

Synthesis, Characterization and Photocatalytic Application of Halloysite-nanotube Supported Fe-Ni Nanostructure

Rahil S. Qureshi¹, V. S. Ashtekar², P. D. Jolhe³

^{1,2}Sinhgad College of Engineering, Department of Chemical Engineering, Vadgaon, Pune -411041

³Sinhgad College of Engineering, Department of Biotechnology, Vadgaon, Pune -411041

Abstract: Fabricated halloysite and halloysite supported Fe-Ni (Fe-Ni@HNTs) nanostructure is successfully fabricated by immobilization of precursor metal over the surface of amino silane modified HNTs. The as-synthesized HNTs supported metal nanostructures were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectrometry (EDX). Peaks patterns obtained from XRD confirm the formation immobilized HNTs and Fe-Ni@HNTs. 12 mol% Fe-Ni@HNTs shows better photocatalytic oxidation of methylene blue (MB) than 6 mol% Fe-Ni@HNTs under the influence of UV irradiation. The effect of loading of catalyst had also been studied under this report.

Keywords: Halloysite, Photocatalytic, Methylene blue, Oxidation.

1. Introduction

In recent times, the preparation of enhanced and advance functional materials with improved properties and characteristics involve hybrid nano-compounds, which comprises nano-size inorganic and organic material derivatives, the important feature is controlling the growth of molecular structure at the atomic and macroscopic level dimensions, resulting a major effect in the performance [1-4]. All of the enhanced properties NCs can be prepared by inorganic solid such as, layered silica clay, hydroxyl-apatite, silicates, metal-oxides, and a variety of bio polymers, which includes polysaccharides, proteins, polypeptides, nucleic acid and much more [5-8]. The synthetic method for the structural templating of the inorganic component normally by means of self assembly, preparation and surface modification of nano-scale inorganic materials [9-11]. They had a wide application in advanced catalysis, controlled drug preparation, advance oxidation processes, water purification, food processing, optics, mechanics, sensors and electronics [12-15].

The fabrication of novel material is now possible due to the development of halloysite based on organic-inorganic enhanced Nanocompounds, which will be used in applications as anti-corrosive agents, nanoreactors to host reactants for synthesis of nanomaterial. Halloysite nanotube (HNT) is a naturally occurred two-layered alumino-silicate clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$) having a hollow tubular shaped structure, which is formed of alumino-silicate minerals and consist of the constituent elements such as aluminium, silicon, and oxygen. The packing disorder and the nanotube curves are due to the adjacent alumina and silica layers with their certain amount of water of hydration and which roll up to form a several layers [16,17]. The hollow tube formation of aluminosilicate is impelled due to the mismatch in the periodicity between the tetrahedral SiO_2 sheets and the adjacent octahedral AlO_6 sheets, it also assist in determining

the positive and negative surface charges of the HNTs [18,19]. Thus, they possess various varied surface chemistry that help to control the physico-chemical properties of these clay nanotubes through the organized chemistry of the constituent elements as well as their morphology. HNTs restrict their wide applications in different fields sometimes due to the hydrophilic surface. Hence organosilane had been used for the modification of the outer surfaces of the HNTs of these nanotubes which results in improved dispersive property of clay materials as well as improves the physical, mechanical, and chemical properties of the nanotubes.

The modification or functionalization of HNTs surfaces with these organosilanes provides the deposition of metal nanoparticles (NPs) all over the surface. where HNTs act as a solid inorganic support and organosilane is a linking molecule that link metal nanomaterial and HNTs and hence, leading to successful formation of HNTs/metal NCs. Due to the unique characteristics and properties of metallic nanoparticles had attracted a huge attention in research field in modern nanoscience technology and had a wide application of catalysis, electrical, electronics, photonics and information storage component [20-23]. Agglomeration had a great impact on their properties and activity which is highly affected and reduced once they start agglomerating. The mixture results in the formation of bulk like material. To avoid this problem of agglomeration and to possess well dispersed particles, Immobilization of these NPs on solid supports or deposit them directly over the supports are the way for preventing agglomeration [12, 24-28]. Halloysite nanoclay is available as abundant natural resource and hence is of low cost, therefore is a best alternate solid support for the deposition of metal NPs. The preliminary objectives of our present study are to synthesize HNTs/metal NCs, and studying its application in the photocatalytic degradation of dye.

