International seminar on Nanoscience and Technology- conference proceedings. Oct- 2016
Volume 3, Special Issue - Available Online: http://ijrset.in/Volume3,Special-Issue-IV.php Pages: 6-11

ISSN 2394-739X

International Journal for Research in Science Engineering and Technology

A SIMPLE ROUTE FOR THE PREPARATION AND CHARACTERIZATION OF NICKEL – COPPER DOPED SILICA NANOCOMPOSITE AND ITS APPLICATION IN DYE DEGRADATION

[1] A. Vanitha, [1] S. Sulochana, [1] A. Sahaya Raja, [1] J. Sathiyabama, [2] V. Prathipa.
[1] PG& Research Department of Chemistry, [2] Department of chemistry,
[1] G.T.N. Arts College, [2] PSNA College Engineering and Technology,
[1, 2] Dindigul, Tamilnadu, India

ABSTRACT- Nanocomposite SiO_2/Ni-Cu was synthesised using simple chemical phase method and their structural characterizations were evaluated by X-ray diffraction (XRD) and Fourier Transform Infra Red (FTIR) spectroscopy techniques. The prepared nanostructure towards Methylene blue dye degradation was evaluated by using UV-Vis spectrophotometer. It has been found that SiO_2/Ni-Cu of Nanocomposite exhibited superior degradation ability owing to the large surface area and high absorption ability of the composite.

Keywords- [SiO_2/Ni-Cu Nanocomposite, Methylene blue dye, XRD, FTIR, UV –Vis Spectroscopy]

1. INTRODUCTION

Nanoscience and technology has become an identifiable, if very broad and multidisciplinary, field of research and emerging applications in recent years. It is one of the most visible and growing research areas in materials science in its broadest sense. The International Technology Research Institute, World Technology Division (WTEC), supported a panel study of research and development status and trends in nanoparticles, nanostructured materials, and nanodevices during 1996–1998[1]. This report attempted to cover the very broad field of nanostructure science and technology. A conclusion of the report is that better understanding of the relationships between nanostructure and properties and how these can be engineered [2-8]. In recent years much attention has been paid to silica (SiO_2) nanoparticles, owing to their large pore volume, high surface area, tunable pore sizes, narrow size distribution, nontoxic nature, good surface permeability, highly ordered hexagonal structure with narrow pore size distribution, and large surface area, which aid the constructive applications of SiO_2 as an effective catalyst in photocatalytic application [9-11]. However, SiO_2 exhibits certain disadvantages such as low chemical stability in aqueous medium, functionality degradation, unfavorable charge distribution, and heterogeneous electron transfer. An extreme interest has been generated by metals, such as Co, Ni, Cu and Fe, since they exhibit superior catalytic activity [12-17].

2. MATERIALS AND METHODS

2.1 MATERIALS

Ethanol, ammonia, tetra ethyl ortho silicate (TEOS), Nickel chloride hexahydrate ($NiCl_2.6H_2O$),Copper Chloride ($CuCl_2$) were purchased from sigma –Aldrich . All reagents were of analytical grade and were used as without further purification. The ethanol is distilled through vacuum distillation and the distilled ethanol is used for the synthesis of silica and silica nanocomposites.

2.2. PREPARATION OF SILICA NANOPARTICLES

The silica nanoparticles were synthesized by using the following procedure. In the mixture of 80 ml absolute ethanol, 2 ml deionized water and 2.6ml ammonia, tetraethyl orthosilicate (TEOS) 1.6 ml was added by drops under constant stirring. The above solution mixture stirred for about 2 h at the room temperature, and the formed white precipitate was centrifugally separated from the suspension, and washed with three times absolute ethanol and water.

2.3 Preparation of Nickel Doped Silica Nanoparticles

To fabricate the Nickel doped composite, 0.1 g of silica was ultrasonically dispersed in 10 mL deionized water to form a suspension, and then 0.05g of Ni Cl_2 and 0.1ml of ammonia were added under stirring. The suspension was heated to 80 °C, and refluxed at that temperature for 2 h. Then, the sample was separated by centrifugation to obtain a green precipitate.

