INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

PRODUCTION WITH PORTRAYAL OF NANOMATERIAL'S: A STUDY

Chemistry

B.SWAPNA   Assistant Professor of Chemistry, Dr.K.V.Subba Reddy Institute of Technology, Kurnool, A.P. India.

ABSTRACT

The paper focuses on the synthesis of Ni and NiCo nanoparticles and their application in the field of magnetism, catalysis & thin film. The characterization of the particles was conducted using TEM, XRD,FTlR,TGA-DSC,UV-vis spectroscopy, EDS. Ni and NiCo nanoparticles have been synthesized using two different mediums i.e aqueous and non aqueous respectively. Heterogeneous synthesis of monodisperse pure nickel nanoparticles in aqueous medium has been carried out using cetyltrimethylammonium bromide and a lower alkylammonium bromide mixture of tetraethylammonium bromide and tetrabutylammonium bromide. The presence of cetyltrimethylammonium bromide alone results in the formation of a mixture of nickel hydroxide and nickel nanoparticles. The particles have been characterized using TEM, EDS, XRD, TGA—DSC and FTIR. The analysis showed that particles were spherical in shape, monodisperse, face centered- cubic with average size about 15 nm and were stable in air up to 325 0C. The nanoparticles have been used as a solid phase catalyst for the reduction of p-nitrophenol and methyl orange in the presence of hydrazine hydrate as reducing agent at different temperatures under varying conditions. The reduction process has been monitored by UV—vis analysis. The present study showed that nanoparticles were not poisoned after their repeated use. TEM analysis also confirms that nanoparticles were stable in the dispersed medium for longer times. The recapping of these nanoparticles has been done with TOPO.

INTRODUCTION:

In non aqueous medium Ni and Ni-Co nanoparticles were prepared by using P VP as stabilizing agent and Hydrazine hydrate as reductant. Three types of NiCo nanoparticles have been synthesized with the ratio of 8: l, 4: l, 2:1. The morphology and structure of the resulting surface capped nickel nanoparticles were analyzed bv means of TEM, XRD, FT-IR, TGA and EDS. As the percentage of co in NiC0 nanoparticles increases, the size of the nanoparticles increases (Ni8C01-3-5nm, Ni4C01-5-l nm, Ni2C0120nm). Below ratio 2:1 the formed nanoparticles get coagulate. The very small size of the synthesized nanoparticles reveals that PVP played a critical role in controlling the radius and dispersibility of the nanoparticles. The catalytic property has been studied for the reduction of p-nitrophenol. Here washing of the nanoparticles also plays an important role during catalysis. Only after fourth washing particles exhibit there catalytic behavior efficiently. Thin film of Ni8C01 nanoparticles has also been formed using LB technique. Characterization of the films has been conducted using AFM and UV-vis spectroscopy. Thin film has the average roughness of 18 nm. Magnetic measurement has been done with vibrational magnetometer of Ni nanoparticles synthesized using CTAB and lower alkyl ammonium salts. Magnetic analysis reveals that with the decrease in size the magnetic character shifts from ferrornagnet to the super paramagnet.

ELEMENTAL OF NANO SCIENCE AND TECHNOLOGY :

Nanoscience and nanotechnology primarily deal with the synthesis, characterization, exploration, and exploitation of nanostructured materials. These materials are characterized by at least one dimension in the nanometer (Inm = 10-9 m) range. Nanostructures constitute a bridge between molecules and infinite bulk systems. Individual nanostructures include clusters, quantum dots, nanocrystals, nanowires, and nanotubes, while collections of nanostructures involve arrays, assemblies, and superlattices of the individual nanostructures .The physical and chemical properties of nanomaterials can differ significantly from those of the atomic-molecular or the bulk materials of the same composition. The uniqueness of the structural characteristics, energetics, response, dynamics, and chemistry of nanostructures constitutes the basis of nanoscience. Suitable control of the properties and response of nanostructures can lead to new devices and technologies. The themes underlying nanoscience and nanotechnology are twofold: one is the bottom-up approach, that is, the miniaturization of the components.

