Sci. & Cult. 77 (11–12) 499-502 (2011)

Metal Nanoparticles Stabilized on Montmorillonite Clay: Synthesis and Reactivities

ABSTRACT : *In situ* generation of metals Cu°-, Rh°- and Au°-nanoparticles into the pores of modified natural Montmorillonite clay and their characterization have been carried out. The modification of Montmorillonite clay was carried out with mineral acids under controlled conditions for generating nanopores on the surface of the clay. Powder XRD, TEM, N2 adsorption, UV-visible Spectroscopy etc. analyses were carried out to characterize the solid materials. The stabilized metals-nanoparticles are found very active as heterogeneous catalysts and exhibit antimicrobial activities.

Key words: *Nanoparticles; Montmorillonite clay; Nanopores; Powder XRD; TEM; Heterogeneous catalysts; Antimicrobial activities.*

Nanoscience and nanotechnology arouse enormous interest in different fields like medicine, environment, electronics, bio-science, opto-electronic etc.[1-2]. Particles of metals, semiconductor or ceramic of size below 100 nm impart new and novel properties. Metal nanoparticles find applications due to their unique high surface to volume ratio[3-8]. Copper, gold and rhodium nanoparticles were extensively focused by Panacek *et al*.[9], Haruta *et al*.[10,11], Borah et al.[12] in different organic transformations. The stabilizers like surfactants, polymers, organic ligands, alkylammonium salts, zeolites, activated carbon, metal oxides, clay minerals are extensively used[12-18]. Attempts are made to stabilise metals Cu°-, Au°- and Rh°-nanoparticles into pores or layers of Montmorillonite[8,12,19-21].

Preparation of Support : Purified Montmorillonite clay (5 g) (Gujarat, India) was dispersed in 100 ml of 4M HCl followed by refluxing for 1 and 2 h. and thereafter washed repeatedly with deionised water until free from Cl^- ion to generate samples AT-Mont.-I and AT-Mont.-II respectively.

Synthesis of Cu°-, Rh°- and Au°-nanoparticles : 0.5 g AT-Mont. was treated with the aqueous salts solutions [$Cu(CH_3COO)_2$, $RhCl_3$, $HAuCl_4$] under vigorous stirring condition for 6 h followed by reduction with $NaBH_4$ under nitrogen to produce Cu°-Mont., Rh°-Mont, and Au°-Mont.

Results and Discussion : *Characterization of Support:* The high surface area of 478 m^2/g with type-IV isotherm and a H3 hysteresis loop at P/P_o ~ 0.4-0.8, [Fig.1 (4 M HCl activated)] is the characteristics of mesoporous solids. The BJH plot [Fig. 1 (inset)] indicated relatively narrow pore size distributions. The parent Montmorillonite clay exhibited a basal spacing 12.5 Å (d_{001}) (Fig. 2) with an intense basal reflection at 7.06° 2θ, which decreases gradually with increasing treatment time. The SEM image of AT-Mont.-I [Fig. 3(A)] shows the formation of pores on the surface of clay matrix. The EDX pattern of the surface [Fig. 3(B)] reveals the predominance amount of Si over Al.

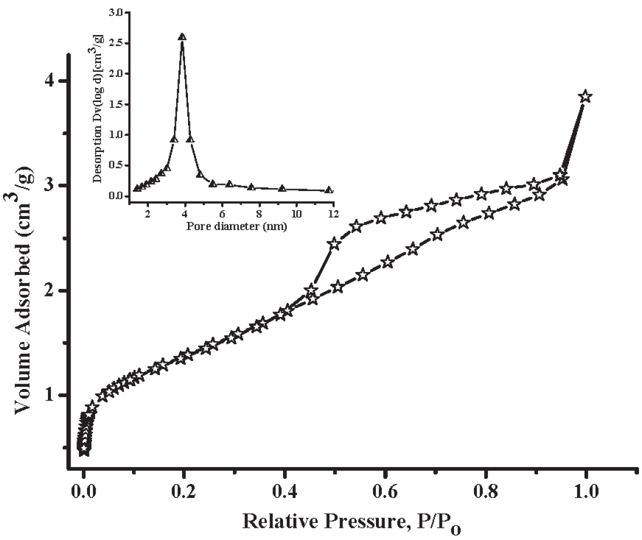


Fig. 1: N_2 adsorption-desorption isotherm and BJH pore size distribution curve (inset) of AT-Mont.-I

