are copper according to EDX pattern (Fig. 2(c)), and the other gray areas are shaggy carbon power in accordance to EDX pattern (Fig. 2(d)). Also, there are some traces of the impure mixture such as oxygen, iron elements and so on.

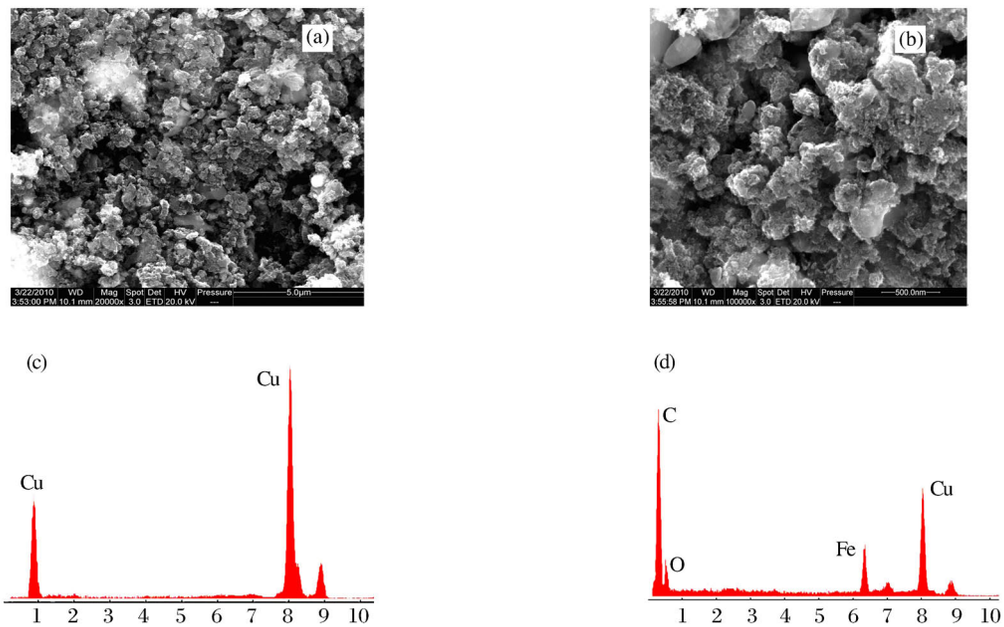


Fig. 2 SEM images and EDX spectrum of graphite-encapsulated copper crystal powders
((a) The × 20 000 SEM of sample No. 2; (b) The × 100 000 SEM of sample No. 2;
(c) The EDX pattern of the bright areas(copper); (d) The EDX pattern of the shaggy areas(main carbonaceous material))

Analysis from the Fig. 3, TEM confirmed that the formation of these composite nanoparticles were derived from the detonation reaction process. The as-obtained composites were dominated by black spherical particles with grayish carbonaceous material coating. The observation of TEM images revealed that the sizes of the spherical particles were in range of 10-40 nm.

Fig. 3(a) and Fig. 3(a) shows TEM images of sample No. 1, indicating that the product mainly consists of well-dispersed copper nanocrystal with the size between 10 and 20 nm and black nanocrystal cores are coated in thin graphite layers about 1-2 nm and particles distribution between amorphous carbon. Furthermore, the carbon coating shell is graphite crystalline; the spacing of the lattice fringes of shell materials is around 0.34 nm (shown in Fig. 3(b)).

As shown in Fig. 3(c) and Fig. 3(d), TEM images reveal that all of the spheroidal particles have an obvious core-shell structure with a big copper nanocrystal core and graphite carbon shell. The carbon layers tightly encapsulate the black core and no obvious voids can be observed between the core and coating layers(Fig. 3(d)). The interlayer distance of graphitic lattice is around 0.34 nm in accord-

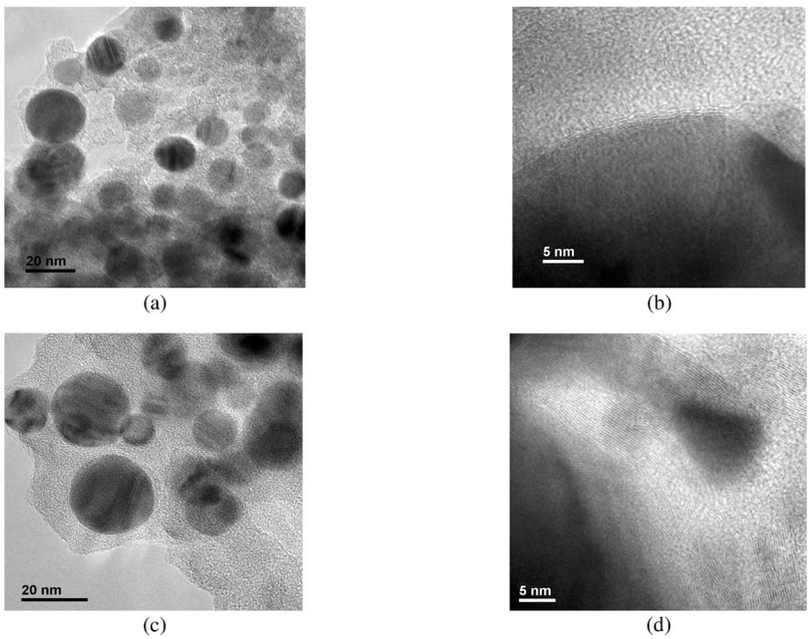


Fig. 3　TEM images of three kinds of GECNPs

((a) and (b) TEM images of sample No. 1;(c) and (d) TEM images of samples No. 2)