HARD NANOPARTICLES

Metal nanoparticles have attracted a great interest in scientific research and industrial applications, owing to their unique large surface-to-volume ratios can be used as catalystsoligonucleotide recognition, electronic, drug delivery, sensors and optical components .The nature of metal colloids remained unclear, until Faraday realized that the gold colloids he studied contained small metallic particles, which he called divided metals. As the size of a metal nanoparticle is decreased, the continuous density of electronic states in its band structure changes until, at small enough sizes, it is finally broken into discrete energy levels. In discrete energy levels the electrons are not freely mobile, and Ohm's law is no longer applicable. A resultant "Coulomb staircase' is observed experimentally in the current—voltage curves for nanoparticles. The shape corresponds to electronic tunneling via discrete energy levels where adding or removing one electron from the nanoparticles creates an excited state. This excited state has a voltage threshold that depends on an electrostatic charging energy.

Ferromagnetic particles, some of which include Fe, Co, and Ni, exhibit a strong magnetic interaction due to unbalanced spins in their Il-sub shells. These materials are characterized by hysteresis on a magnetization vs. applied field plot when the applied field is increased and then decreased in both a positive and negative direction. The hysteresis is characteristic of two processes that occur in the sample: the initial movement of magnetic domains in the sample at small applied magnetic fields and then, at sufficient energy, the rotation of the sample magnetization vector to align in the direction of the applied field until saturation, Ms, is reached. The energy required to bring the net magnetization in the sample back to zero in the reverse direction is given by the coercively, Hc, where K is the anisotropy constant, which is characteristic of the energy required to align the magnetization of the sample along a particular direction. The anisotropy could arise from the particle structure (crystalline anisotropy), shape, stress, surface, or interaction with other particles. Equation (a) is applicable for systems without thermal activation. If the size of a ferromagnetic particle is reduced to a few nanometers, it will have a single magnetic domain. Single domain particles exhibit greater coercively values than larger multidomain particles because a greater applied field is needed to align only the magnetization vector. For spherical iron particles, the diameter where the transition to a single magnetic domain occurs has been proposed by Kittel to be approximately 15 nm. Single domain particles with some form of anisotropy may exhibit an

unusually large coercivity, sometimes indicating only two values of the magnetic moment, and thus are ideal for digital recording. As the size of ferromagnetic particles is decreased even further, the particles may exhibit a change from ferromagnetic to super paramagnetic behavior. This is observed as a lack of hysteresis (zero coercivity) and occurs for particles where the thermal energy is sufficient to overcome anisotropy barriers.

PRODUCTION OF METALLIC NANOPARTICLES
A large variety of synthetic methods for nanoparticles have been developed. Recently, the emphasis of synthesis has been on the preparation of monodisperse particles, with well-defined size, shape and surface properties. Control over these parameters is crucial for a successful utilization of the size dependent properties that are unique to nanoparticles, and is particularly important in assembly of monolayer protected nanoparticles into crystalline arrays of one-, two- or three-dimensions. Such assemblies are of interest for future generation nanoelectronics . Particles intended as catalysts are generally not sensitive to the particle size, however, the particle surface must be readily available to the reactant, and thus, any protective agents that are used must not adsorb too strongly. Metal nanoparticles have been prepared by a wide variety of techniques such as laser ablation, nucleation from vapor , thermal decomposition of organ metallic compounds, sonolysis , pulse radiolysis , electrochemical reduction and chemical reduction of the corresponding metal salts. Reduction of metal salts in the presence of a suitable protecting agent is the most commonly used technique. Generally, a reluctant, such as borohydride, hydrotriorganoborates , hydrogen or citrate , is added to a solution of the corresponding metal salt. An easily oxidized solvent may function both as the electron donor and the dispersing medium. Such particles are of particular interest for catalysis, as the metal surface is readily accessible.