2. Experimental

2.1 Functionalization of HNTs

Preparation of functionalized HNTs was approached using the following experimental procedure. 40 mL of toluene and 4 gms of HNT's was charged in a 250 ml three neck round bottom flask equipped with reflux condenser, thermowell for thermometer and stopper. The reaction mass in flask was heated using a heating mantle to achieve temperature of 60°C. As 60°C is achieved 5 mL of (3-aminopropyl triethoxy silane) is added to the reaction mass. The reaction mass is heated to gain reflux temp of 120 °C, and reflux was carried out for next hrs. After 12 hrs, the reaction mass is cooled and then the material is centrifuged with simultaneous washing with toluene first and then with ethanol. The washed product is then dried at 80 °C for 5 hrs.

2.2 Preparation of Fe-Ni@HNTs

For the preparation Fe-Ni @ HNTs 9.95 gm $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is added to 25 ml of water in a beaker and agitated for 15 minutes at the agitation speed of 1200 rpm using a magnetic stirrer. After that 1 gm of functionalized halloysite is added to the solution then stirred continuously for 2 hr. 600 mg of NaBH_4 is added to the reaction mass and stirred for 30 minutes. 0.05 mole % and 0.125 mole % of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is added to the reaction mass and mixed for 30 minutes. The obtained product is then washed with distilled water and ethanol to wash off the reactant residue, centrifuged and dried at at 80 °C for 5 hrs. The obtained product is Fe-Ni@HNTs

2.3 Photocatalytic experiments

In all photocatalytic experiments, 100 ml of dye solution and appropriate quantity Fe-Ni@HNTs of are taken in a beaker. The dye and catalyst suspension was agitated for 20 mins in dark chamber so that the adsorption equilibrium is reached. Then after 20 mins the UV radiation are illuminated on to the solution. At various time intervals 1 ml from dye catalyst suspension is withdrawn and then is diluted to 10 ml of solution by adding distilled water then centrifuge to separate suspended catalyst and its absorbance is measured. The absorbance is due to the colour of dye and it helps to calculate the concentration and degradation of dye.

3. Results and Discussion

3.1 Photocatalyst characterization

The XRD images shown in Fig. 1 give the XRD patterns of the modified HNTs and the prepared Fe-Ni@HNTs catalysts. For HNTs the peaks of diffraction is obtained at 27.5°, 38.6°, 56.66°, and 64.06° at 2θ corresponding to (111), (200), (220), and (311) that is allotted to hexagon structure of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, the main skeleton of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ is Al_2O_3 and SiO_2 . Where as in 5 mol % Fe-Ni@HNTs and 12 mol % Fe-Ni@HNTs the diffraction peak is obtained at 26.9°, 34.8°, 46.76°, 54.06° and 27.2°, 39.6°, 48.63°, 58.06° at 2θ corresponding to (111), (200),

(220), and (311) successful deposition of Fe-Ni over the surface of HNTs have been observed. It's also shows that several by products hav also been formed due may be due to the back reaction or the improper washing of the prepared catalyst. XRD patterns verify the F.C.C structure of the loaded Fe-Ni NPs.

