www.amlett.com, www.amlett.org, DOI: 10.5185/amlett.2012.11465 Published online by the VBRI press in 2013

Magnetically tunable superparamagnetic cobalt doped iron oxide colloidal nanocluster

S. Ravi[1*], A. Karthikeyan[2]

[1]*Department of Physics, Mepco Schlenk Engineering College, Sivakasi 626005, India*
[2]*Department of Nano science and technology, Mepco Schlenk Engineering College, Sivakasi 626005, India*

[*]Corresponding author. Tel: (+91) 4562235691; Fax: (+91) 4562235111; E-mail: sravi_phygri@yahoo.com, sravi@mepcoeng.ac.in

Received: 17 November 2012, Revised: 29 December 2012 and Accepted: 07 January 2013

ABSTRACT

Magnetically tunable colloidal nano clusters (CNC's) have been fabricated using superparamagnetic cobalt doped iron oxide CNCs for the first time. This has the regular interparticle spacing and strongly diffracts light, which is being controlled by an external field. The size of the nanoclusters varies from 10nm–200nm. It reveals that it can be used for wide magnetic tunability. The response to the magnetic field was studied using reflection spectra by varying field sample distance. This shows good response in the UV and visible region. We obtained eight prominent peaks in the UV region which enhances the prosperity of our CNC's sensing the UV predominately. Hysteresis behavior shows the presence of superparamagnetic nature, which is promising candidate for drug delivery, bioseperation and magnetic resonance imaging. Copyright © 2013 VBRI press.

Keywords: Colloidal nanocluster; superparamagnetism; magnetically tunable; cobalt doped iron oxide; self-assembly nanocluster.

S. Ravi is currently Assistant Professor of Department of Physics at Mepco Schlenk Engineering College, Sivakasi, India. He obtained his PhD in the year 2008 from Gandhigram Rural University, Gandhigram, India. He has been awarded as Young Scientist Fellowship from Department of Science & Technology, Government of India during the year 2010. He has published 15 papers with average impact factor and citations of 1.922 and 4.2 respectively. His area of interest includes Nanomagnetism & spintronics and nanomaterials for energy storage devices

A. Karthikeyan obtained his MTech degree (Nanoscience and Technology) from Mepco Schlenk Engineering College, Sivakasi, India and presently working under the corresponding author's group for his Ph.D.

Introduction

Colloidal crystals, periodic structures typically self-assembled from monodisperse colloidal building blocks, are one class of photonic band gap materials that can be fabricated at low cost and on a large scale **[1–3]**. The main advantage of using colloidal crystal is that their properties can be modified by applying any stimuli. In principle, the properties of the colloidal nanocluster (say colour) can be changed by the external stimuli. The stimuli can be electric field, magnetic field, stress, temperature, etc. **[4]**. Recent years, magnetic nano-crystals have attracted much attention owing to their colour tunability in response to the magnetic field. The other advantage is that they can self-assemble in the magnetic field and hence their size and shapes can be controlled. Shell of organic compounds, surfactants or polymers is constructed around nanoparticles of various materials in order to add stability to them preventing their aggregations and minimizing surface energies **[5]**. Asher and co-workers explored this approach by fabricating colloidal photonic crystals using highly charged polystyrene microspheres containing superparamagnetic nanoparticles **[6, 7]**. In this case the magnetic force exerted on the particles is weak and have delayed response. This can be overcome by using polymer microspheres with increase in magnetic loading. Direct use of iron oxide nanoparticles will lead to enhance the strong response but the superparamagnetic to ferromagnetic transition occurs when they grow into larger domains. A nanoparticle with polymer capped is a better idea which enhances the prosperity of having good magnetic response.