RANGE OF NICKEL NANOPARTICLES:-
- Metal nanoparticles especially nickel has potential application in biomedical sensors, drug delivery, magnetic resonance imaging, data storage, nanoelectronics, etc.
- Two applications, which are being heavily investigated by several research groups are: detoxification of contaminated personnel for the military drug delivery and treatment.
- Nickel is very reactive therefore its synthesis in pure form is still a challenge.
- Synthesis of nickel is cheaper than Pt, Pd, Ag and Au, and then also it is equally useful in catalysis.
- The method we used to synthesize the Ni and NiCo alloys nanoparticles is the Wet Chemical Method

CONCLUSION:
Additionally, the thiol ligands may be exchanged for functionalized thiols, allowing flexible variation of the properties and the use of the particles as building blocks in chemistry. This synthesis has become very popular and reference is the most cited paper in Chemical Communications to date. Although the size of nanoparticles cannot be exactly controlled during synthesis, it is possible to narrow the size distribution by controlling the reaction conditions. Complete control over the size distribution requires size selection techniques, such as size-selective precipitation. This method is based on a so-called solvent/non-solvent pair that is mutually miscible, but differs in their ability to dissolve the particles. The particles can be precipitated by varying the ratio of the solvents. The method is applicable only to reversibly precipitative particles. Several studies has been done for the synthesis of metallic nanoparticles (Ni) in non aqueous medium and comparatively very little in aqueous medium. In present study nanoparticles has been synthesized in aqueous medium using heterogeneous method in which platinum chlorate has been used as nucleating agent. Also for synthesis various combinations of salt, reducing agent, capping agent (ammonium salts) has been used to synthesize monodispersed nanoparticles of varying size. In another study NiCo and Ni nanoparticles has also been synthesized in 3-5 nm range using non aqueous medium using PVP as capping agent