2.4. PREPARATION OF NICKEL – COPPER DOPED SILICA NANOPARTICLES

0.1g of silica was ultrasonically dispersed in 10ml of ethanol and 0.025g of Ni Cl_2 and 0.025g of $CuCl_2$.Then 0.1ml of ammonia added to the mixture stir for 4 hours. Then, the sample was separated by centrifugation to obtain a dark green precipitate.

2.5 EVALUATION OF MB DYE DEGRADATION.

The prepared Nanocomposite material was evaluated for the degradation of MB. 25 mg Nanocomposite material were mixed with 50 ml 10 mg/L MB solution. Afterwards, the mixture was magnetically stirred in the dark for 1 h to reach the complete absorption-desorption equilibrium, the prepared Nanocomposite material were separated by centrifugation in a dark environment. The concentration of the remained MB was analyzed by measuring the absorption intensity at featured wavelength of 664 nm.

3. RESULTS AND DISCUSSION

3.1. XRD PATTERN

The XRD patterns of as-synthesized SiO_2 /Ni and SiO_2 /Ni–Cu nanostructures are depicted in Fig. 1 .The sharp peak found at 24.08, which is related to the (100) reflection plane of SiO_2. In addition to the characteristic broad peaks at 46.6, 52.4, 68.2 ^{o} corresponding (111), (200) and (220) planes indicate the presence of Ni in the prepared SiO_2 /Ni nanosturctures.

SiO_2 /Ni-Cu preserved the (100) reflection plane of SiO_2 and (111), (200) and (220) planes of the Ni. The additional (111) plane found at 40.2 ^{o} is confirm the presence of Cu in the prepared SiO_2 /Ni-Cu composite.

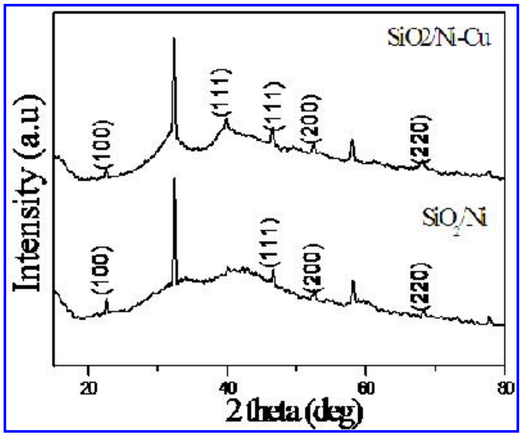

Figure 1- XRD patterns of SiO_2 / Ni and SiO_2 / Ni–Cu composites

3.2. FT-IR STUDIES

The FT-IR spectra of SiO_2, SiO_2/Ni and SiO_2/Ni–Cu are provided in Fig.2. SiO_2 exhibited a broad band at 3447 cm^{-1}, which is attributed to the stretching vibration of Si–OH groups. The Si–O–Si symmetric stretching and Si–O bending vibrations of SiO_2 were observed at 1098 and 800 cm^{-1}, respectively. For the SiO_2/Ni–Cu composite, the bands observed at 960 and 570 cm^{-1} signify the Si–O–Ni and Si–O–Cu stretching vibrations, respectively, further demonstrating that silanol groups are effectively involved in the composite formation of metal nanoparticles with SiO_2.

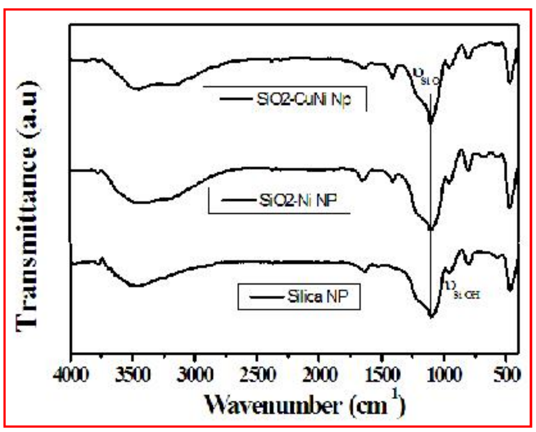

Figure 2- FTIR spectrum of SiO_2, SiO_2 / Ni and SiO_2 / Ni–Cu composites

3.3. MB DYE DEGRADATION EVALUATION STUDIES

The photocatalytic activities of prepared nanostructures toward MB dye degradation in the presence of H_2O_2 under solar light irradiation were monitored by using UV-*Vis* spectroscopy and the results are shown in **Fig.3**. The photocatalytic decomposition of MB was calculated by using the formula:

$$\% \text{ of degradation} = \left(\frac{Co - Ct}{Co}\right) \times 100$$

where C_o is the initial MB concentration and C_t is the concentration of MB at time t. The characteristic SPR bands of MB were located at 664 and 614 nm, which are attributed to the n-π* and 0-1 vibration transitions, respectively. The aforementioned significant SPR bands of MB dye were gradually decreased upon the addition of H_2O_2 as evidenced from the absorption intensity values. The dissociation of H_2O_2 under the sun light generated free hydroxyl ($^{\cdot}OH$) radicals, which attacked the MB framework at different sites including unsaturation points and initiated the MB dye degradation.

$$H_2O_2 + h\gamma \longrightarrow 2\,^{\cdot}OH$$

Although MB was degraded by H_2O_2, the observed degradation rate was found to be minimum (49.1 %) (Fig. 4a) with the minimal decolorization, which urges the need for the exploration of catalytically active nanostructures to enhance the degradation rate.

Hence, SiO_2 nanostructure was employed as an active catalyst for the degradation of MB dye and the degradation rate was increased to 60.3 % (Fig.4b). The existence of OH groups over the surface of SiO_2 nanostructures effectively interacted with cationic MB through the electrostatic interaction and hydrogen bonding, which enhanced the effective adsorption of MB dye. However, the degradation process was limited in SiO_2 nanostructures. This limitation was tackled with the aid of SiO_2/Ni catalyst, wherein the degradation rate was significantly improved to 65,4% (Fig.4c). The enhancement in the photocatalytic performance is associated with the visible light responsiveness of peroxidise behaviour of Ni in the SiO_2/Ni composite. But SiO_2/Ni nanostructures suffer with high agglomeration in an aqueous medium and limited electrical conductivity, which restricted its MB degradation rate.

The aforementioned significant limitations were effectively trounced by SiO_2/Ni–Cu composite. The improvement of the photocatalytic activity can be suggested to enhance the charge separation derived from the coupling of the Ni-Cu nanoalloy and SiO_2 nanoparticles. Two advantages, extending the photoresponse of large bandgap SiO_2 and effectively separating the photogenerated electrons and holes, exist in this system. The small energy levels of the conduction and valence bands allow the Ni-Cu alloy to act as visible-light sensitizers for nano- SiO_2 in the degradation of MB and gave rise to the 92.7% of degradation (Fig. 4d). In addition, Ni-Cu alloys are favorable for photogenerated electrons from SiO_2, which hinders the recombination of photogenerated electrons and holes. Thus, pure SiO_2 and SiO_2/Ni only exhibits weak visible light photocatalytic activity, but the photoresponse could be extended into the visible region after coupling with Ni-Cu.

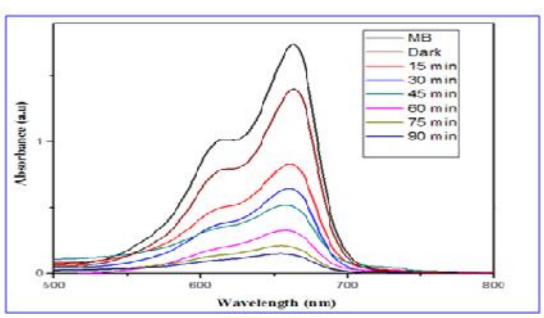

Figure 3- UV–Vis spectra of MB degradation process influenced by SiO_2/Ni-Cu observed at a time interval of 15 min