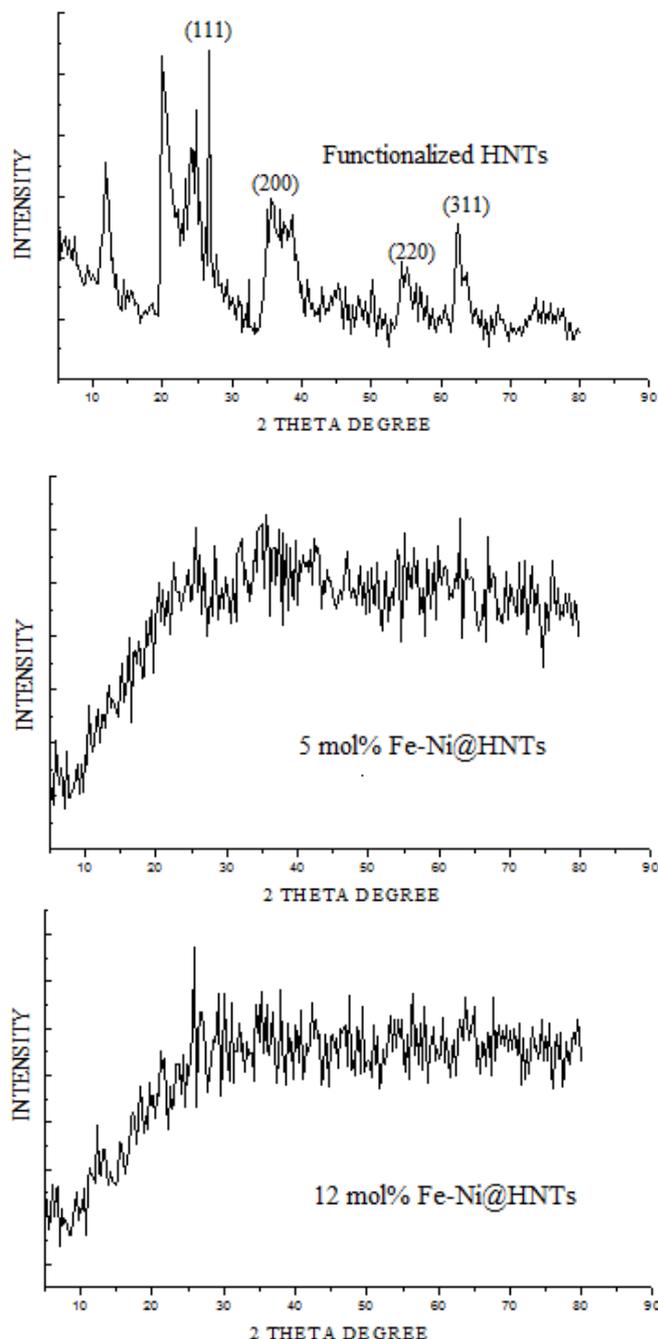


Figure 1: XRD patterns of functionalized HNTs and prepared 5 mol% Fe-Ni@HNTs and 12mol% Fe-Ni@HNTs.

Figure 2 and 3 shows the FE-SEM and EDX results of the prepared Fe-Ni@HNTs the morphologies and chemical composition of this prepared HNT/Fe-Ni. This shows that the Fe and Ni is completely im-mobilized and well deposited over the surface of HNTs having particle sizes 9.0 ± 1.5 for Au and 9.0 ± 1.0 for Ag NPs. Characterization by EDX analysis and the corresponding elemental mapping again reveals the formation of HNTs/Fe-Ni NCs.

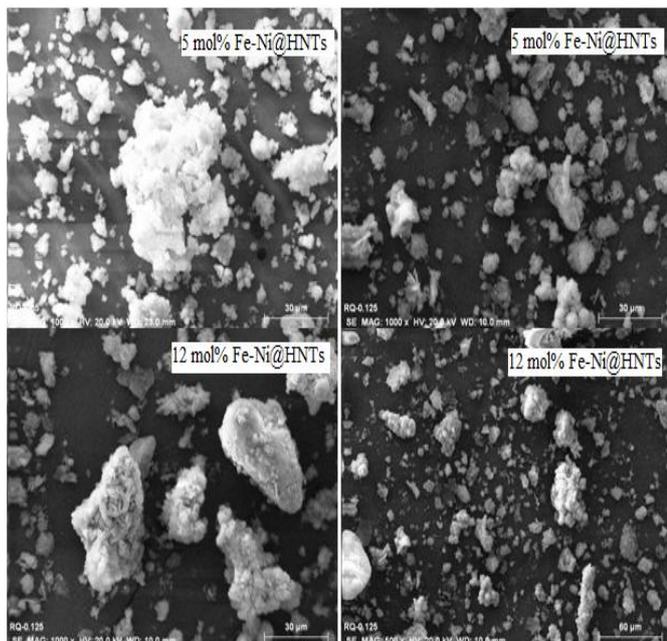


Figure 2: FE-SEM Images of 5 mol% and 12 mol% Fe-Ni@HNTs at magnification of 30 μm and 60 μm

