



Chemical Synthesis and Characterization of Ni/Cu Metal Doped Silica Nanosphere Composites and Its Application in Hazardous Textile Dye Degradation

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ARTICLE DETAILS

Article history:

Received 16 January 2017

Accepted 01 May 2017

Available online 24 July 2017

Keywords:

SiO₂/Ni-Cu Nanocomposite
Methylene Blue Dye
Spectral Analysis

ABSTRACT

The research and development of nanomaterial and the nanotechnology fields have been greatly improved by the fabrication of Nano devices and their unique properties of nanomaterial. Silica nanoparticles and their composites (SiO₂/Ni and SiO₂/Ni-Cu) were synthesized using simple chemical phase method and their morphological and structural characterizations were evaluated by scanning electron microscopy (SEM), energy dispersive x-ray diffraction (EDAX), X-ray diffraction (XRD), Fourier transform infra-red (FTIR) spectroscopy techniques. The photo catalytic behaviour of prepared nanostructure toward Methylene blue dye in the presence of solar light was evaluated using UV-Vis spectrophotometer. It has been found that the SiO₂/Ni-Cu catalyst exhibited superior degradation ability over SiO₂/Ni nanoparticles. Thus the proposed effort has not only provided a simple approach to synthesize the SiO₂ based composites but also the effective and economically viable approach for the complete degradation of hazardous organic dye.

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 (SiO₂) 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 SiO₂ as an effective catalyst in photocatalytic application [9-11]. However, SiO₂ 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. Experimental Methods

2.1 Materials

Ethanol, ammonia, tetra ethyl ortho silicate (TEOS), nickel chloride hexahydrate (NiCl₂·6H₂O), copper chloride (CuCl₂) 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 (SiO₂/Ni and SiO₂/Ni-Cu).

2.2. Preparation of Silica Nanoparticles

The silica nanoparticles and their composites (SiO₂/Ni and SiO₂/Ni-Cu) and photocatalytic activity were synthesized by using the following flow charts Figs. 1-4.



Fig. 1 Preparation of silica nanoparticles

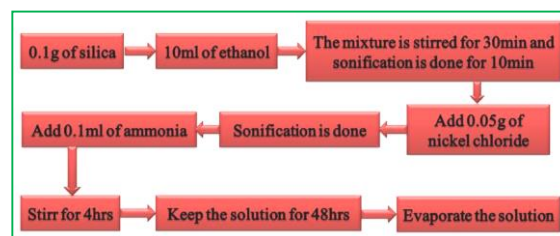


Fig. 2 Preparation of nickel doped silica nanoparticles

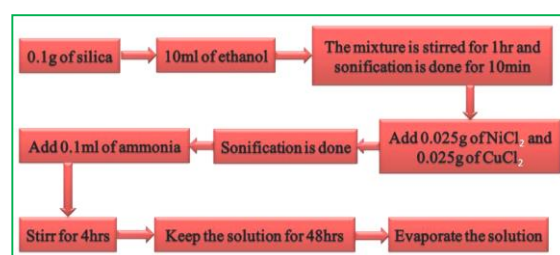


Fig. 3 Preparation of nickel – copper doped silica nanoparticles

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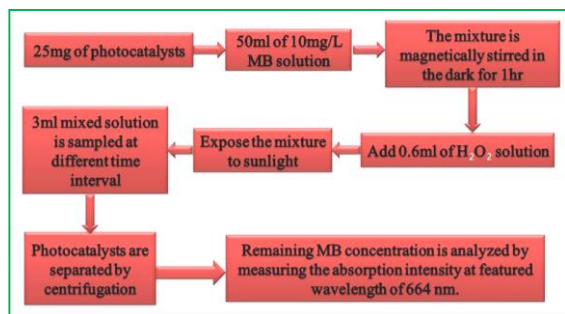