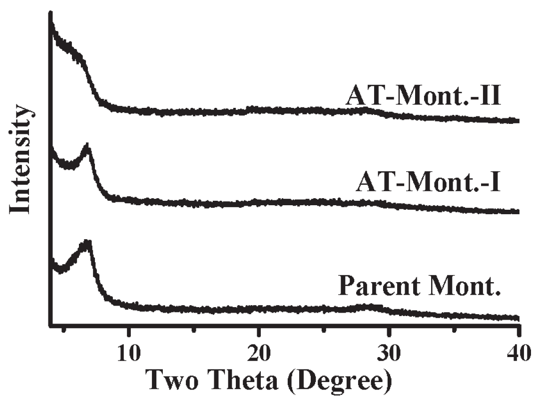


Fig. 2: Powder XRD pattern of different Montmorillonite clay before and after acid activation.

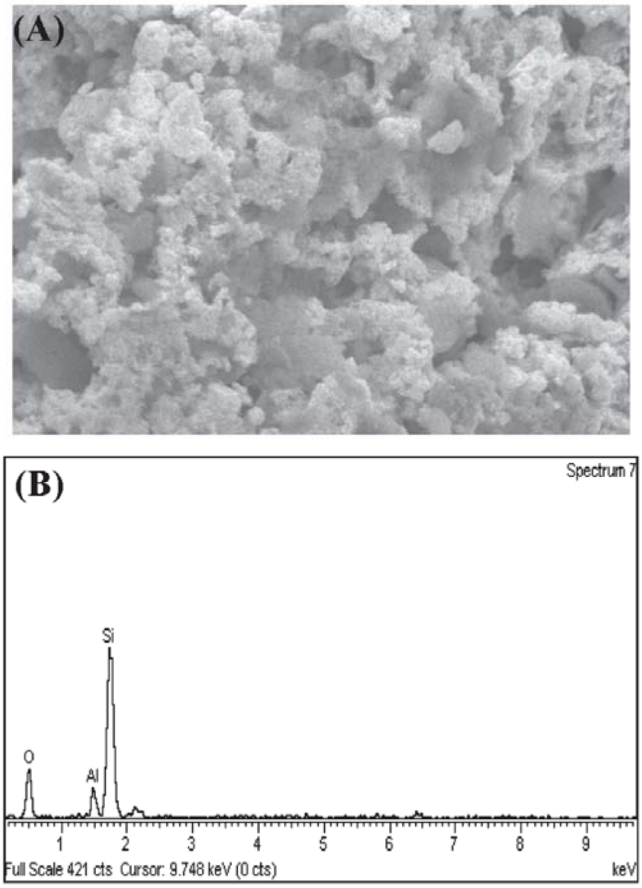


Fig. 3: (A) SEM image of the surface of AT-Mont.; (B) EDX analysis of the surface.

Characterization of Cu°-, Rh°-, Au°-nanoparticles : The peaks [Fig. 4(A)] at 43.3, 50.3 and 74.1° are due to (111), (200) and (220) indices of metallic Cu. In Fig. 4(B), the broad peaks at 41 and 68° are due to the (100) and (200) indices of metallic Rh. The peaks in Fig. 4(C) correspond to (111), (200), (220) and (311) diffraction of metallic Au. Face centered cubic (fcc) geometry prevails in all cases.

The Cu°-, Rh°-, Au°-nanoparticles are of spherical shape having size 0-10 nm and formed in the pores of Montmorillonite clay matrix [Fig. 5]. The HRTEM image [Fig. 5(inset)] shows the reticular lattice planes indicating crystalline nature.