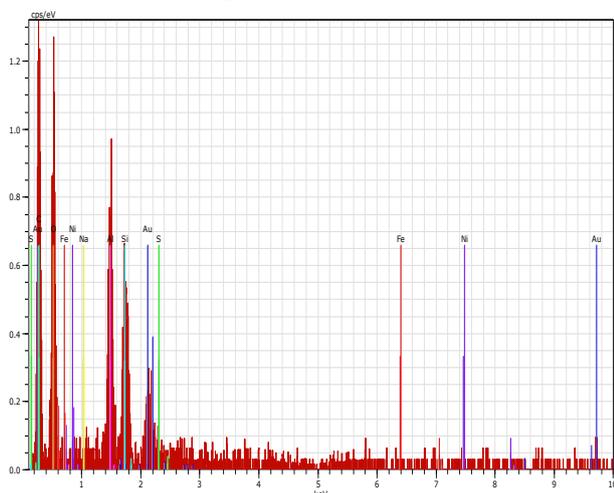


Figure 3: HNTs/Fe-Ni NCs and its EDX spectra, demonstrating the presence of Fe-Ni in HNTs/Fe-Ni.

3.2 Photocatalytic activity

3.2.1 Effect of Catalyst Loading

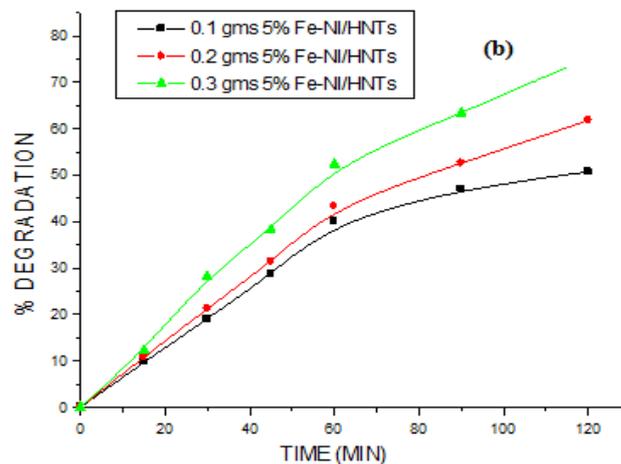
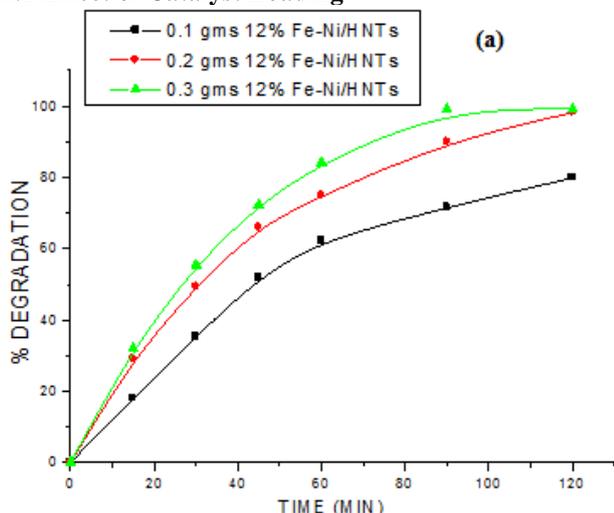


Figure 4: Figure 4 shows the photocatalytic degradation of [MB] by varying the amount of catalyst loading of catalyst (a) 5 mol% Fe-Ni/HNTs (b) 12 mol% Fe-Ni/HNTs

The photocatalytic degradation of methylene blue is achieved by synthesized HNT/Fe-Ni. Fig 4 shows that the degradation of MB increases with increase in mole of Ni in the Fe-Ni@HNTs dopant with respect to irradiation time. It shows that the MB degrades over the surface of Fe-Ni@HNTs. The photocatalytic degradation of [MB] is carried out for 120 minutes. Figure 4 relates the degradation of [MB] using various catalysts loading of 5 mol% Fe-Ni@HNTs and 12 mol % Fe-Ni@HNTs the maximum degradation occurs at loading of 0.3 gms of 0.3 gms 12 mol % Fe-Ni@HNTs that is (99%) followed by 0.2 gms of 12 mol % Fe-Ni@HNTs that is (98%).

4. Conclusion

In summary, modified HNTs and Fe-Ni@HNTs is successfully fabricated by immobilization of precursor metal over the surface of amino siliane modified HNTs and confirmed by XRD, FE-SEM, and EDX characterization technique. Prepared photocatalyst were applied for photocatalysis of methylene blue under UV radiations. Percent degradation 0.3 gms of 12 mol% Fe-Ni@HNTs (99 %) is 3.6 times greater than 5 mol% Fe-Ni@HNTs (75%) may be due to the increase in concentration of Fe-Ni.

