Highly stable carbon-protected cobalt nanoparticles and graphite shells†

An-Hui Lu, Wen-Cui Li, Nina Matoussevitch, Bernd Spliethoff, Helmut Bönnemann and Ferdi Schüth*

Received (in Cambridge, UK) 16th September 2004, Accepted 26th October 2004
First published as an Advance Article on the web 17th November 2004
DOI: 10.1039/b414146f

The fabrication of carbon-shell protected cobalt nanoparticles and hollow graphitic shells has been achieved *via* a pyrolysis process by using monodispersed cobalt nanoparticles as a template. These materials are mesoporous and highly stable under strong acidic and basic conditions.

Nanoengineering core–shell nanoparticles with tailored chemical compositions is the focus of numerous research efforts. A commonly employed approach is the templating strategy, *i.e.* using colloidal particles made of polymer, carbon, metal or silica as templates which are then coated with various materials, both organic or inorganic.[1] To achieve capsules or hollow shell particles, the template cores are usually sacrificed by solvent treatment or by calcination. Due to their unique structures and properties, core–shell nanoparticles have broad applications in photonics, catalysis, drug delivery and controlled release, or magnetic data storage; in addition, sometimes the shell does not induce a specific property with respect to an application, but just serves to protect the core particle.[2]

Metallic nanoparticles such as Fe, Co, and Ni, are useful in various application fields of magnetism, including magnetic data storage, ferrofluids, and biotechnology.[3] The main difficulty for the use of pure metals arises from their instability towards oxidation in air and dissolution in acid, which becomes much easier as the size gets smaller. In addition, metallic nanoparticles have extremely high surface energies that lead to easy agglomeration of these particles. It is thus highly important to develop methods to improve the chemical stability of such particles. One approach is to use the core–shell strategy to deposit a protecting shell on the nanoparticle's external surface that prevents the oxidation reaction.[4] In practice, surface-grafted polymer species, silica coatings or carbon deposition are often used.[5] Presently, most studies are focused on polymer and silica shells. Compared to these, however, carbon exhibits a much higher stability in various chemical and physical environments such as acid or base media, and at high temperature and pressure. In order to meet the demands of nanoparticle applications, the synthesis of carbon-protected metallic nanoparticles was explored in this study.

In general, the Huffman-Krätschmer carbon arc process and chemical vapor deposition are employed to synthesize carbon-coated metallic nanoparticles.[5c,6] However, the obtained nanoparticles have broad size distributions, phase inhomogeneity, and are formed in low yield. Moreover, reports about stability of these nanoparticles in strong acidic and alkaline conditions are very scarce.

In the following we report a different approach to obtain carbon-protected cobalt nanoparticles with a cobalt core and a graphitic shell. In a support anchored form such particles have been prepared recently by us to create magnetic nanocomposites.[7] Here the synthesis of pure carbon protected cobalt particles is described. This material exhibits chemical stability in concentrated HNO_3 (53 wt%) and in 1 M NaOH solution. The synthesis is described as follows: Monodispersed cobalt nanoparticles were freshly prepared according to ref. 8. Cobalt nanoparticles suspended in dry toluene were first slightly oxidized to make them air stable, and then washed with dry toluene and ethanol to remove the aluminium species. Afterwards, the cobalt nanoparticles were mixed with an excess amount of Pluronic surfactant P_{123}. P_{123} has two functions: it prevents the agglomeration of cobalt nanoparticles, and acts as the carbon source for surface coating of the cobalt nanoparticles. After drying, the solids were thermally treated at 1000 °C for 2 h under a flow of argon to achieve carbon-protected nanoparticles denoted as Co@C-1. The obtained samples were immersed in an excess amount of highly concentrated HNO_3 (53 wt%) solution for 1 month at room temperature. After this harsh treatment, these particles are still magnetic, as revealed by the attraction of these particles to a magnet. After the acidic or alkaline treatment, only a few empty shells were found in the TEM. Most of the cobalt particles were well protected by a dense carbon shell. In Fig. 1a, the high-resolution TEM image shows the cobalt nanoparticles with an average size of 10 nm, surrounded by carbon cages throughout the sample. Strikingly, the nanoparticles, as shown in Fig. 1b, are completely embedded in curved and layered graphite structures with roughly five to ten curved graphitic sheets, which resemble larger fullerene cages. This demonstrates that carbon-coated cobalt nanoparticles are protected against acid erosion. The EDX and XRD patterns of this sample are shown in the supplementary information.†

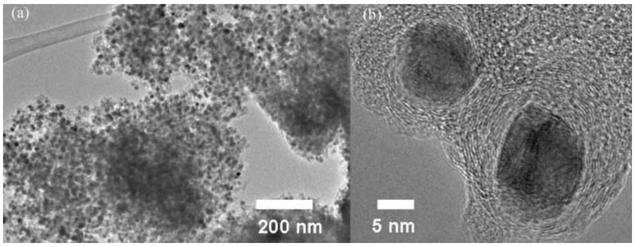

Fig. 1 TEM images of Co@C-1 after 1 month treatment in 53% HNO_3.