Au°-nanoparticles, exhibiting broad surface plasmon band [Fig. 6] at ~520 nm, reveals the formation of Au°-nanoparticles.

Reactivities: The Cu°-, Rh°-, Au°-nanoparticles are active as catalyst precursors. For example : Borah et al.[12] showed that Cu°-nanoparticles-Montmorillonite serve as

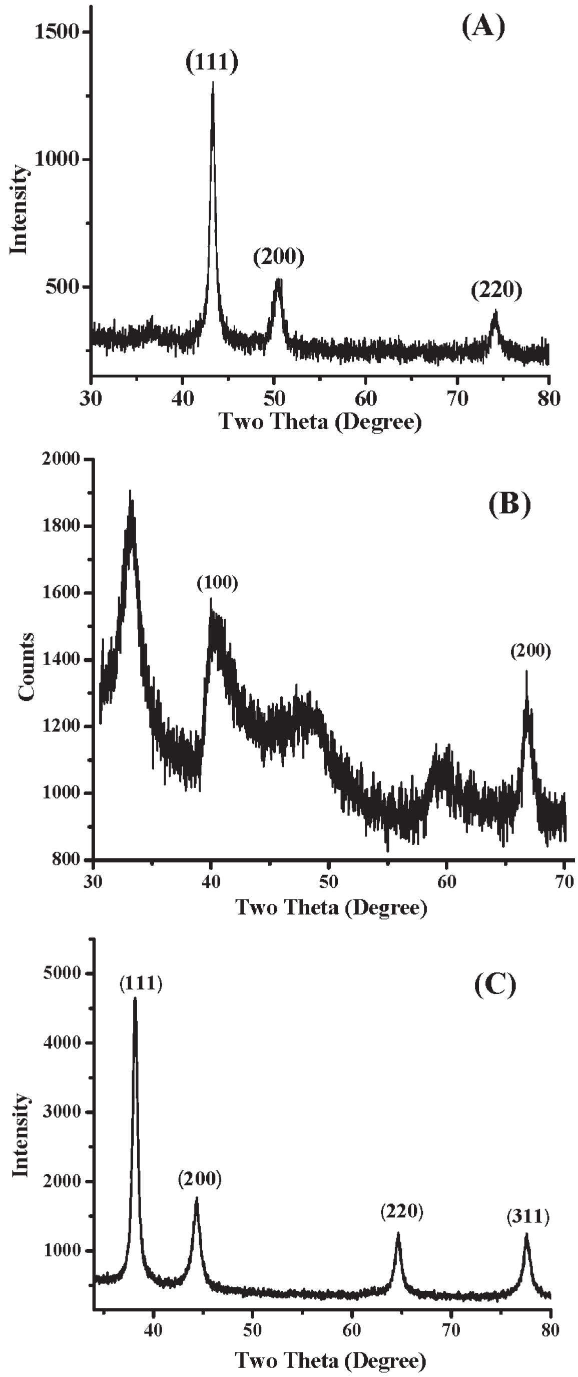
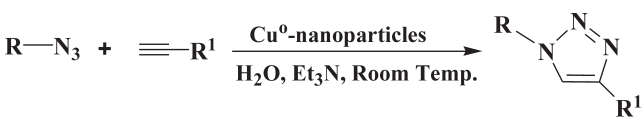


Fig. 4: Powder XRD pattern of (A) Cu°-Mont.; (B) Rh°-Mont; (C) Au°-Mont.

efficient *Green* catalyst for the "Click" azide-alkyne cycloaddition to afford highly regioselective 1,4-disubstituted 1,2,3-triazoles with excellent yields (95%) and selectivity (100%).



