Synthesis of Snowball Flower-like Ni Nanoparticles by Negatively Charged Micelles

Madhuri Mandal* and Kalyan Mandal
Material Sciences Division, S. N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700 098, India

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Snowball-like nanoflowers of Ni have been synthesized directed by negatively-charged micelles. Positively-charged or neutral micelles can not evolve such structure. Initially, negatively-charged micelles incorporate the positively-charged Ni-ion onto its head group by electrostatic attraction and again further attraction of surfactant on the Ni^{+2} form a layer by layer structure and in a repetitive fashion the surfactant and positively-charged Ni salts form flower-like structure. By the reduction of Ni salts the Ni nanoflowers are formed. The sizes of nanoflowers are ca. 30 nm. The particles are superparamagnetic.

In recent years, the preparation and characterization of nanostructured magnetic materials are receiving immense interest from researchers because they exhibit unique and tunable magnetic properties due to inherent magnetic anisotropy. The practical application of these magnetic nanoparticles in the field of nanotechnology is an attractive topic among researchers. Among the different magnetic nanoparticles studied to date, Ni nanoparticles attract special attention due to their tunable magnetic properties, antimicrobial effects, and catalytic functions. People have synthesized Ni/NiO core–shell nanoparticles,[1] Pt anchoring carbon-encapsulated Ni nanoparticles,[2] Ni/Ni_3C core–shell nanochain,[3] etc. These kinds of material is of interest because they are good catalyst,[4] useful in making nanodevices due to excellent magnetic properties,[3] and applicable to nanomedicine.[5] People are currently interested in size- and shape-controlled synthesis of nanomaterials. We have synthesized many kinds of nanomaterials with different size and shape by exploiting different micelles as template.[6] In this paper we have reported synthesis of Ni nanoparticles of snowball-like shape by a simple chemical process using sodium dodecyl sulfate (SDS) micelles. Our method is simpler than other's. We have used negatively-charged micelles in an intelligent way to synthesize snowball flower-like particles.

All chemicals were analytical grade and used without purification. A typical experiment was as follows. 30-mL acetone and 30-mL ethyl alcohol were taken in a round bottom flask under N_2 atmosphere. Nickel acetate (0.01 M) was dissolved in 30-mL sodium dodecyl sulfate micelles (SDS) solution. This nickel acetate solution was added to the round bottom flask containing acetone and ethyl alcohol. Then the desired amount of hydrated hydrazine solution was added to it under heating (70 °C) and stirring. Then a drop of sodium borohydride solution of very low concentration was added to initialize the reduction of nickel acetate salt. Initially hydrated hydrazine can not reduce the nickel acetate. But after addition of a drop of sodium borohydride the mixture turned to black indicating formation of Ni nanoparticles. Sodium dodecyl sulfate micelles consist of negatively-charged head groups. To understand the mechanism of formation of flower-like particles a similar reaction was also performed in the presence of some other micelles, like positively-charged cetyltrimethylammonium bromide (CTAB) and nonionic Triton X-100 (TX-100) micelles. Only in SDS medium snowball flower-like Ni nanoparticles are formed. But when the synthesis is carried out in positive or nonionic micelles such flower-like nanoparticles are not formed. On the basis of these experiments we presume a mechanism for the formation of flower-like particles in negatively-charged SDS micelles. In the salt "nickel acetate" the Ni is positively charged. Therefore Ni^{+2} are attached to negatively-charged head of the SDS micelles and again SDS surfactant are attracted to positively-charged Ni ions, then in a repetitive way layer by layer, surfactant and Ni salts form a flower-like structure as shown in flow chart Figure 1. After addition of reducing agent, the Ni^{+2} ions are reduced to Ni atoms and due to confinement of Ni clusters inside the SDS micelles flower-like structures of Ni nanoparticles are formed.

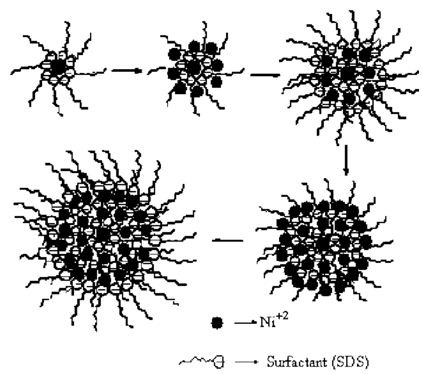

Figure 1. Flowchart diagram of formation mechanism of flower-like Ni nanoparticles.

TEM image of these flower-like nanoparticles are shown in Figure 2. From the TEM image it is evident that all the particles are snowball flower like and almost of uniform size on the order of ca. 30 nm. The closure view of one flower-like structure shows, it again consists of many smaller particles around 2–3 nm. EDX analysis shows particles are purely Ni. No other metals are present.

The structure of the sample was confirmed by taking XRD spectra from X-ray diffractometer (X'Pert Pro, Panalytical) using Cu Kα radiation source. The XRD pattern taken from these flower-shaped nanoparticles is shown in Figure 3. XRD pattern is indexed. It shows only (111) peak corresponding to Ni. The peak is broad in nature which indicates very small particles. From Scherer analysis particle size was calculated and found to be ca. 3 nm. This value is consistent with the actual size of the smaller Ni nanoparticles confined inside the micelles forming snowball flower-like shape.