References:
1. K. E. Drexler, Nanosystems: molecular machinery, manufacturing, and computation, Wiley Interscience, London, 1992.
2. A. Henglein, Chem. Rev., 1989, 89, 1861.
3. G. Schmid, Chem. Rev., 1992, 92, 1709.
4. C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, P. P. Edwards, Chem. soc. Rev., 2000, 2927.
5. A. C. Templeton, W. P. Wuelfing, R. W. Murray, Acc. Chem. Res., 2000, 33, 27.
6. G. Markovich, P. Collier, S. E. Henrichs, F. Remacle, R. D. Levine, J. R. Heath, Acc. Chem. Res., 1999, 32, 415.
7. L. N. Lewis, Chem. Rev., 1993, 93, 2693.
8. R. Elghanian, J. J. Storhoff. R. C. Mucic, R. L. Letsinger. C. A. Mirk'in, Science, 1997, 277, 1078.
9. D. l. Gittins, D. Bethell, D. J. Schiffrin, R. J. Nichols, Nature, 2000, 408, 67.
10. S. W. Koch, A. Knorr, Science, 2001, 293, 2217.
11. Y. F. Cheng, D. J. Schiffrin, J. Chem. Soc., -Faraday Trans 1996, 92, 3865.
12. J. A. Mellor, A comprehensive treatise on inorganic and theoretical chemistry, Longmans, Green & Co, London, 1923.
13. M. Faraday, Philos. Trans. soc. London, 1857, 197, 145.
14. G. Sch"on, U. Simon, Colloid Polym Sci., 1995, 273, 101.
15. G. Schmid, M. B"aumle, M. Geerkens, I. Heim, C. Osemann. T. Sawitowski, Chem. soc. Rev., 1999, 28, 179.
16. G. Schmid, R. Ugo (Ed.), Vol. 7 of Aspects of homogeneous catalysis, Kluwer Academic Press, 1991, pp. 1—36.
17. P.-A. Buffat, M. Fl"ueli, P. Stadelmann, J.-P. Borel, Faraday Discuss. Chem. soc., 1991, 92,173.
18. J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," p. 241. Academic Press, London, New York, 1967.
19. G. Bond and D. Thompson, Catal. Rev. sci. Eng., 1999, 41, 319.
20. T. K. sau, A. Pal, and T. Pal, J. Phys. Chem. B, 2001,105, 9266.
21. S. Link and M. A. El-Sayed, J. Phys. Chem. B, 1999, 103, 4212.
22. S. Galvagno and G. Parravano, J. Catal., 1978, 55, 178.
23. N. W. Cant and W. K. Hall, J. Phys. Chem., 1971, 75, 2914.
24. M. W. Robert and T. I. Stewart, "Chemisorption and Catalysis,'
25. D. Andreeva, V. Idakiev, T. Tabakova, and A. Andreev, J. Catal. 1996, 158, 354.
26. G. J. Hutchings, Gold Bull., 1996, 29, 123.
27. T. Aida, R. Higuchi, and H. Niiyama, Chem. Lett., 1990, 1990, 2247,
28. C. H. Lin, S. H. Hsu, M. Y. Lee, and S. D. Lin, J. Catal., 2002, 209, 62.
29. H. Liu, A. I. Kozlov, A. P. Kozlova, T. Shido, K. Asakura, and Y. Iwasawa, J. Catal., 1999, 185, 252.
30. J. wu and P. Harriott, J. Catal., 1975, 39, 359.
31. R. Santen and C. J. Catal., 1986,530.
32. Balint, A. Miyazaki, and K. Aika, Appl. Catal., B, 2002, 37, 217.
33. Y. Takasy, Y. Fujii, K. Yasuda, Y. Iwanaga, and Y. Matsuda, Electrochim.Acta, 1989, 34, 453.
34. B. G. Ershov, E. Janata, M. Michaelis, and A. Henglein, J. Phys. Chem., 1991, 95, 8996.
35. R. Kramer and H. Zuegg, J. Catal., 1983, 80, 446.
36. J. H. Fendler (Ed.), Nanoparticles and nanostructured Films': Preparation, Characterization and Applications, Wiley-VCH, 1998.
37. Y. Wang, J. Ren, K. Deng, L. Gui, Y. Tang, Chem. Mater., 2000. 12 1622.
38. R. W. Devenish, T. Goulding, B. T. Heaton, R. Whyman, J. Chem. Soc., -DaltonTrans., 1996,673.
39. J. R. Thomas, J. Appl. Phys., 1966, 37, 2914.
40. C. H. Griffiths, H. P. O'Horo, T. W. Smith, J. Appl. Phys., 1979, 50, 7108.
41. T. Tano, K. Esurni, K. Meguro, J. Colloid Int. sci., 1989,133, 530.
42. T. Tano, K. Esumi, K. Meguro, Colloid surf., 1992, 62. 255.
43. N. Arul Dhas, H. Cohen, A. Gedanken, J. Phys. Chem. B, 1997, 101, 6834.
44. N. Arul Dhas, A. Gedanken, J. Mater. Chem., 1998, 8, 445.
45. A. Henglein, J. Phys. Chem., 1993, 97, 5457.
46. M. T. Reetz, W. Heibig, J. Am. Chem. soc., 1994, 1 16, 7401.
47. M. T. Reetz, S. A. Quaiser, Angew. Chem. Int. Edit. , 1995, 34, 2240.
48. M. T. Reetz, M. Winter, R. Breinbauer, T. Thurn-Albrecht, W. Vogel, Chem.Eur.J., 2001, 7, 1084.
49. H. B"onnemann, W. Brijoux, R. Brinkmann, R. Fretzen, T. Joussen, R. Korall, P. Neiteler, J. Richter, J. Mol. Catal., 1994, 86, 129.
50. J. Turkevich, G. Kim, J. Macromol. Sci. -Chem., 1970,169, 873.
51. H. Hirai, Y. Nakao, N. Toshima, J. Macromol. Sci. -Chem. A, 1979, 13, 727.
52. M. Komiyama, H. Hirai, Bull. Chem. Soc. Jpn., 1983, 56, 2833.
53. H. Hirai, Y. Nakao, N. Toshima, J. Macromol. Sci. -Chem. A, 1979, 13, 633.
54. W. Hoogsteen, L. G. J. Fokkink, J. coll. Int. sci., 1995. 175, 12.
55. L. D. Rampino, F. F. Nord, J. Am. Chem. soc., 1941, 63, 2745.
56. A.Henglein, M. Giersig, J. Phys. Chem. B. 1999, 103. 9533.
57. H. B"onnernann, R. Brinkmann, R. K"oppler, P. Neiteler, J. Richter, Adv. Mater.,1992, 4, 804.
58. C. Petit, P. Lixon, M. P. Pileni, J. Phys. Chem., 1993, 9, 12974.
59. A. Taleb, C. Petit, M. P. Pileni, Chem. Mater., 1997, 9, 950.
60. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, J. Chem. Soc.   Chem. Commun., 1994, 801.
61. M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, C. Kiely, J. Chem. Soc. -Chem. Commun., 1995, 1655.
62. M. Brust, D. Bethell, D. J. Schiffrin, C. J. Kiely, Adv. Mater., 1995, 7, 795.
63. S. Chen, R. S. Ingram, M. J. Hoestetler, J. J. Pietron, R. W. Murray, T. G. Schaaff, J. T. Khoury, M. M. Alvarez, R. L. Whetten, Science, 1998, 280, 2098.
64. W. L. Wilson, P. F. Szajowski, L. E. Brus, Science, 1993, 262, 1242.
65. C. B. Murray, D. J. Noris, M. G. Bawendi, J. Am. Chem. soc., 1993, 1 15, 8706.
66. T. G. Schaaff, M. N. Shafigullin, J. T. Khoury, 1. Vezmar, R. L. Whetten, W. G.Cullen, P. N. First, C. Gutierrez-Wing, J. Ascensio, M. J. Jose-Yacaman, J.m Phys. Chem. B, 1997, 101, 7885.
67. C.J. Brinker, and C.W. Scherer, Sol—Gel Science, Academic Press, San Diego, CA, 1990.
68. L. V. Interrante, and M.J. Hampden-Smith, Eds., Chemistry of Advanced Materials —An Overview, Wiley-VCH, New York, 1998.
69. M.J. Hudson, and J.A. Knowles, J, Mater. Chem., 1996, 6, 89.
70. M.D. Fokema, E. Chiu, and J.Y. Ying, Langmuir, 2000, 16, 3154.
71. H. Lu, C. Hsu, 1. Lin, C. weng, U.S. Patent Application, US 2003/021 1032 Al, 2003.
72. Capek, Adv. Colloid Interface Sci., 2004, 1 10, 49.
73. H. Huang, G.Q. xu, W.S. Chin, L.M. Gan, and CH. Chew, Nanotechnolov, 2002,13, 318.