---

† Electronic supplementary information (ESI) available: EDX and XRD patterns of Co@C-1 and XRD pattern of graphite shells. See http://www.rsc.org/suppdata/cc/b4/b414146f/

*schueth@mpi-muelheim.mpg.de

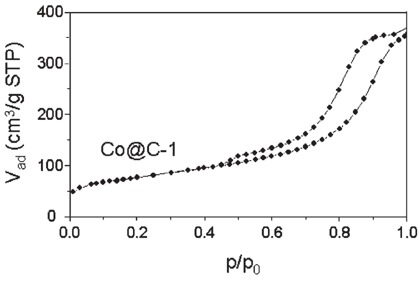

Fig. 2 Nitrogen sorption isotherm of Co@C-1.

Interestingly, these core–shell nanoparticles show mesoporous properties, as determined by nitrogen adsorption. As seen in Fig. 2, the isotherm of Co@C-1 exhibits a typical type IV shape, which is strong evidence of the mesoporous characteristics of such a material. The mesoporous properties can be further verified by the calculated textural parameters. The BET surface area and the total pore volume are 265 $m^2\ g^{-1}$ and 0.53 $cm^3\ g^{-1}$. The mesopore surface area and micropore volume calculated by the α_s-plot method (Cabot BP 280 as reference)[9] are 238 $m^2\ g^{-1}$ and 0.05 $cm^3\ g^{-1}$, respectively. Obviously, the surface area and pore volume can mainly be attributed to the mesopores. Combining the porosity of carbon and the magnetic properties of the encapsulated cobalt nanoparticles, one can expect the integration of adsorption and magnetic separation to generate new and effective adsorbents and catalyst supports.

In another series of experiments, cobalt nanoparticles, after removal of the solvent, were treated under identical conditions as Co@C-1 in order to produce carbon-coated cobalt nanoparticles. In this case the carbon source was the KoratinSH surfactant which protects and isolates the cobalt nanoparticles in the fluid. The obtained black powder, exhibiting magnetic properties, was immersed in HNO_3 solution (53 wt%). Intensive reaction occurred with gas evolution and the solution became dark red, indicating that cobalt nanoparticles were being leached by the acid. Within a few minutes, all solid material had dissolved. This proved the easy leaching of cobalt particles in an acidic solution. KoratinSH, the regular surfactant used in the synthesis, cannot provide a sufficient amount of carbon to coat the cobalt-core. Thus, in order to prevent dissolution of cobalt particles in acidic solution, high amounts of carbon are needed.

As for the supported materials,[7] we have also used furfuryl alcohol as a carbon precursor to test its efficiency for coating the free cobalt nanoparticles with a carbon-shell. For this process, cobalt nanoparticles were mixed with furfuryl alcohol in the presence of oxalic acid as the polymerization catalyst. The polymerization was carried out at 90 °C. After the analogous thermal treatment as in the above experiment, a shiny black powder was obtained. No visible reaction occurred when the powder was immersed in HNO_3 (53 wt%) solution. Even when stored in acid solution for 2 months, the solution remained nearly colorless, indicating that the cobalt-core was well protected by the furfuryl alcohol derived carbon. Nitrogen sorption measurement shows the BET surface area to be 9 $m^2\ g^{-1}$, which is very low compared to that of Co@C-1. This implies that the nature of the carbon precursor plays an important role in the formation of the carbon-shell and the porosity.

The aforementioned experiments show that cobalt nanoparticles can be protected by a carbon-shell against acid erosion. One might expect that if the cobalt cores were removed from the core–shell particles, a graphitic carbon-shell could be created. Such types of shells should have unusual properties such as low density, shell permeability and improved electron conductivity, and may find applications in chemical storage, drug delivery and electronic devices. Thus an experiment was designed analogously to the conditions used for Co@C-1, but using a surfactant which was thought to produce a thinner, possibly not completely closed carbon shell. Fresh cobalt nanoparticles were mixed with cetyltrimethylammonium bromide (CTAB) as both the surfactant and the carbon source. After thermal treatment at 850 °C for 2 h under argon, the obtained black powder shows magnetic properties that can easily be detected with a magnet. Subsequently, the black powder was immersed in an excess amount of HNO_3 (53 wt%) solution at room temperature for 1 day. Empty graphitic shells were obtained after washing with distilled water and ethanol and drying at 90 °C. High-resolution TEM reveals that a large number of 'hollow' shells free of cobalt-cores had formed, as shown in Fig. 3a. Surprisingly, such hollow shells have diameters of 100–200 nm, which is much larger than the diameter of the extracted cobalt nanoparticles. This indicates that the cationic surfactant CTAB with a positively charged head group might preferentially facilitate the assembly of cobalt nanoparticles into large clusters. During the carbonization process, the carbon species generated from CTAB would then be decomposed catalytically to give graphite sheets. A representative single shell particle is shown in Fig. 3b. A high-resolution image (Fig. 3b, insert) reveals that the carbon-shell consists of 8–10 nm thick assemblies of graphitic layers. Moreover, the graphitic characteristic was further examined by X-ray diffraction. The XRD pattern (background has been subtracted) of such shells is shown in Fig. 4. The (002), (101) and (004) peaks can be clearly seen, corroborating the TEM data. Thus, XRD and TEM both confirmed that the CTAB derived carbon was transformed into a graphite shell in the presence of cobalt nanoparticles. The broad peak that appears at $2\theta = 22^\circ$ is due to the presence of silicone grease used for the preparation of the sample in a transmission XRD measurement. For comparison, the original XRD pattern is shown in supplementary information.†