Colloidal nano clusters (CNCs) of iron oxide that changes colour in response to the magnetic field could lead to improved technology for making flat panel displays **[8–17]**, drug delivery agents in anticancer activity **[18]** and has a good cellular response **[19–20]**. The key thing is to design the structures through a simple chemical route so that they self-assemble in a magnetic field. The nanoparticles need to be superparamagnetic and have a high surface charge, high magnetic moment and optimal size **[21–23]**. Each nanocrystal supports a single magnetic domain, but the domain is so small that when the magnetic field is removed, they become thermally randomized across the sample, leaving net magnetic moment zero. Single nanocrystal of the same size cluster would permanently magnetize. Altering the external field changes the spacing and hence light of different wavelength could be reflected **[13]**. Earlier reports regarding pure iron oxide CNCs diffract visible light to a wide range of starting from violet to red **[21–24]**. The application could be extended if we develop a CNC that have optical tunability over a wide range of the electromagnetic spectrum. We have attempted this by doping cobalt with iron oxide. Herein, we report the synthesis of nanocluster using highly charged polyacrylate capped cobalt doped iron oxide. Our approach is simple, inexpensive and possesses good response to magnetic field. Several approaches are used to synthesize iron oxide nanoparticles, which are given in the review article [**25**]. But for having nanoclusters that responses magnetic field, bio-synthesis is a better way. The advantage of our synthesize process over other methods is quite simple. We have used polymer agent and capped the nanoparticle using Diethylene glycol as reducing agent. The stability of the nanoparticles are more compared to the other methods and we can use this for even several months. The other advantage of our report is that we have modified the photonic bandgap by doping it with cobalt, which paves way for new technological applications.

Experimental

Materials

Poly(acrylic acid) (99.99%) and diethylene glycol (99%) were purchased from Sigma Aldrich, India. Iron (III) chloride, cobalt (II) chloride and sodium hydroxide were obtained from Merck (AR Grade), India.

Methods

The synthesis of superparamagnetic nanoparticle is a complex process because of their colloidal nature **[25]**. The method adopted in the synthesis of cobalt doped iron oxide is similar to the earlier report **[22]**. A strong NaOH is mixed with diethylene glycol (DEG) of appropriate ratio and heated over 120°C for 1 hour under atmospheric pressure and kept at 70°C. This is considered as a stock solution. Appropriate quantities of Poly Acrylic Acid (PAA), iron chloride, DEG and cobalt chloride were added and heated with rapid stirring. The NaOH/DEG stock solution was then injected more rapidly in to this heated solution. The final product was washed with water/ethanol and finally dispersed with deionized water.

Characterization

XPERT- PRO X-ray diffractometer using Cu Kα Radiation (wavelength λ = 1.54016 A°) at 40 keV was used to confirm the formation of cobalt doped iron oxide nanocluster. Park system XE 70 AFM/MFM was used to study the topography and magnetic contrast image of cobalt and iron in our CNC's. TEM analysis was done by FEI/Philips CM12 to study the morphology and size distribution. Particle size measurement was analysed using Zeta Sizer nano series ZS90. Magnetic measurement was made using a S700X SQUID Magnetometer. Reflection spectra was carried out using Mini LED reflection spectrometer using an 18F 4520 in the UV-Visible range equipped with back scattering probe.

Results and discussion

Water soluble cobalt doped iron oxide nanoclusters were produced through a high temperature hydrolysis reaction of iron chloride and cobalt chloride with NaOH. It has been shown that the size of the nanoclusters can be changed by the percentage of NaOH **[21]**. The Diethylene glycol acts as polar solvent which reduces the Fe^{3+} and produces Fe_2O_3 through dehydration. PAA acts as surfactant, which controls precise size and shape of nanoparticles. The strong coordination of carboxylate groups of PAA with iron cation on the magnetite surface leads to well defined structures which can be tuned. The PAA coating also confers stability of nanoparticles which can be stored for several months. This is one of the great advantages of our methods compared to other reports [**26-36**]. Also the bio-synthesis approach readily makes it to use in the field of biology & medicine. Under optimized condition, uniform CNC's of wide sizes are produced. The XRD pattern of cobalt doped iron oxide nanocluster was presented in **Fig. 1**.

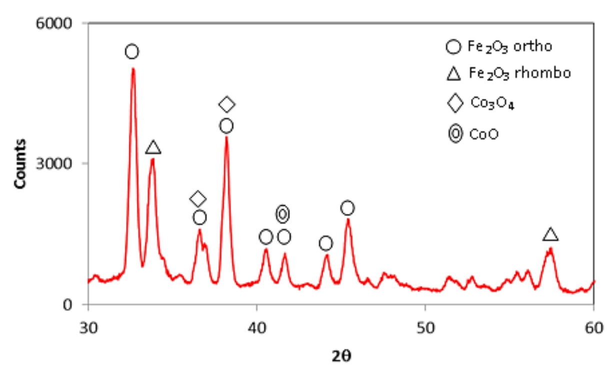

Fig. 1. XRD Pattern for cobalt doped iron oxide CNC.