ing with XRD pattern. The above results showed that the different nature and structure of these composites were prepared during the detonation reaction process, through adjusting the effective element mole ratio (n_{carbon} : n_{copper}). These spherical, core-shell structural composites were composed of the same copper crystal core and different carbon coating shell. It is provided for us good experience to effectively synthesize these kinds of composite nanoparticles.

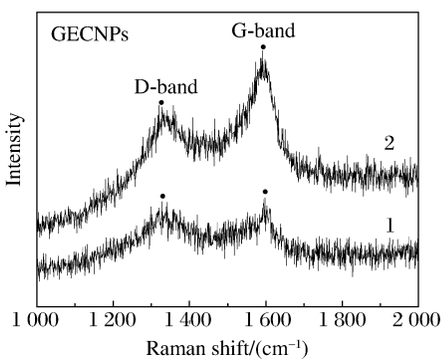


Fig. 4　RS pattern of GECNPs

3.3　Component Analysis

In order to obtain reliable component analysis results, further quantitative investigations of as-obtained composite nanoparticles were measured by XRF. The basic elemental components of detonation products were listed in Table 3. The results showed that the amounts of main elements such as carbon and copper were to 89.43%, 90.49% and 91.14% from sample No. 1 to No. 3 respectively and the others elements were relatively much smaller about 10%, which mainly contain a small amount of elements such as oxygen, iron, silicon and so on.

It is well-known that the RS is one of the most frequently used non-destructive, fast, high-resolution techniques for carbon materials. The intensity of D- and G-peaks can be used to estimate the size of small crystalline graphite or to scale the disorder degree of graphite, comparing to the two typical carbon peak distribution of 1 360 cm^{-1} amorphous carbon and 1 585 cm^{-1} graphitic carbon[22]. The surface of detonation products were investigated by RS to detect carbon covering the surface. Clearly shown in Table 4 and Fig. 4, the RS pattern of as-obtained products revealed the distribution of amorphous carbon and graphitic carbon, which D-band 1 349 cm^{-1} and G-band 1 600 cm^{-1} (sample No. 1) and also D-band 1 353 cm^{-1} and 1 595 cm^{-1} (sample No. 2).

The intensity ratio of D-band to G-band (I_D/I_G) for the raw graphite is 0.543[23], while for the

detonation soot the I_D/I_G is from 0.96 to 0.84, implying that the as-obtained sample No. 2 are more preferable well-crystallized graphite than that of the sample No. 1.

Table 3 The main element contents of GECNPs by XRF

Samples No.	C K_α	Cu K_α	Others K_α
1	35.47%	55.02%	9.51%
2	42.62%	48.52%	8.86%

Table 4 Raman spectroscopy data for GECNPs

Samples No.	D-band	G-band	I_D/I_G
1	1349	1600	0.96
2	1353	1595	0.84

4 Mechanism Preliminary Analysis

4.1 Complexation Mechnism

The citric acid, copper nitrate, ethylene glycol were used as raw materials. The sol-gel explosive precursors were prepared by citric acid roots complexing action with a certain mole ratio of $n_{carbon} : n_{copper}$. Because citrate has a strong adsorption capacity and effect on the surface of the metal, it is more likely to form stable metal ionic compounds. Meanwhile, the adsorption of citric acid ions in the crystal surfaces has special directionality. The combination of citric acid molecules and the copper surface feature was subject to the external environment such as pH level. During the formation of the sol-gel explosive precursors, chelation between polyhydroxyl and copper ions formed coordination compounds with H_2O, OH and O_2. The special chemical properties of the citric acid derived from unique molecular structure and played important role in synthesis of nanometer materials. In the end, the semitransparent stable sol-gel complex system was formed under the action of promoting agents (ethylene glycol). The reaction schematic sketch of citric acid and copper nitrate as follows: (1) the complexing reaction between citric acid boot and copper ions; (2) the good stability complex system were prepared with active group in citric acid and copper ions (shown in Fig. 5).