References

- [1] C. Sanchez, B. Julián, P. Belleville and M. Popall, *J. Mater.Chem.*, 2005, 15, 3559–3592.
- [2] G. L. Drisko and C. Sanchez, *Eur. J. Inorg. Chem.*, 2012, 5097–5105.
- [3] Z. Ahmad and J. E. Mark, *Mater. Sci. Eng., C*, 1998, 6, 183–196.
- [4] K. H. Wu, T. C. Chang, Y. T. Wang and Y. S. Chiu, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, 37, 2275–2284.
- [5] B.K.G. Theng, *Formation and Properties of Clay Polymer Complexes*, Elsevier, New York, 1979.
- [6] X. Ding and S. M. Henrichs, *Mar. Chem.*, 2002, 77, 225–237.
- [7] Y. Chen and J. O. Iroh, *Chem. Mater.*, 1999, 11, 1218–1222.

- [8] C. C. Chang and W. C. Chen, *Chem. Mater.*, 2002, 14, 4242–4248.
- [9] S. L. Burkett, S. D. Sims and S. Mann, *Chem. Commun.*, 1996, 1367–1368.
- [10] M. A. Ogawa, *Chem. Commun.*, 1996, 1149–1150.
- [11] D. G. Shchukin, G. B. Sukhorukov, R. R. Price and Y. M. Lvov, *Small*, 2005, 1, 510–513.
- [12] S. Jana, S. Praharaaj, S. Panigrahi, S. Basu, S. Pande, C.-H. Chang and T. Pal, *Org. Lett.*, 2007, 9, 2191–2193.
- [13] A. F. Thunemann, D. Schutt, L. Kaufner, U. Pison and H. Mohwald, *Langmuir*, 2006, 22, 2351–2357.
- [14] S. J. Tans, A. R. M. Verschueren and C. Dekker, *Nature*, 1998, 393, 49–52.
- [15] S. Lelu, C. Novat, A. Guyot and E. Bourgeat-Lami, *Polym. Int.*, 2003, 52, 542–547.
- [16] E. Joussein, S. Pitit, J. Churchman, B. Theng, D. Righi and B. Delvaux, *Clay Miner.*, 2005, 40, 383–426.
- [17] Y. M. Lvov, D. G. Shchukin, H. M. Mohwald and R. R. Price, *ACS Nano*, 2008, 2, 814–820.
- [18] E. Abdullayev, A. Joshi, W. Wei, Y. Zhao and Y. Lvov, *ACS Nano*, 2012, 6, 7216–7226.
- [19] G. Cavallaro, G. Lazzara and S. Milioto, *J. Phys. Chem. C*, 2012, 116, 21932–21938.
- [20] D. B. Ingram, P. Christopher, J. L. Bauer and S. Linic, *ACS Catal.*, 2011, 1, 1441–1447.
- [21] J. S. Lee, P. A. Ulmann, M. S. Han and C. A. Mirkin, *Nano Lett.*, 2008, 8, 529–533.
- [22] L. R. Hirsch, R. J. Stafford, J. A. Bankson, S. R. Sershen, B. Rivera, R. E. Price, J. D. Hazle, N. J. Halas and J. L. West, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, 100, 13549–13554.
- [23] C. J. Murphy, A. M. Gole, S. E. Hunyadi and C. J. Orendorff, *Inorg. Chem.*, 2006, 45, 7544–7554.
- [24] J. Dai and M. L. Bruening, *Nano Lett.*, 2002, 2, 497–501.
- [25] S. Ivanova, V. Pitchon, Y. Zimmermann and C. Petit, *Appl. Catal., A*, 2006, 298, 57–64.
- [26] S. Jana and S. Das, *RSC Adv.*, 2014, 4, 34435–34442.
- [27] K. Esumi, R. Isono and T. Yoshimura, *Langmuir*, 2004, 20, 237–243.
- [28] J. C. Garcia-Martinez, R. Lezutekong and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, 127, 5097–5103.
- [29] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet and B. Delmon, *J. Catal.*, 1993, 144, 175–192.