It shows the high crystallinity and no indication of any other impurities in the sample. From the observed peaks, it is clear that the iron oxide exist in two phases. Ortho phase exist as evident from strong peak at 32.78 (122) plane [JCPDS NO. # 89-7047] and rhombo phase with 2θ value of 33.842 (104) plane [JCPDS NO. # 89-8104]. All other peaks are from orthorhombic phase. Cobalt oxide peaks are mostly overlapped with the iron oxide. So it is difficult to resolve. But the peak at 36.7 shows the existence of Co_3O_4 in (311) plane [JCPDS NO. # 65-3103]. The detailed structural values were presented in **Table 1**.

Table 1. Crystalline details of cobalt doped iron oxide nanocluster.

2θ	(hkl)	Crystal structure	Crystalline size (nm)	d spacing (Å)
32.780	(122)	$(Fe_2O_3)_{ortho}$	13.37	2.7380
33.842	(104)	$(Fe_2O_3)_{rhombo}$	10.4	2.6466
36.710	(210)	$(Fe_2O_3)_{ortho}$ and Co_3O_4	7.2	2.4462
38.303	(004)	$(Fe_2O_3)_{ortho}$ and Co_3O_4	13.37	2.3480
40.639	(132)	$(Fe_2O_3)_{ortho}$	13.47	2.2238
41.701	(212)	$(Fe_2O_3)_{ortho}$ and CoO	13.37	2.1642
44.250	(140)	$(Fe_2O_3)_{ortho}$	13.37	2.0453
45.418	(222)	$(Fe_2O_3)_{ortho}$	11.69	1.9953
57.525	(122)	$(Fe_2O_3)_{rhombo}$	7.8	1.6009

The average crystalline is found to be 11 nm. **Fig. 2** gives the AFM image cobalt doped iron oxide CNC. The AFM image shows the core shell structure and size homogeneity of the nanoparticles. The average particle size was found to be about 100 nm, which was in close agreement with the size obtained by TEM studies. MFM image was given in **Fig. 2** (Bottom), which clearly shows the contrast colour change, indicating the different magnetization for cobalt and iron. Cobalt possess different magnetic moment and relaxation mechanism than iron and this provides the necessitate condition for different wavelength propagation inside the CNC.

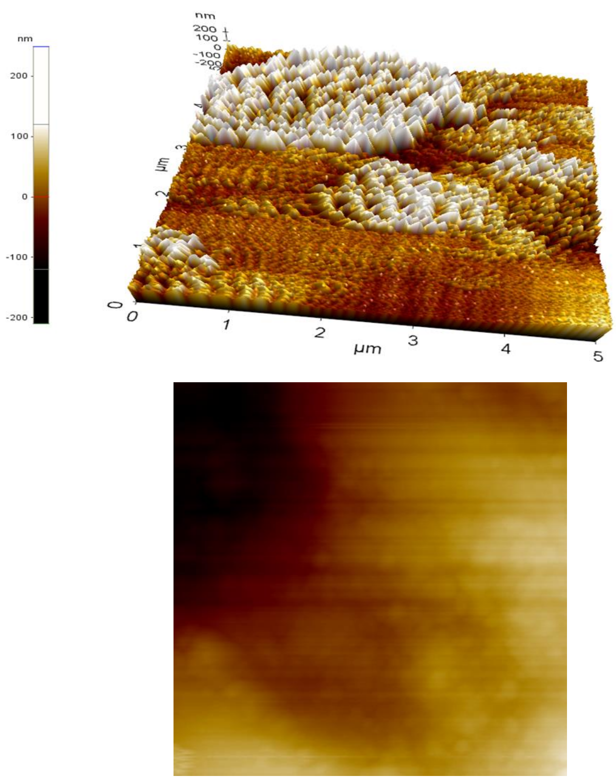

Fig. 2. (Top) AFM image of cobalt doped iron oxide nanocluster showing morphological view of CNC with different spacing. (Bottom) MFM image is showing contrast distribution of cobalt and iron in cobalt doped iron oxide CNC.

Under an optimized conditions, the nanoclusters aggregate to form a periodic grain like distribution. It is evident that each grain like distribution may be considered as a nanocluster, which is clearly seen in the TEM image shown in the **Fig. 3**. Close inspection of these images reveals that each nanocrystal has a different dimension. The cluster size is approximated to 100nm (from TEM) and each cluster may be distributed with number of nanocrystals possessing size in the range 8–12nm.