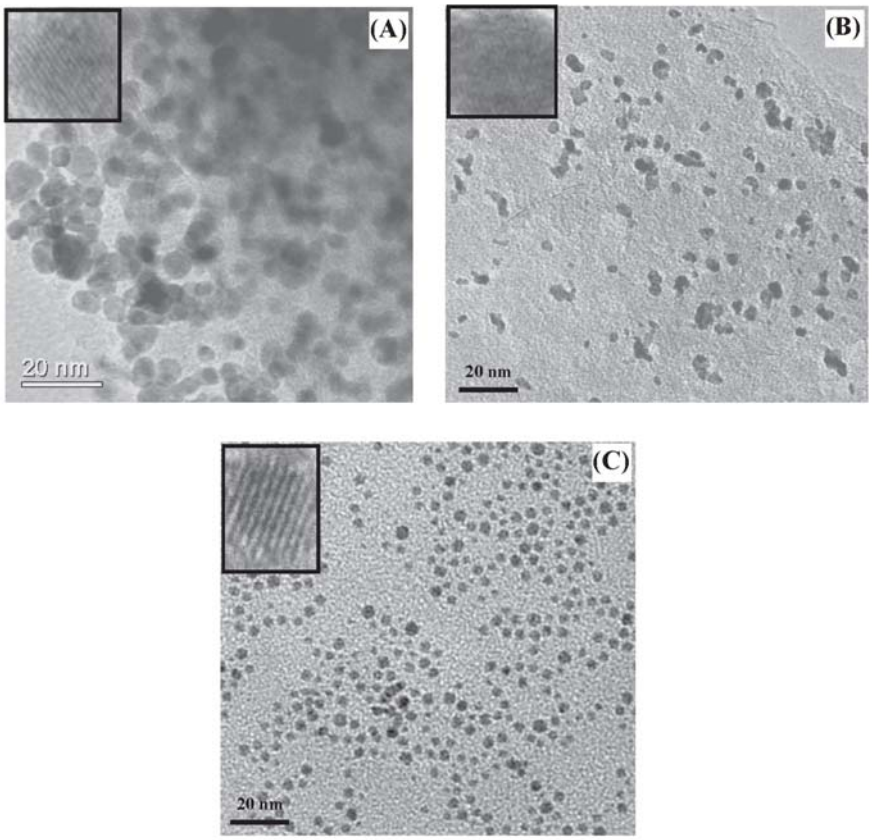
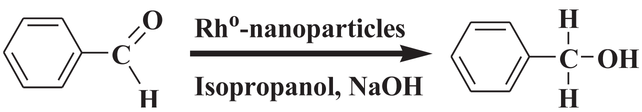


Fig. 5: TEM and HRTEM (inset) images of (A) Cu°-Mont.; (B) Rh°-Mont; (C) Au°-Mont.

The Rh°-nanoparticles serve as efficient catalyst for hydrogenation of carbonyl group to corresponding alcohols (yield 100%) e.g.



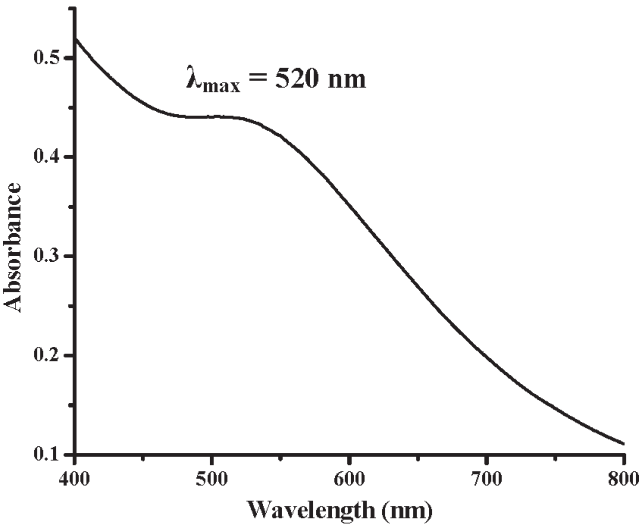


Fig. 6: UV-visible spectrum of Au°-Mont

Recently, Borah et al.[22] reported that the Au°-nanoparticles act as antimicrobial agent against some Gram(+) and Gram(-) bacteria and the nanoparticles are more active against the former e.g. *Staphylococcus aureus* than the latter e.g. *Escherichia Coli*.

