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Effects of NiTiO₃ nanoparticles supported by mesoporous MCM-41 on photoreduction of methylene blue under UV and visible light irradiation

M.S. Sadjadi^{a,*}, M. Mozaffari^a, M. Enhessari^a, K. Zare^{a,b}

^a Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
^b Department of Chemistry, University of Shahid Beheshti, Eveen, Tehran, Iran

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ABSTRACT

In this work, we report the synthesis of nickel titanate nanoparticles loaded on nanomesoporous MCM-41 nanoparticles to determine the effect of MCM-41 nanoparticles on the photocatalytic activities of nickel titanate (NiTiO₃) nanoparticles by using simple solid-state dispersion (SSD) method. Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and UV–Vis diffuse reflectance spectra (DRS) analysis were used to characterize the size and morphology of the obtained nanocomposite. The photocatalytic activity (PA) of the as-prepared NiTiO₃ loaded on MCM-41 was evaluated by degradation of the methylene blue under irradiation of UV and visible light. The results showed that NiTiO₃ loaded on nanosize MCM-41 has higher photocatalytic activity than that of NiTiO₃ nanoparticles.

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1. Introduction

Various industries such as textiles, paint and varnishes, ink, plastics, pulp and paper and cosmetics use different types of organic dyes and dye intermediates. However, such colored dye effluents pose a major threat to the surrounding ecosystem. Some of the dyes are extremely toxic [1]. Dye effluents can be treated by biological methods, flocculation, reverse osmosis, adsorption on activated charcoal, chemical oxidation methods and advanced oxidation processes [2]. Biological methods have been proved to be ineffective [3–5]. Flocculation, reverse osmosis and adsorption methods transfer

* Corresponding author. Tel.: +98 2122285032. E-mail address: msadjad@gmail.com (M.S. Sadjadi).

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the pollutants to other media, thus causing secondary pollution [6,7]. Chemical oxidation methods are not cost effective [8]. Hence there is considerable current interest in developing attractive and more cost-effective methods. Semiconductor heterogeneous photocatalysis is well reported in the photodegradation of organic of pollutants. Many semiconductor oxides like TiO₂, Fe₂O₃, ZnO, ZrO₂, Nb₂O₅, WO₃, Bi₂O₃, SnO₂, etc. have been employed as photocatalysts in the wastewater treatment, organic synthesis and water splitting reactions [9–13]. When semiconductors are illuminated with light of an appropriate wavelength they become powerful oxidants and convert most of the organic molecules into carbon dioxide and water. Recent studies have demonstrated that heterogeneous photocatalysis using TiO₂ as photocatalyst appears as the most emerging destructive technology [14]. But, large band gap energy (3.2 eV) for anatase TiO₂ (excitation wavelength <387.5 nm) limits its practical application under the condition of natural solar light [15].

To develop more solar light efficient catalysts, it is very urgent to develop photocatalytic systems which are able to operate effectively under visible light irradiation. Recently, it has been reported that mesoporous (MCM-41), microporous β -zeolite and pillared structure (montmorillonite) supported TiO₂ exhibited good photodegradation efficiency of orange II under UV light [16]. Support materials with high surface area and good acidic properties adsorb organic pollutants in vicinity to the active sites that results in enhanced photocatalytic degradation rate. Furthermore the photocatalytic efficiency is also improved by decreasing the electron-hole recombination, facilitating the interfacial charge transfer from the surface of the photocatalyst to the substrate. The metal titanates based oxides including metals such as nickel, cobalt, ferrite, zinc, copper and lead are universally known as inorganic functional materials with wide applications. These compounds with ilmenite structure in trigonal system are important as chemical and electrical materials due to their weak magnetism and semiconductivity [17,18]. NiTiO₃ belong to the ilmenite structure. Ni and Ti atoms both prefer octahedral coordination with alternating cation layers occupied by Ni and Ti alone [19]. Since NiTiO₃ samples are heavily colored, the reflection spectra were dominated by the broad intense absorption in the visible region around 600 nm and have the band gap energy of 3.02 eV which may be suitable for photocatalysis shift to visible region.