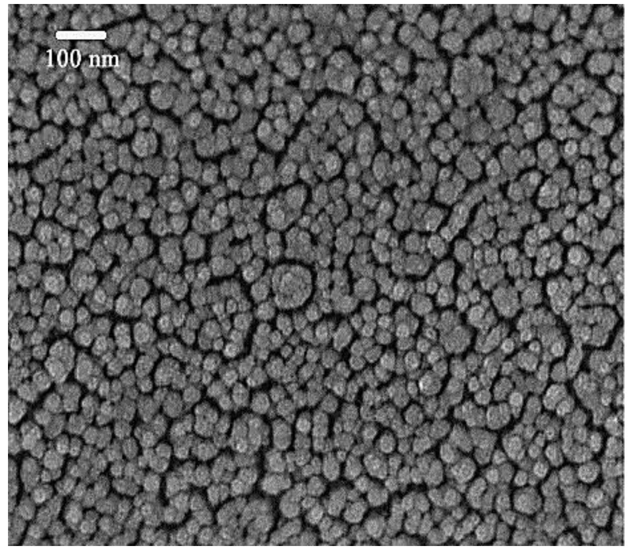

Fig. 3. TEM image of cobalt doped iron oxide nanoclusters showing the distribution of different sizes.

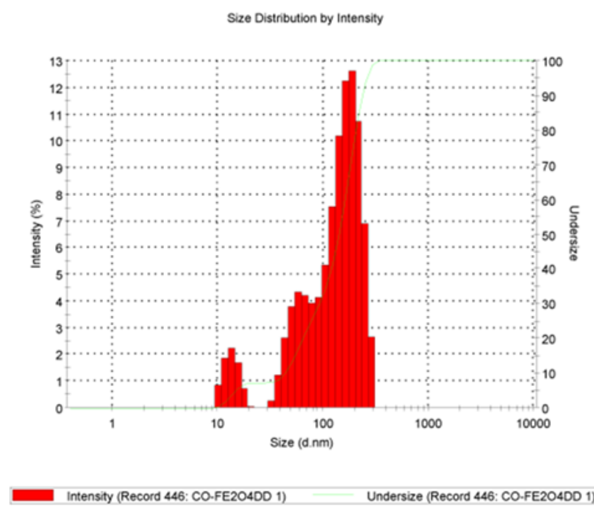

Fig. 4. Size distribution of CNC's using Zeta analyzer showing wide range of size.

The particle size distribution of the CNC's is measured using a particle size analyzer (ZETA Analyser). **Fig. 4** shows the particle size distribution using a Zeta Analyzer. The plot between size and intensity is shown in the histogram format. It reveals that the size range in 10nm are in intensity of 2% and size range in 100–200 nm are in 12% intensity. It is reasonable to presume that nanocrystals having the size in the range of 10nm possess intensity of 2% (since they are not isolated, leading to low intensity value), where nanoclusters shows good intensity of 12%. Since nanocrystals are not isolated (as evident in TEM image), this shows the particle size in the range of 10nm–200nm with combined nanocrystals as well as nanocluster.

In order to fabricate CNC that responds to the magnetic field, the CNC should exhibit an important property called Superparamagnetism. Cobalt possesses an excellent spin mechanism for superparamagnetic nature even at the lowest concentration. CNC's that changes colour or diffract wavelength in response to a magnetic field must possess this property. The key thing is to design the nanocluster so that they self-assemble in a magnetic field. To evaluate the magnetic response of the CNC's to an external field, the mass magnetization was measured at room temperature by the cycling –5 to 5 kOe. **Fig. 5** shows that the CNC's are superparamagnetic at room temperature. The application of a magnetic field to a superparamagnetic colloids results in magnetic packing force and magnetic dipole interaction. There will be also an electrostatic repulsive force. When the electrostatic repulsive force and magnetic force reaches a balance, the CNC form a chain like structure along the external field with regular interparticle spacing which is responsible for controlling and manipulating light propagation. The regular interparticle spacing can be varied by an external field so that it can influence the diffracting wavelength.

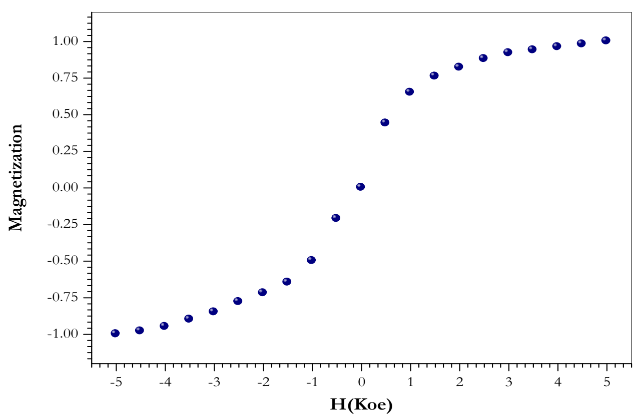

Fig. 5. Mass Magnetization as a function of applied field at room temperature measured of cobalt doped iron oxide CNC showing the existence of superparamagnetic behaviour.