Conclusion **:** The synthesized metals (Cu, Rh, Au) nanoparticles (< 10 nm) stabilized on Montmorillonite clay find applications as catalysts in some specific organic transformations. These nanocatalysts are very active, stable and exhibit antimicrobial activities. ❒

DIPAK KUMAR DUTTA*,
BIBEK JYOTI BORAH,
PODMA POLLOV SARMAH,
AND DIPANKA DUTTA

Materials Science Division,
CSIR-North East Institute of Science and Technology,
Jorhat, 785 006, Assam, India

*E-mail: dipakkrdutta@yahoo.com

Received : 14 November, 2011

1. B. Bhusan, *Introduction to nanotechnology*, (Springer Handbook of Nanotechnology), (2004).
2. C. P. Poole Jr and F. J. Owens, *Introduction to Nanotechnology*, (Wiley-Science Pub.), (2003).
3. H. Goesmann and C. Feldmann, *Angew. Chem. Int. Ed.* **49**, 1362-1395 (2010).
4. G. Schmid and B. Corain, *Eur. J. Inorg. Chem.*, 3081-3098 (2003).
5. C. N. R. Rao, G. U. Kulkarni, P. J. Thomas and P. P. Edwards, *Chem. Soc. Rev.* **29,** 27-35 (2000).
6. D. L. Feldheim and C. A. Foss, Jr (Eds.), *Metal Nanoparticles: Synthesis, Characterization and Application* (CRC Press, New York), (2002).
7. M. R. Das, R. K. Sarma, R. Saikia, V. S. Kale, M. V. Shelke and P. Sengupta, *Colloids & Surf. B: Biointerf.* **83**, 16-22 (2011).
8. O. S. Ahmed and D. K. Dutta, *Langmuir* **19,** 5540-5541 (2003).
9. A. Panacek *et al. J. Phys. Chem.* **B. 110,** 16248-16253 (2006).
10. M. Haruta, *Chem. Rec.* **3,** 75-87 (2003).
11. M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett*. 405-408 (1987).
12. B. J. Borah, D. Dutta, P. P. Saikia, N. C. Barua and D. K. Dutta, *Green Chem.* (2011), DOI: 10.1039/C1GC16021D.

13. C. –J. Jia and F. Schuth, *Phys. Chem. Chem. Phys.* **13,** 2457-87 (2011).

14. W. W. Weare, S. M. Reed, M. G. Warner and J. E. Hutchison, *J. Am. Chem. Soc.* **122,** 12890-12891 (2000).

15. R. Tatumi, T. Akita and H. Fujihara, *Chem. Commun.* 3349-3351 (2006).

16. L. O. Brown and J. E. Hutchison, *J. Am. Chem. Soc.* **121**, 882-883 (1999).

17. M. Brust, M. Walker, D. Bethell, J. D. Schiffrin and R. Whyman, *J. Chem. Soc. Chem. Commun.* 801-802 (1994).

18. K. R. Gopidas, J. K. Whitesell and M. A. Fox, *J. Am. Chem. Soc.* **125**, 6491-6502 (2003).

19. B. J. Borah, D. Dutta and D. K. Dutta, *Appl. Clay Sci.* **49**, 317-323 (2010).

20. D. Dutta, B. J. Borah, L. Saikia, M. G. Pathak, P. Sengupta and D. K. Dutta, *Appl. Clay Sci.* **53**, 650-656 (2011).

21. D. K. Dutta, D. Dutta, P. P. Sarmah, S. K. Bhorodwaj and B. J. Borah, *J. Biomed. Nanotech*., **7**, 76-77 (2011).

22. B. J. Borah, A. Yadav and D. K. Dutta, *J. Biomed. Nanotech.*, **7**, 152-153 (2011).