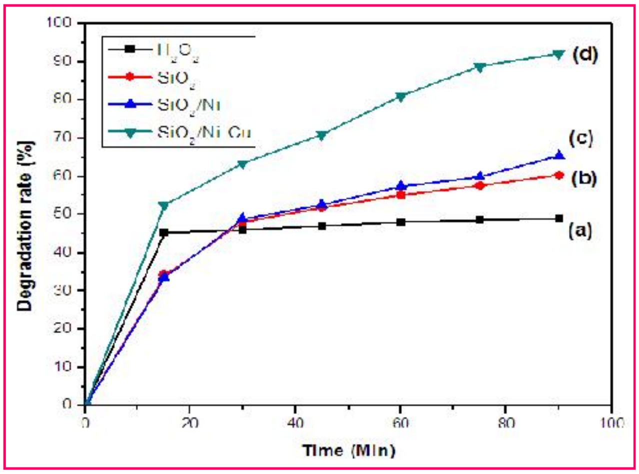

Figure 4- The effect of ((a) H_2O_2 and H_2O_2 mediated (b) SiO_2 nanoparticles, (c) SiO_2/Ni and (d) SiO_2/Ni-Cu on the degradation of MB dye as a function of time

CONCLUSION

SiO_2/Ni-Cu Nanocomposite with large surface area and pore volume were synthesised using a simple and effective chemical method. The XRD patterns revealed the highly crystalline nature of the prepared samples. Owing to the larger surface area, extended catalytic active sites and the synergic effects, SiO_2/Ni-Cu exhibited a faster degradation rate (92.7%) toward MB dye degradation under the identical conditions. Thus the proposed research strategy has not only widened the scope of preparing the SiO_2 supported Ni-Cu alloy material but has also explored their applications in dye degradation technology with the time and cost efficient path way.

ACKNOWLEDGEMENT

The authors are thankful to their respective management, Principal, G.T.N. Arts College, Dindigul, Tamil Nadu, India for providing the required facilities for completion of the work.

REFERENCES

[1]. C. P. Poole, Jr. and F. J. Owens, Introduction to Nanotechnology, Wiley, 2003.
[2]. H. Bonnemann and F. J. M. Richards, Eur. J. Inorg. Chem., 2001, 2455.
[3]. C. M. Niemeyer, Angew. Chem. Int. Ed., , 40 (2001) 4129.
[4]. A.M. Smith and S. Nie, Analyst, 129 (2004) 672.
[5]. C.R. Martin, Acc. Chem. Res., , 28 (1995) 61.
[6]. Reach, G.; Wilson, G. S. Anal. Chem. 64 (1992) 381A.
[7]. Wang, J. Electroanalysis 13 (2001) 983.
[8]. Clark, L., Jr.; Lyons, C. Ann. NY Acad. Sci. 102 (1962) 29.
[9]. Guimon, C.; Auroux, A.; Romero, E.; Monzon, A. Appl. Catal., A251 (2003) 199−214.
[10]. Choudary, V. R.; Rajput, A. M. J. Catal. 139 (1993) 326−328.
[11]. Burattin, P.; Che, M.; Louis, C. J. Phys. Chem. B 103 (1999) 6171−6178.
[12]. Sivaiah, M. V.; Petit, S.; Barrault, J.; Batiot-Dupeyrat, C. Valange, S. Cat. Today 157 (2010) 397−403.
[13]. Sivaiah, M. V.; Petit, S.; Beaufort, M. F.; Eyidi, D.; Barrault, J. Batiot-Dupeyrat, C.; Valange, S. Microporous Mesoporous Mater.140 (2011) 69−80.
[14]. Owens, L.; Tillotson, T. M.; Hair, L. M. J. Non-Cryst. Solids 186 (1995) 177−183.
[15]. Tkachenko, O. P.; Klementiev, K. V.; van den Berg, M. W. E.; Gies, H.; Grünert,

W. Phys. Chem. Chem. Phys. 8 (2006) 1539−1549.
[16]. Tkachenko, O. P.; Klementiev, K. V.; Koc, N.; Yu, X.; Bandyopadhyay, M.; Grabowski, S.; Gies, H.; Grünert, W. Stud. Surf. Sci. Catal. 154 (2004) 1670−1678.
[17]. Tu, C. H.; Wang, A. Q.; Zheng, M. Y.; Wang, X. D.; Zhang, T.Appl. Catal., A 297 (2006) 40−47.