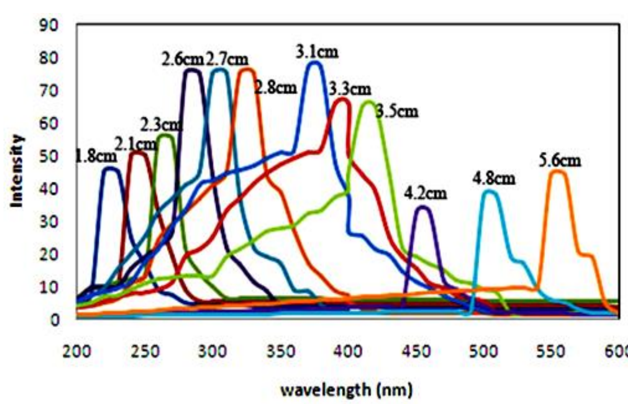

Fig. 6. Reflection spectra of cobalt doped iron oxide CNC showing good response in the UV-vis region.

Fig. 6 shows the reflection spectra of cobalt doped iron oxide CNC by varying field sample distance. The field sample distance was varied from 1.8cm to 5.6cm. Below 1.8cm and beyond 5.6 cm there was no response and the CNC acts as a photonic crystal with stop gate. The reflection spectra shows only four peaks in the visible region and many peaks in the UV region. Thus it shows a good optical tunability in the UV-Visible range.

Conclusion

The colour of the CNC is due to its reflection. Tuning color by varying the magnetic field finds application in the flat panel displays. Iron oxide CNC shows good response in the visible region and used as a targeted drug delivery agent [18]. In our studies, we have shown that cobalt doped iron oxide CNC shows good response in both UV and visible regions. The advantages of using iron oxide are mainly because of its non-toxic nature, availability and good response to the magnetic field. In our work, we have slightly modified the photonic bandgap by doping with cobalt and shown that it can be tuned from UV to visible region. This may find application in targeted tissue/cancerous cell removal in a better way than pure iron oxide.

References:

1. Schroden, R.C.; Al-Daous, M,; Blanford, C.F.; Stein, A. Chem. Mater. **2002**, 14, 3305
   DOI: 10.1021/cm020100z.
2. Lopez, C. J. Opt. A **2006**, 8, R1.
   DOI: 10.1088/1464-4258/8/5/R01.
3. Halaoui, L.I.; Abrams, N.M.; Mallouk, T.E. J. Phys. Chem. B **2005**, 109, 6334.
   DOI: 10.1021/jp044228a.
4. Barry, R.A.; Waltzes, P. Langmuir **2006**, 22, 1369.
   DOI: 10.1021/la0519094.
5. Intelligent Nanomaterials, Wiley-Scrivener Publishing LLC, USA, **ISBN:** 978-04-709387-99, 2012
6. Xu, X.; Friedman, G.; Humfeld, K.D.; Majetich, S.A.; Asher, S.A. Adv. Mater. **2001**, 13, 1681.
   DOI: 10.1002/1521-4095(200111)13:22<1681.
7. Xu, X.; Friedman, G.; Humfeld, K.D.; Majetich, S.A.; Asher, S.A. Chem. Mater. **2002**, 14, 1249.
   DOI: 10.1021/cm010811h
8. Ge, J.; Hu, Y.; Zhang, T.; Huynh, T. Langumir **2008**, 24, 3671.
   DOI: 10.1021/la7039493
9. Fudouzi, H.; Xia, J. Langumir **2003**, 19, 9653.
   DOI: 10.1021/la034918q
10. Van Blaaderen, A. MRS Bull. **1998**, 23, 39.
11. Prasad, T.; Mittleman, D.M.; Colvin, V.L. Opt. Matter. **2006**, 29, 56.
   DOI: 10.1016/j.optmat.2006.03.008
12. Asher, S.A.; Sharma, A.C.; Goponeko, A.V.; Ward, M.M. Anal Chem. **2003**, 75, 1676
   DOI: 10.1021/ac026328n
13. Braun, P.V.; Rinne, S.A.; Garcia- Santamoria, F. Adv. Matter. **2006**, 18, 2665.
   DOI: 10.1002/adma.200600769
14. Lawrence, J.R.; Ying, Y.; Jing, P.; Foulger, S.H. Adv. Matter. **2006**, 18, 300.
   DOI: 10.1002/adma.200501833
15. Tian, E.; Wang, J.; Zheng, Y.; Song, Y.; Jiang, L.; Zhu, D. J. Matter Chem. **2008**, 18, 1116.
   DOI: 10.1039/B717368G
16. Arsenault, A.C.; Puzzo, D.P.; Manners, I.; Ozin, G.A. Nat. Photon. **2007**, 1, 468.
   DOI: 10.1038/nphoton.2007.140
17. Kuai, S.L.; Budder, G.; Ashrit, P.V. Appl. Phys. Lett. **2005**, 86, 221110.
   DOI: 10.1063/1.1929079
18. Chertok, B.; Moffat, B.A.; David, A.E.; Yu, F.; Bergemann, C.; Ross, B.D.; Yanga, V.C. Biomaterials **2008,** 29, 487.
   DOI: 10.1016/j.biomaterials.2007.08.050