The magnetic properties i.e., change of magnetization were measured by a vibrating sample magnetometer (Lakeshore,

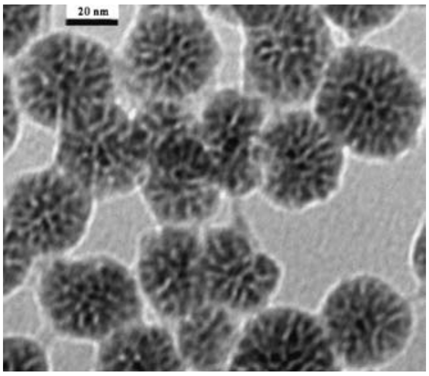

Figure 2. TEM image of snowball nanoflower of Ni nanoparticles.

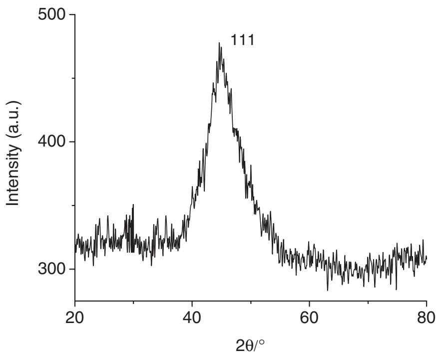

Figure 3. XRD spectrum of snowball flower-like Ni nanoparticles.

model 7144) at room temperature (300 K) with applied magnetic field from −15 to +15 kOe. The curve is shown in Figure 4. It shows hysteresis with no coercive field and remanence which indicates superparamagnetic characteristic of particles. As individual Ni nanoparticles are very small in size they are superparamagnetic in nature. It is well known that small ferromagnetic single domain particles behave as superparamagnetic entities. As flower-like particles are composed of small ferromagnetic clusters of Ni, where the clusters are so small that they can randomly flip direction under thermal fluctuations. As a result, magnetization of the material as a whole become zero when externally applied magnetic field is zero and with increase of applied magnetic field magnetization of material increases and reach a saturation value thus they behave as superparamagnetic.

Snowball flower-like Ni nanoparticles were synthesized in a negatively-charged micelles SDS and its structure, shape, and

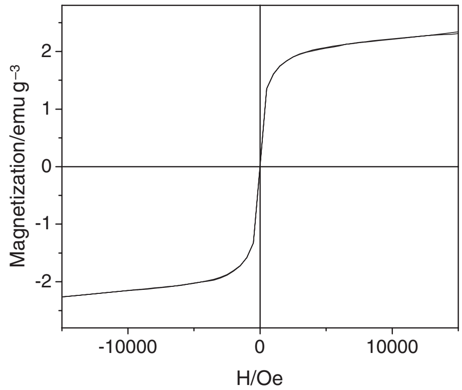

Figure 4. Magnetic hysteresis loop measured for Ni nanoflower.

magnetic properties were investigated. Particles show superparamagnetic behavior. This kind of SDS micelles incorporated biofunctionalized, superparamagnetic material may show a potential applicability in biology in near future and method can be utilized for synthesis of other nanomaterials for extensive comparative study.

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References

1 T. Seto, H. Akinaga, F. Takano, K. Koga, T. Orii, M. Hirasawa, *J. Phys. Chem. B* **2005**, *109*, 13403.

2 Y. Ma, B. Yue, L. Yu, X. Wang, Z. Hu, Y. Fan, Y. Chen, W. Lin, Y. Lu, J. Hu, *J. Phys. Chem. C* **2008**, *112*, 472.

3 W. Zhou, K. Zheng, L. He, R. Wang, L. Guo, C. Chen, X. Han, Z. Zhang, *Nano Lett.* **2008**, *8*, 1147.

4 M. Chen, J. Zhou, L. Xie, G. Gu, L. Wu, *J. Phys. Chem. C* **2007**, *111*, 11829.

5 a) B. Z. Tang, Y. Geng, J. W. Y. Lam, B. Li, X. Jing, X. Wang, F. Wang, A. B. Pakhomov, X. X. Zhang, *Chem. Mater.* **1999**, *11*, 1581. b) M. Kryszewski, J. K. Jeszka, *Synth. Met.* **1998**, *94*, 99. c) V. F. Puntes, P. Gorostiza, D. M. Aruguete, N. G. Bastus, A. P. Alivisatos, *Nat. Mater.* **2004**, *3*, 263. d) M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss, A. P. Alivisatos, *Science* **1998**, *281*, 2013.

6 a) M. Mandal, M. Shamsuzzoha, D. E. Nikles, *J. Magn. Magn. Mater.* **2008**, *320*, 630. b) M. Mandal, S. K. Ghosh, S. Kundu, K. Esumi, T. Pal, *Langmuir* **2002**, *18*, 7792. c) M. Mandal, S. Kundu, T. K. Sau, S. M. Yusuf, T. Pal, *Chem. Mater.* **2003**, *15*, 3710.

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