Synthesis and formation mechanism of carbon-encapsulated copper nanoparticles in detonation process

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Summary The paper firstly describes that carbon-encapsulated copper nanoparticles(CECNPs) are synthesized by detonation experiment and the numerical simulation reproduce the detonation chemistry reaction environment for its formation mechanism. The results showed that the CECNPs were grown from nitrates only produced metal core and from organic carbon radicals only produced graphitic carbon crystals. The numerical simulation that the CECNPs growth from metal ions or organic carbon radicals source material at above 2000℃ and about ten several GPa pressure by gas-solid coupling program. It is believed that the CECNPs growth environment of detonation technology is superior and the CECNPs is good in quality with uniformity and spherical core-shell structure materials.

RESEARCH BACKGROUND

The breakthrough in this regard was the discovery of carbon coated nanocapsules [1], an intriguing by product of carbon capsules filled with metal or metal carbide was also investigated [2,3]. These metals or metal carbides are entirely encapsulated by the multilayer carbon capsules, which are thus expected to be protected from corrosion by the external environment. Because that copper nanocrystal particles are nonmagnetic and expected to have widespread application such as magnetic fluid, electro-catalytic properties, thermal conductive nano-fluid, nano-lubricants additives, coating materials[3-5]and so on. Since detonation synthesis of nanodiamond, detonation technique has the advantage of high efficiency, simple and lower energy consumption, which have attracted many scholars' attention. The detonation synthesis of the magnetic composites were performed as described in our previous work [6]. Recently, in our experiments, CECNPs were prepared using the sol-gel precursor by the detonation technique in the closed explosive vessel. The CECNPs were synthesized by detonation decomposition of the sol-gel precursor, which are composed of copper nitrate, citric acid, ethylene glycol and trinitro-1-3-5-triazine. A large amount of CECNPs were obtained under a certain condition. The numerical simulation results showed that the formation of CECNPs were at above 2000℃ and ten several GPa pressure by the gas-solid coupling program. The principle of program design are on the basis of detonation fluid dynamics equation and equations of state (gas, Cowan and metal solid), coupling with by Gibbs free energy of the theory of minimum.

RESULTS AND DISCUSSION

The as-obtained samples were observed with transmission electron microscope (TEM) and high-resolution TEM (HR-TEM).

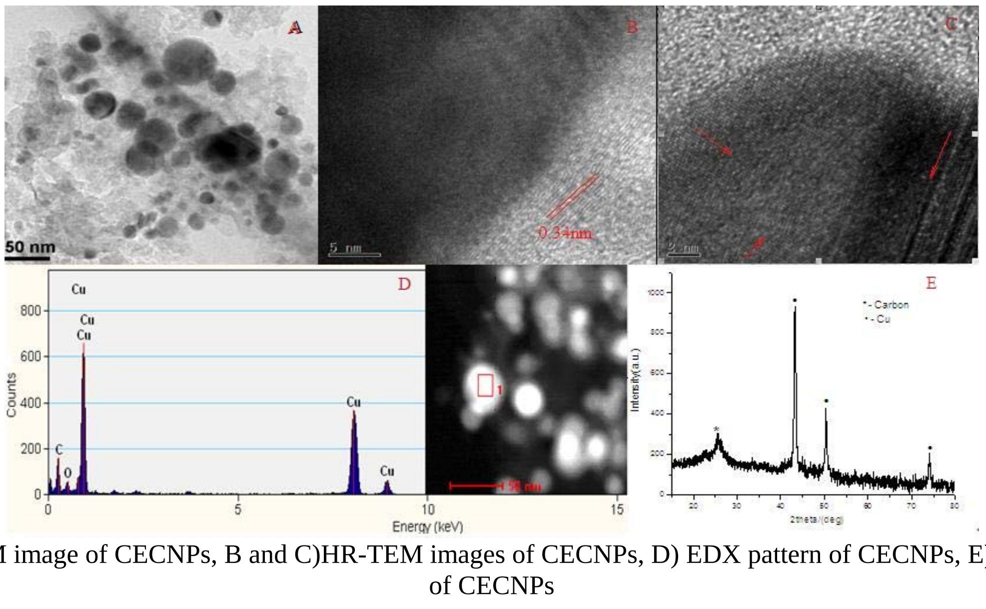

Fig. 1 A)TEM image of CECNPs, B and C)HR-TEM images of CECNPs, D) EDX pattern of CECNPs, E)XRD pattern of CECNPs