19. Jain, T.K.; Morales, M.A.; Sahoo, S.K.; Leslie-Pelecky, D.L.; Labhasetwar, V. Mol. Pharm. **2005**, 2(3), 194.
DOI: 10.1021/mp0500014
20. Kumar, S.; Bhanjana, G.; Dilbaghi, N.; Manuja, A. Adv. Mat. Lett. **2012**, 3(4), 345
DOI: 10.5185/amlett.2012.5342
21. Ge, J. Hu, Y.; Biasini, M.; Beyer mann, W.P.; Yin, Y. Angew Chem. Int. Ed. **2007**, 46, 4342.
DOI: 10.1002/anie.200700197
22. Ge, J.; Hu, Y.; Yin, Y. Angew Chem. Int. Ed. **2007**, 46, 7428.
DOI: 10.1002/anie.200701992
23. Ge, J.; Yin, Y. Adv. Matter. **2008**, 20, 3485.
DOI: 10.1002/adma.200800657
24. Ge, J.; Yin, Y. J. Mater. Chem. **2008**, 18, 5041.
DOI: 10.1039/B809958H
25. Jadhav, S.A.; Bongiovanni, R. Adv. Mat. Lett. **2012**, 3(5), 356
DOI: 10.5185/amlett.2012.7381
26. Blanco-Andujar, C.; Ortega, D.; Pankhurst, Q. A.; Thanh, N. T. K. J. Mater. Chem. 2012, 22, 12498.
DOI: 10.1039/C2JM31295F
27. Ahmed, N.; Michelin-Jamois, M.; Fessi, H.; Elaissari, A.; Soft Matter, 2012, 8, 2554.
DOI: 10.1039/C2SM06872A
28. Ciobanu et al. Chemistry Central Journal 2012, 6, 17.
DOI: 10.1186/1752-153X-6-17
29. Bychko, I.; Kalishyn, Y.; Strizhak, P. Advances in Mater. Phy. Chem. 2012, 2, 17.
DOI: 10.4236/ampc.2012.21003
30. Guardia, P.; Perez, N.; Labarta, A.; Batlle, X. Langmuir 2010, 26, 5843.
DOI: 10.1021/la903767e
31. European patent WO/2012/018240.
32. Darbandi M. et al. J. Phys. D: Appl. Phys. 2012, 45, 195001.
DOI: 10.1088/0022-3727/45/19/195001
33. De Guire, M. R.; Hu, M. Z.; Gogotsi, Y.; Lu, S. W. Ceramic Nanomaterials and Nanotechnology II, Volume 2012, 148.
DOI: 10.1002/9781118406083.ch12
34. Bae et al. Nanoscale Res. Lett. 2012, 7, 44.
DOI: 10.1186/1556-276X-7-44
35. Wang, X. Y.; Zhou, J.; Miao, C.; Wang, Y. M.; Wang, H. F.; Ma, C.; Sun, S. Q. J. Nanopart. Res. 2012, 14, 783.
DOI: 10.1007/s11051-012-0783-y
36. Zhang, S.; Zhang, Y, Wang Y, Liu S, Deng Y, Phys Chem. Chem. Phys. 2012, 21, 5132.
DOI: 10.1039/C2CP23675C

