SYNTHESIS AND CHARACTERISTICS OF CARBON ENCAPSULATED NANOPARTICLES MODIFIED BY NOBLE METALS

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Introduction

New carbon nanomaterials of different morphologies (nanotubes, fullerenes, graphene) are among the most popular nano-objects under intense investigation during the recent decades. However, in our opinion, not only search for and discovery of the new forms of carbon may be rather interesting from the scientific and practical points of view. Investigation of the physical and chemical properties of already known carbon nanostructures like metal core – carbon shell may turn out to be useful, too. This will allow one to establish the mechanisms of reactions that occur during chemical transformations of composite carbon nanomaterials, and also to find a new application areas. In this work we proposed a new method for deposition of noble metals nanoparticles on the surface of the shells of carbon encapsulated nickel particles using the galvanic replacement reaction/

Experimental

Low pressure dc arc discharge (100 A, 25V) was used to produce the carbon-metal (Ni, Fe, Ag, Cu, Bi) samples, carried out in He at 25 torr. The anode was a graphite rod (7 x 80 mm) having a 5 mm hole drilled and packed with a mixture of metal and graphite powder (metal = 10% by weight). Due to the high arc temperature, the anode was completely consumed and a feeding mechanism was used to maintain a stable arc discharge plasma. Some of vaporized atoms precipitate on the cathode but the main part diffuses into the background He. On cooling, the evaporated material deposits on a cooled shield. After arc discharge the materials were collected for investigations. The deposited materials consisted of spherical amorphous carbon-coated copper particles (fig. 1) with small amount of graphitic carbon

The deposition of the nanoparticles of noble metals (platinum, gold, silver) was performed using the galvanic replacement reaction which is widely used to obtain hollow metal nanostructures[1-4]. In this case, unlike for the widespread methods of metal deposition on carbon surface, no additional surface modification was required. Aqueous suspensions of the powder containing metal nanoparticles encapsulated in amorphous carbon shells were treated with the solutions of hydrochloroauric or hydrochloroplatinic acids or with silver nitrate solution at a temperature of 40-50^{o}C for 1-4 hours. It was established that the following chemical transformations take pace in these cases (for example, for carbon encapsulated nickel nanoparticles):

$3Ni_{(s)} + 2HAuCl_{4\,(aq)} \rightarrow 2Au_{(s)} + 3NiCl_{2(aq)} + 2HCl_{(aq)}$

$2Ni_{(s)} + H_2PtCl_{6(aq)} \rightarrow Pt_{(s)} + 2NiCl_{2(aq)} + 2HCl_{(aq)}$

$Ni_{(s)} + 2AgNO_{3(aq)} \rightarrow 2Ag_{(s)} + Ni(NO_3)_{2(aq)}$

For investigation in a transmission electron microscope the arc discharge and modified by noble metals nanoparticles were sonicated in ethanol and dropped onto a standard copper grid. Transmission electron microscopic studies of the arc discharge and oxidized powders were carried out with a JEM-2000FX II electron microscope with 200 kV acceleration voltage.

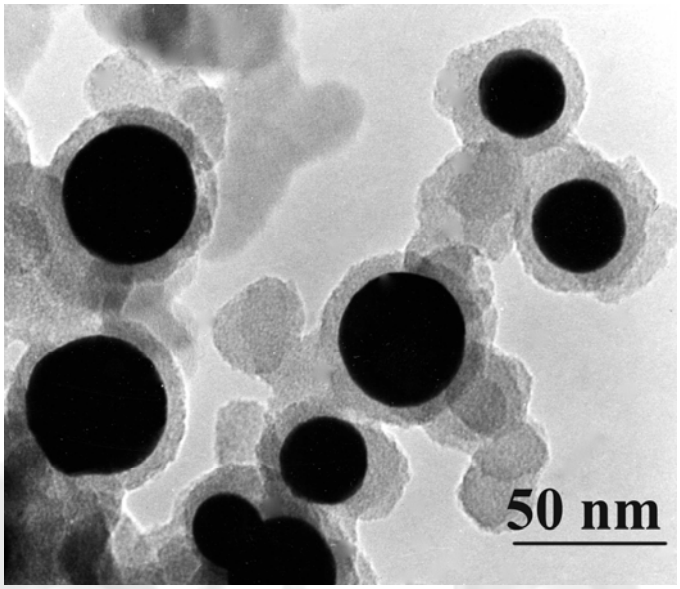

Fig. 1 Typical TEM images of carbon encapsulated metal nanoparticles.

Results and Discussion

The formation of the nanoparticles of noble metals in the galvanic replacement reaction was detected on the basis of the appearance of X-ray reflections of metals in the diffraction patterns of the solid products of treatment of carbon-encapsulated metal (fig 2) and on the basis of the presence metals (Ni^{2+}, Fe3+, Ag+, Cu^{+}, Bi^{3+}) ions in the solution.