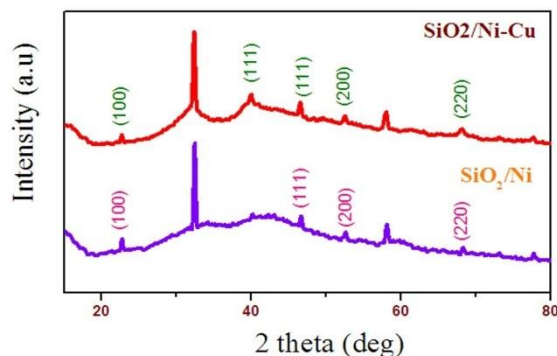
Fig. 4 Photocatalytic activity evaluations

3. Results and Discussion

3.1 XRD Pattern

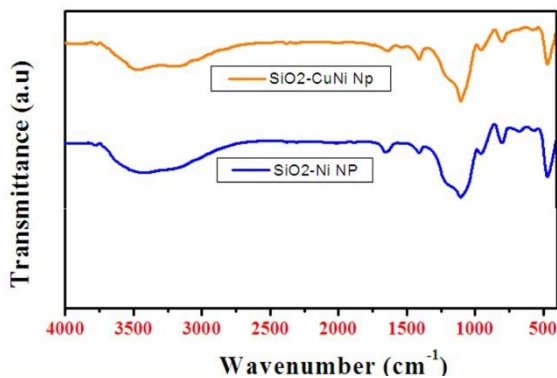
The XRD patterns of as-synthesized SiO_2/Ni and $\text{SiO}_2/\text{Ni-Cu}$ nanostructures are depicted in Fig. 5. The sharp peak found at 24.08° , which is related to the (100) reflection plane of SiO_2 . In addition to the characteristic broad peaks at $46.6, 52.4, 68.2^\circ$ corresponding (111), (200) and (220) planes indicate the presence of Ni in the prepared SiO_2/Ni nanostructures.

$\text{SiO}_2/\text{Ni-Cu}$ 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° is confirm the presence of Cu in the prepared $\text{SiO}_2/\text{Ni-Cu}$ composite.

Fig. 5 XRD patterns of SiO_2/Ni and $\text{SiO}_2/\text{Ni-Cu}$ composites

3.2 FT-IR Studies

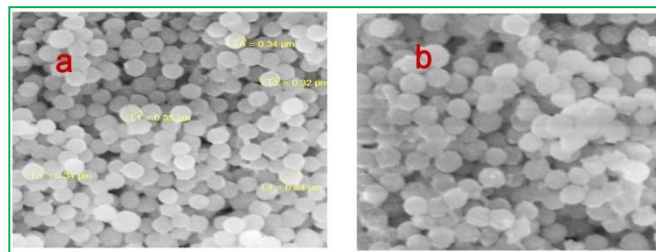
The FT-IR spectra of SiO_2 , SiO_2/Ni and $\text{SiO}_2/\text{Ni-Cu}$ are provided in Fig. 6. SiO_2 exhibited a broad band at 3447 cm^{-1} , which is attributed to the stretching vibration of Si-OH groups. The Si-O-Si symmetric stretching and Si-O bending vibrations of SiO_2 were observed at 1098 and 800 cm^{-1} , respectively. For the $\text{SiO}_2/\text{Ni-Cu}$ 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 .

Fig. 6 FTIR spectrum of SiO_2/Ni and $\text{SiO}_2/\text{Ni-Cu}$ composites

3.3 Morphological Properties (SEM)

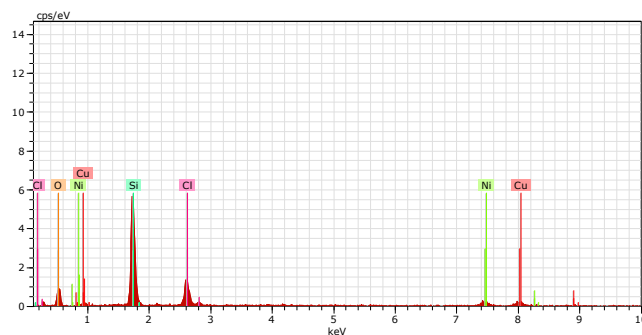
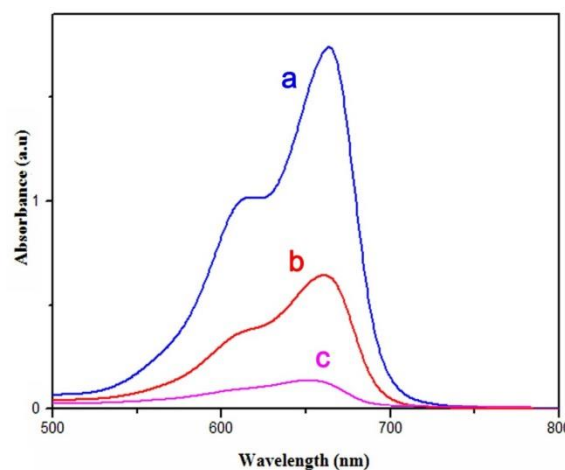
The morphological features of prepared nanostructures elucidated by using SEM are depicted in Figs 3(a&b). The monodispersed, well separated and spherical shaped SiO_2/Ni nanoparticles with smooth surface were obtained under chemical phase route and the average diameter of obtained spheres is in the range of 350 nm (Fig. 7a). The morphological