In summary, a synthetic strategy *via* a pyrolysis process has been established for the fabrication of carbon-shell protected cobalt nanoparticles or graphitic shells by using monodispersed cobalt nanoparticles as templates. This pathway is a versatile approach to the fabrication of magnetic materials highly stable under strongly acidic and basic conditions. Work to produce such materials with controlled shell thicknesses is in progress.

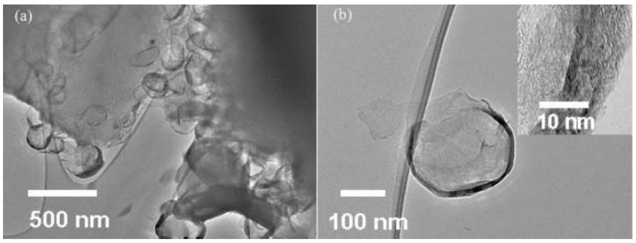

Fig. 3 TEM images of graphite shells.

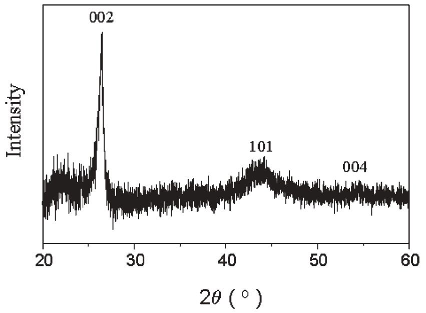

Fig. 4 XRD (transmission) pattern of graphite shells.

A.-H. Lu would like to thank the Alexander von Humboldt Foundation for a fellowship. The authors would like to thank Dr. W. Schmidt and Dr. C. Weidenthaler for helpful discussions, and thank the Leibniz-program and the FCI for support in addition to the basic funding provided by the Institute.

An-Hui Lu, Wen-Cui Li, Nina Matoussevitch, Bernd Spliethoff, Helmut Bönnemann and Ferdi Schüth*
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim, Germany. E-mail: schueth@mpi-muelheim.mpg.de; Fax: +49 0208-3062995

Notes and references

1 (*a*) C. Graf, D. L. J. Vossen, A. Imhof and A. van Blaaderen, *Langmuir*, 2003, **19**, 6693; (*b*) X. Sun and Y. Li, *Angew. Chem., Int. Ed.*, 2004, **43**, 3827; (*c*) T. Cassagneau and F. Caruso, *Adv. Mater.*, 2002, **14**, 34; (*d*) X. Xu and S. A. Asher, *J. Am. Chem. Soc.*, 2004, **126**, 7940.
2 F. Caruso, *Adv. Mater.*, 2001, **13**, 11.
3 (*a*) P. Tartaj, M. P. Morales, S. Veintemillas-Verdaguer, T. Gonzalez-Carreno and C. J. Serna, *J. Phys. D: Appl. Phys.*, 2003, **36**, R182; (*b*) S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. Li, *J. Am. Chem. Soc.*, 2004, **126**, 273.
4 D. K. Kim, M. Mikhaylova, Y. Zhang and M. Muhammed, *Chem. Mater.*, 2003, **15**, 1617.
5 (*a*) X. Gao, K. M. K. Yu, K. Y. Tam and S. C. Tsang, *Chem. Commun.*, 2003, 2998; (*b*) M. Wu, Y. D. Zhang, S. Hui, T. D. Xiao, S. Ge, W. A. Hines and J. I. Budnick, *J. Appl. Phys.*, 2002, **92**, 491; (*c*) T. Hayashi, S. Hirono, M. Tomita and S. Umemura, *Nature*, 1996, **381**, 772.
6 W. Teunissen, F. M. F. de Groot, J. Geus, O. Stephan, M. Tence and C. Colliex, *J. Catal.*, 2001, **204**, 169.
7 (*a*) A.-H. Lu, W. Li, A. Kiefer, W. Schmidt, E. Bill, G. Fink and F. Schüth, *J. Am. Chem. Soc.*, 2004, **126**, 8616; (*b*) A.-H. Lu, W. Schmidt, N. Matoussevitch, H. Bönnemann, B. Spliethoff, B. Tesche, E. Bill, W. Kiefer and F. Schüth, *Angew. Chem., Int. Ed.*, 2004, **43**, 4303.
8 H. Bönnemann, W. Brijoux, R. Brinkmann, N. Matoussevitch, N. Waldöfner, N. Palina and H. Modrow, *Inorg. Chim. Acta*, 2003, **350**, 617.
9 M. Kruk, M. Jaroniec and K. P. Gadkaree, *J. Colloid Interface Sci.*, 1997, **192**, 250.