Electron microscopic studies showed that for the short time of treatment with the solutions of $HAuCl_4$, H_2PtCl_6 or $AgNO_3$, respectively, the nanoparticles of metal gold, platinum and silver several nanometers in size are deposited on the outer surface of carbon shells of the encapsulated metal particles (fig 3). With an increase in the time of treatment of encapsulated nickel nanoparticles, the formation of a noble metal layer on the surface of carbon shells and almost complete dissolution of the metal core were observed. It may be assumed that the surface of carbon shells may contain functional groups able to reduce noble metals from solution. To confirm that the main contribution into the reduction of noble metals is made by metal nanoparticles (according to reactions 1-3), we treated the encapsulated particles with the solution of hydrochloric acid, which caused dissolution of encapsulated metals cores and the formation of hollow carbon

nanocapsules containing no metal. It was established that the treatment of thus obtained hollow capsules with the solutions of $HAuCl_4$, H_2PtCl_6 or $AgNO_3$ does not lead to the deposition of noble metals

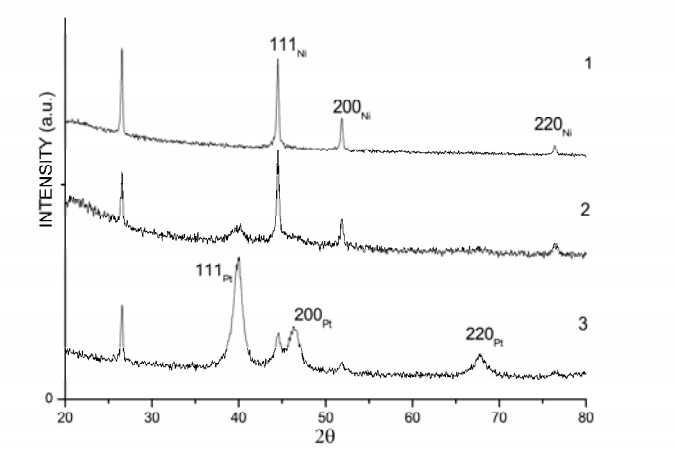

Fig. 3 X-ray diffraction patterns of carbon encapsulated nickel nanoparticles: after arc discharge (1), after treatment by H_2PtCl_6 for 1 h (2) and after treatment by H_2PtCl_6 for 4 h (3).

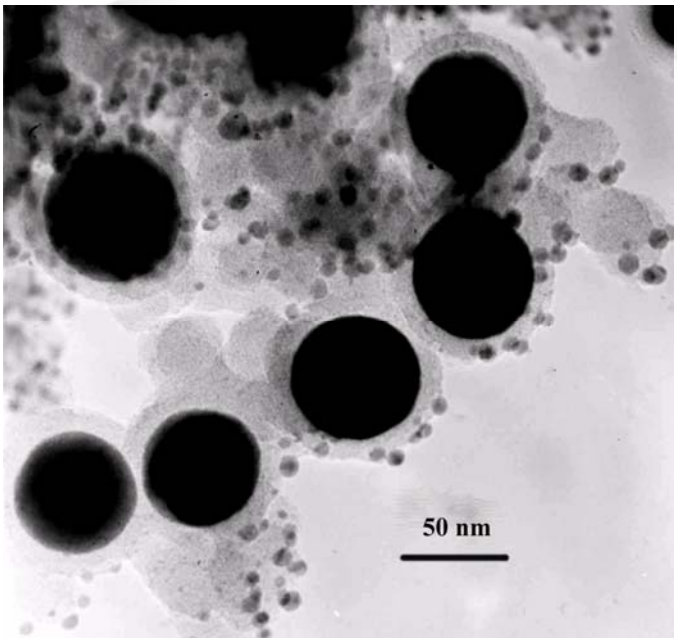

Fig. 3 TEM image of carbon encapsulated metal nanoparticles after treatment after treatment by H_2PtCl_6 solution for 1 h.

The stage sequence of the formation of nanosized gold, platinum or silver particles during the treatment of carbon-encapsulated metal particles may be represented with the following scheme (fig.4). The initial stage of the process is connected with the redox reaction that proceeds via electron transfer through the carbon shell from metal atoms of the core of nanoparticle to noble metals ions adsorbed on the outer surface of the carbon shell ($Me^0 - e \rightarrow Me^+$ and $Pt^{4+} + 4e \rightarrow Pt^0$ or $Au^{3+} + 3e \rightarrow Au^0$). Because metals ions ($Me^+$) in this process are formed inside the carbon capsule, they are to diffuse through carbon shells in order to form the metal-chloride phase.

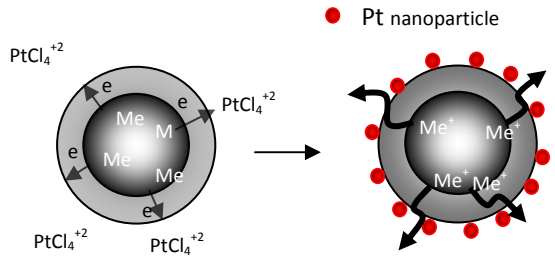

Fig. 4 Schematic of deposition of platinum nanoparticles during treatment of carbon encapsulated metal by H_2PtCl_6 solution.

Conclusions

The obtained results show the possibility to use the galvanic replacement reaction for modification of carbon encapsulated metal nanoparticles with the nanoparticles of noble metals; this opens rather broad outlooks for the direct preparation and design of composite carbon-based nanomaterials of different composition for practical applications. In our opinion, the nanoparticles of this morphology and composition may turn out to be rather promising from the viewpoint of application in catalytic reactions and medicine.

References

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