74. T. Hirai, T. Saito, and 1. Komasawa, J. Phys. Chem. B, 2001,105, 9711-9714.
75. A. Harutyunyan, L. Grgorian, and T. Tokune, U.S. Patent Publication, US 2004/0099092 Al, 2004.
76. T. Miyao, T. Sawaura, and S. Naito, J. Mat. Sci. Leil., 2002, 21, 867-870.
77. W.R. Moser, U.S. Patent 5,466,646, Assigned to Worcester Polytechnic Institute, 1995.
78. F. Fievet, J. P. Lagier, and M. Figlaez, Mat. Res. Soc. Bull. , 1989, 14, 29.
79. P. Y. Silvert, and K. Tekaia-Elhsissen, Solid State Ionics, 1995, 82, 53.
80. L. K. Kurihara, G. M. Chow, and P. E. Schoen, Nanaos•l. Mat.. 1995. 5, 607.
81. G. M. Chow, P. E. Schoen, and L. K. Kurihara, Nanostructured Metallic Powders and Films Via an Alcoholic Solvent Process, Navy Case No. 76,572,US Patent 2, 1998).
82. G. M. Chow, L. K. Kurihara, K. M. Kemner, P. E. Schoen, W. T. Elam, A. Ervin, S. Keller. Y. D. Zhang, J. Budnick, and T. Ambrose, J. Maler Res., 1995, 10:1546.
83. G. M. Chow, L. K. Kurihara, and P. E. Schoen, Navy Case No. Patent application pending (1996).
84. L. K. Kurihara, G. M. Chow, S. H. Lawrence, P. E. Schoen, The Minerals, Metals,and Materials Society, Warrendale, PA (1996).
85. M.S. Hed ue, D. Larcher, L. Dupont, B. Beaudoin, K. Tekaia-Elhsissen and J. M., Tarascon, Solid State Ionics,1997, 93, 33.
86. G. Viau, F. Fievet-Vincent, F. Fievet, P. Toneguzzo, F. Ravel, and O. Acher, J.Appl. Phvs., 1997, 81, 2749.
87. Ph. Toeguzzo, O. Acher, G. Viau, F. Fievet-Vincent, and F. Fievet, J. Appl. Phys., 1997, 81, 5546.
88. N. Toshima, and P. Lu, Chem. Lett., 1996, 729.
89. N. Toshima, and Y. Wang, Langmuir, 1994, 10, 4574.
90. N. Toshima, and Y. Wang, Chem. Lett., 1993, 161 1.