images of $\text{SiO}_2/\text{Ni-Cu}$ composite clearly demonstrated that tiny particles Cu deposited on spherical SiO_2/Ni particles without any obvious aggregation (Fig. 7b). The size of the spherical structure almost remain same as SiO_2/Ni denoting the presence of Cu has not influenced any morphological change in the composite. The addition of NiCl_2 and CuCl_2 to the negatively charged SiO_2 matrices, produces intermediate (Si-O-Ni²⁺ and Si-O-Cu²⁺ and) bonds through electrostatic interactions, and the subsequent addition of ammonia leads to the reduction of Ni²⁺ and Cu²⁺ to Ni⁰ and Cu⁰ respectively. From Figures it is clear that Ni and Cu nanoparticles were effectively embedded in the SiO_2 pore channels, and no other scattered particles were found outside of the channels, indicating the strong interaction between the Ni-Cu nanoparticles and the porous SiO_2 matrix.

Fig. 7 SEM images of SiO_2/Ni (a) and $\text{SiO}_2/\text{Ni-Cu}$ (b) composites

3.4 EDAX Patterns

The EDAX patterns of prepared nanostructures are depicted in Fig 4. The prepared $\text{SiO}_2/\text{Ni-Cu}$ nano composite was composed of Si (33.79%), O (44.47%), Ni (5.64%) and Cu (6.20%) element, ensuring the formation $\text{SiO}_2/\text{Ni-Cu}$ product. There is a small amount of Cl ions as impurity in $\text{SiO}_2/\text{Ni-Cu}$ nanoparticles.

Fig. 8 EDAX spectra of $\text{SiO}_2/\text{Ni-Cu}$ compositeFig. 9 UV-Vis spectra (a) Methylene Blue (MB) UV-Vis spectra of MB degradation process influenced by (b) SiO_2/Ni Nano Composite (c) $\text{SiO}_2/\text{Ni-Cu}$ Nano Composite.

3.5 MB Degradation Evaluation Studies

The photocatalytic activities of prepared nanostructures toward MB dye degradation in the presence of prepared nano composite under solar light irradiation were monitored by using UV-Vis spectroscopy and the results are shown in Figs. 9a-c. The photocatalytic decomposition of MB was calculated by using the formula:

$$\% \text{ of degradation} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100$$

where C_0 is the initial MB concentration and C_t is the concentration of MB at time t (90min). The characteristic of MB were located at 664 and 614 nm (Fig. 9a).

MB was degraded by SiO₂/Ni Composite, the observed degradation rate at the end of 90 min was found to be minimum (65.4%) with the minimal decolorization (Fig. 9b).

SiO₂ /Ni-Cu nanostructure was employed as an active catalyst for the degradation of MB dye and the degradation rate was increased to 92.7% (Fig. 9c).

4. Conclusion

SiO₂/Ni and SiO₂/Ni-Cu were synthesised using a simple and effective chemical method. The morphological characterizations revealed that the SiO₂/Ni and SiO₂/Ni-Cu nanocomposites composed of spherical structure with Cu nanoparticle impinged on it. 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, SiO₂/Ni-Cu exhibited a faster degradation rate toward MB dye degradation in comparison with SiO₂/Ni nanostructures under the identical conditions. Thus the proposed research strategy has not only widened the scope of preparing the SiO₂ 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 The Principal, Head of the Department of Chemistry and my guide, M.V. Muthiah Government Arts College for Women, Dindigul Tamil Nadu, India for providing the required facilities for completion of the work.