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Elemental analyses of the encapsulated materials were carried out with an energy-dispersive X-ray (EDX) Elemental analysis of the filled particles was carried out by an EDX analyzer and X-ray powder diffraction. Fig.1-A show a TEM image of the as-obtained CECNPs. The CECNPs diameters shown here are on the order of 10-40 nm and also the observed thickness of graphitic coating is 5~8nm around the particles with much disordered carbon. A HR-TEM image of graphitic layers encapsulated a metal crystalline is shown in Fig.1-B and C. Fig.1-D shows an EDX spectrum from area 1, which mainly reveals the presence of copper and carbon. Precisely measuring lattice fringe spacing of the copper crystals indicated that they have different size: one is 2.08Å (43.36°), the other is 1.80Å (50.48°) and the another is 1.27Å (74.80°) according to lattice constant: a=b=c=3.61,which can be ascribed to the diffraction of the planes of face centered cubic (fcc-)copper nanocrystal (Fig. 1-E).
It is well known that detonation reaction can provide a high energy (high temperature and high pressure) with the tremendously fast chemical reaction time about a few microseconds. The powerful shock waves come into being and propagate in the precursors (Fig.2, Part-2), meanwhile a significant amount of heat and tens of GPa pressure was produced for the construction of various nanostructures, so the sol-gel precursor decomposed into radical carbon species and active copper ions(Fig. 2, Part-3). The metal copper (1357.70K) ions and surplus carbon molecules were in gas state or in similar gas state. The numerical simulation of detonation pressure and temperature was calculated by self-made gas-solid coupling program[7]. The results showed that under the 10.08GPa pressure and 2291.40K temperature, the density of carbon and copper at C-J interface are about 0.5606g/cm^3 and 0.1078g/cm^3, respectively. The reliability of calculated results show a good agreement with experimental results and calculated results using BKW program[8]. With the temperature reducing sharply, the liquid copper species agglomerate into copper particles with a certain size and carbon species adsorbed on the surface(Fig. 2, Part-4). 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 CECNPs were produced during the detonation reaction process(Fig. 2, Part-5).No evident copper oxide particles exist from the image of as-obtained results and the oxygenated chemicals may be adsorbed on the surface in carbon during the preparation.

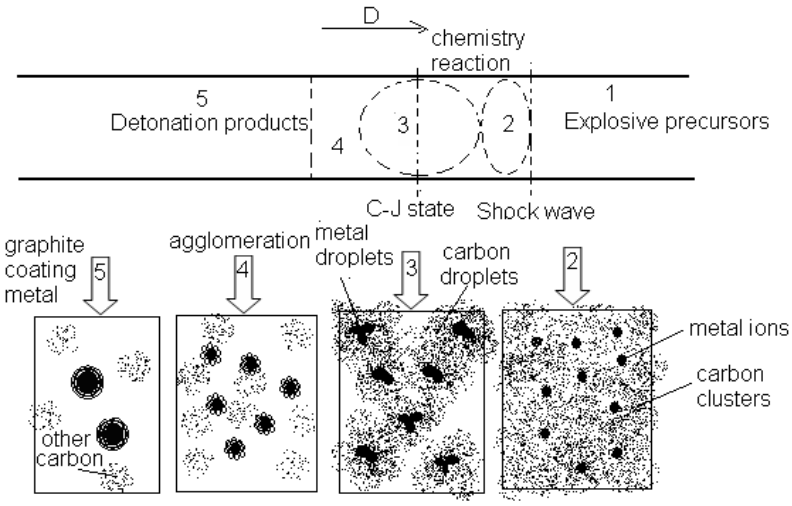

Fig. 2 Possible formation mechanism of detonation synthesis for Carbon-encapsulated metal Nanoparticles

CONCLUSIONS

Our experiments may provide a new way to synthesize carbon-encapsulated particles with the diameters in the range of 10-40nm. The experimental and simulation results show that the CECNPs can be prepared at about 2291.40K and 10.08GPa in the detonation decomposition of the sol-gel precursor. We believe that this method may be a step towards mass production of carbon-encapsulated particles.

References

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