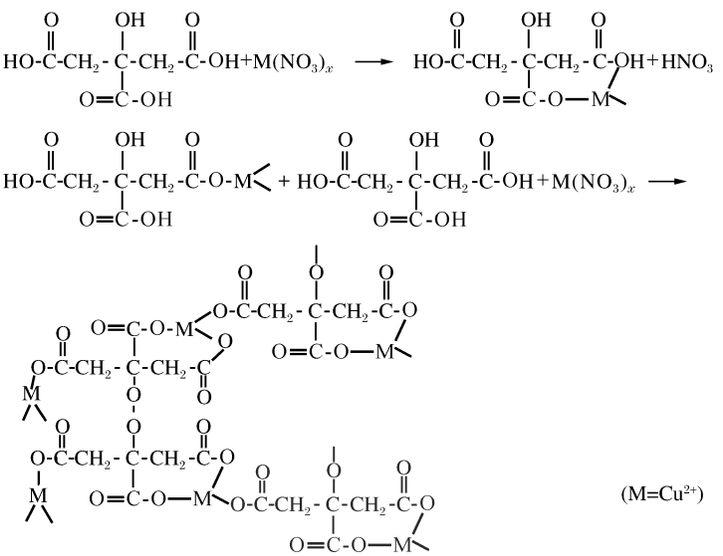


Fig. 5 Schematic plot of complex reaction with citrate acid/copper nitrate

4.2　Formation Mechnism of GECNPs

With adjusting and optimizing composition of the raw materials, the active group of citric acid and Cu ions effectively uniform mixed at molecular level by liquid phase with proper temperature and a certain pH condition. In order to uniform the sol-gel explosive precursors, the ethylene glycol solution and trinitro-1-3-5-triazine were put into semitransparent sol-gel complex system. And then as-prepared sol-gel explosive precursors were ignited by a detonator in argon gas in the closed explosive vessel. The powerful shock waves come into being and propagate in the precursors, meanwhile a significant amount of heat and tens of GPa pressure was produced for the construction of various nanostructures. The detonation pressure and temperature was calculated by self-made gas-solid coupling program [24]. The calculated results showed a good agreement with experimental results and calculated results using BKW program[25]. Under the tens of GPa pressure and more than two thousand kelvin temperature, the metal copper (1 357.7 K) ions and surplus carbon ions were in gas state or in similar gas state. During the detonation process in argon gas, the detonation temperature was rapidly decreasing with the tremendously fast detonation chemical reaction time (about a few microseconds). Copper ions firstly condensed and then active carbon group ions were adsorbed on the surface of hot copper crystal core and carbon cluster transformed from long-chain molecules to rings, wrapped up layer by layer to prevent the agglomeration of copper crystal, so that the ultimate objective nanosize composites were produced during the detonation reaction process(as shown in Fig. 6).

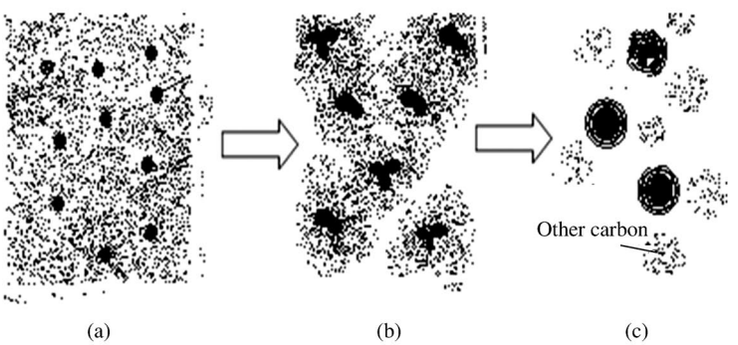


Fig. 6　Formation mechanism of detonation synthesis for CECNPs

(a) Copper ions and surplus carbon ions in gas state;

(b) Agglomeration of copper crystal and active carbon group condensed;

(c) The ultimate objective CECNPs formation

5　Conclusions

In conclusion, the spherical and different nature of core-shell structural GECNPs have been successfully synthesized by detonation decomposition of sol-gel explosive precursors. The above results revealed that the cores of the as-prepared composites were copper crystal core and the carbon coatings of composite nanoparticles were mainly transformed amorphous carbon to graphite through effective adjusting the element mole ratios, OBs and density in the precursors. The obtained composite particles have a diameter ranging between 10 and 40 nm with a perfect core-shell structure and the carbon coating layers in these samples. Based on above experimental and theoretical analysis results, a simple route to synthesize GECNPs can be mapped. The synthesis of the similar materials is practicable by a detonation method.

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采用凝胶炸药前驱体制备石墨包覆铜纳米颗粒的研究

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摘要: 采用凝胶炸药前驱体爆轰合成了石墨包覆铜纳米颗粒。凝胶炸药前驱体主要以柠檬酸、二乙醇为促进剂、黑索金为碳源材料与硝酸铜为金属源材料以一定的工艺条件制备得到。采用X射线衍射、扫描电子显微镜、透射电子显微镜、能量弥散X射线探测器、X射线荧光光谱和拉曼光谱等,对爆轰产物进行形貌、结构及性能分析。结果表明,采用凝胶炸药前驱体成功合成了球形、核壳结构的石墨包覆铜纳米颗粒,粒径分布在10～40 nm。并初步证实复合纳米颗粒的粒径分布及包覆层石墨厚度,可通过调整炸药前驱体中各组分的有效比例获得。

关键词: 石墨包覆铜纳米颗粒;凝胶炸药前驱体;爆轰法;微观结构

中图分类号: O389;TB34　　**文献标识码:** A