References

- [1] C.P. Poole Jr, F.J. Owens, Introduction to nanotechnology, John Wiley & Sons, Inc., Hoboken, New Jersey, Canada, 2003.
- [2] H. Bonnemant, R.M. Richards, Nanoscopic metal particles– synthetic methods and potential applications, *Eur. J. Inorg. Chem.* 10 (2001) 2455-2480.
- [3] C.M. Niemeyer, Nanoparticles, proteins, and nucleic acids: biotechnology meets materials science, *Angew. Chem. Int. Ed.* 40 (2001) 4128-4158.
- [4] A.M. Smith, S. Nie, Chemical analysis and cellular imaging with quantum dots, *Analyst* 129 (2004) 672-677.
- [5] C.R. Martin, Template synthesis of electronically conductive polymer nanostructures, *Acc. Chem. Res.* 28 (1995) 61-68.
- [6] G. Reach, G.S. Wilson, Can continuous glucose monitoring be used for the treatment of diabetes?, *Anal. Chem.* 64 (1992) 381A-386A.
- [7] J. Wang, Glucose Biosensors: 40 Years of advances and challenges, *Electroanal.* 13 (2001) 983-988.
- [8] L.C. Jr Clark, C. Lyons, Electrode systems for continuous monitoring in cardiovascular surgery, *Ann. NY Acad. Sci.* 102 (1962) 29-45.
- [9] C. Guimon, A. Auroux, E. Romero, A. Monzon, Acetylene hydrogenation over Ni-Si-Al mixed oxides prepared by sol-gel technique, *Appl. Catal. A: Gen.* 251 (2003) 199-214.
- [10] V.R. Choudhary, A.M. Rajput, B. Prabhakar, Nonequilibrium oxidative conversion of methane to CO and H₂ with high selectivity and productivity over Ni/Al₂O₃ at low temperatures, *J. Catal.* 139 (1993) 326-328.
- [11] P. Burattin, P.M. Che, M.C. Louis, Metal particle size in Ni/SiO₂ materials prepared by deposition-precipitation: influence of the nature of the Ni(II) phase and of its interaction with the support, *J. Phys. Chem. B* 103 (1999) 6171-6178.
- [12] M.V. Sivaiah, S. Petit, J. Barrault, C. Batiot-Dupeyrat, S. Valange, CO₂ reforming of CH₄ over Ni-containing phyllosilicates as catalyst precursors, *Cat. Today* 157 (2010) 397-403.
- [13] M.V. Sivaiah, S. Petit, M.F. Beaufort, D. Eyidi, J. Barrault, C. Batiot-Dupeyrat, S. Valange, Nickel based catalysts derived from hydrothermally synthesized 1:1 and 2:1 phyllosilicates as precursors for carbon dioxide reforming of methane, *Microporous Mesoporous Mater.* 140 (2011) 69-80.
- [14] L. Owens, T.M. Tillotson, L.M. Hair, Characterization of vanadium/silica and copper/silica aerogel catalysts, *J. Non-Cryst. Solids* 186 (1995) 177-183.
- [15] O.P. Tkachenko, K.V. Klementiev, M.W.E. Van den Berg, H. Gies, W. Grünert, The reduction of copper in porous matrices—the role of electrostatic stabilization, *Phys. Chem. Chem. Phys.* 8 (2006) 1539-1549.
- [16] O.P. Tkachenko, K.V. Klementiev, N. Koc, X. Yu, M. Bandyopadhyay, et al., The reduction of copper in porous matrices, *Stud. Surf. Sci. Catal.* 154 (2004) 1670-1678.
- [17] C.H. Tu, A.Q. Wang, M.Y. Zheng, X.D. Wang, T. Zhang, Factors influencing the catalytic activity of SBA-15-supported copper nanoparticles in CO oxidation, *Appl. Catal. A: Gen.* 297 (2006) 40-47.