In this work, nanosized MCM-41 was firstly synthesized and used then as a support to disperse NiTiO₃ photocatalyst and the formed nanocomposite is showing enhanced activity. The structure activity correlation of NiTiO₃ and NiTiO₃/MCM-41 catalysts is well discussed in the present investigation. The results obtained from XRD, TEM, UV–Vis and Brunauer–Emmert–Teller (BET) experiments are reported.

2. Experimental

2.1. Preparation of NiTiO₃/MCM-41 photocatalysts

Sodium silicate solution (25.5-28.5 wt% SiO₂ and 7.5-8.5 wt% Na₂O, MERK), cetyltrimethylammonium bromide (CTAB, 99%, BDH), acetic acid glacial (100%, analytical regent grade), nickel stearate, tetrabutyl titanate, and stearic acid used in this work, all were of analytical grade.

Mesoporous MCM-41 silica, was synthesized using a gel mixture with a composition of $4SiO_2$:1CTAB:250 H₂O. In this purpose, a required amount of the CTAB was dissolved in an appropriate amount of water and sodium silicate solution slowly and stirred for 30 min. pH of the mixture was now adjusted to 10 by adding acetic acid and the gel obtained was put in a polypropylene bottle and refluxed at 100 °C for 24 h. After cooling and adjusting the pH at 10 with acetic acid the mixture was refluxed again for 24 h at 100 °C. The pH adjustment and subsequently heating operations were repeated several times for 5 days and resulted gel was filtered and washed with distilled water and dried in an oven to obtain a white MCM-41 nanopowders.

NiTiO₃ nanoparticles were prepared by a modified wet-chemistry synthesis method which is described in the literature [20]. In this way, an amount of stearic acid was first melted in a beaker at 80 °C, and added by appropriate amount of nickel stearate to form a transparent green solution. This solution was then stirred after addition of required amount of tetrabutyl titanate, to form a homogeneous light green solution. Slowly cooling down to room temperature and drying in an oven



Fig. 1A. Low angle XRD patterns of (a) MCM-41 (b) NTM-1 (c) NTM-2 (d) NTM-3.

at 120 °C for 24 h gives rise to a dried gel and subsequently calcined in air at 750 °C for 2 h (increasing the temperature at 5 °C/min) gives nickel titanate nanoparticles.

NiTiO₃/MCM-41 nanocomposite systems were finally prepared via simple solid-state dispersion (SSD) method by mixing different amounts of NiTiO₃ nanoparticles (5, 10 and 15 wt%) with required nanosized mesoporous MCM-41 in a minimum quantity of n-butyl alcohol. The mixture was dried in an oven at 100 °C overnight followed by calcination at 750 °C for 2 h. The products were named NTM-1, NTM-2 and NTM-3, respectively.



Fig. 1B. Wide angle XRD patterns of (a) NTM-1 (b) NTM-2 (c) NTM-3.

2.2. Structural characterization

Powder X-ray diffraction patterns of the samples were recorded using a Bruker Advance D8 Diffractometer with Cu K_{α} radiation ($\lambda = 0.154$ nm). The FT-IR spectra were recorded using a Perkin Elmer FT-IR spectrometer by employing KBr pellet technique. Specific surface areas and pore size distribution were measured by BET techniques in liquid N2 temperature. The UV–Vis diffuse reflectance spectroscopy (DRS) was performed on a Varian Cary 500 with BaSO₄ as a reference. The TEM measurements were performed on a Philips CM 200 FEG/HRTEM (high resolution transmission electron microscope) instrument operated at 200 kV.

2.3. Measurement of photocatalytic activity

Photocatalytic activity of the prepared materials was evaluated for degradation of Methylene Blue (MB) as a model compound. The photoreaction was carried out in a 100 ml pyrex vessel which is

positioned at 10 cm under a high pressure mercury UV lamp (125 W, 254–365 nm) and a blue light emitting diode (LED) bulb (1 W, 400–500 nm) as UV and visible-light sources respectively. In a typical experiment, 0.1 g of the samples were suspended in 100 ml of the MB solution (6.74×10^{-6} M) and magnetically stirred for 30 min in the darkness to reach to the maximum absorbance equilibrium. Then, the lamp was switched on to initiate the illumination. During illumination, the suspension was stirred at 600 rpm at 25 °C. The residual MB in the solution was analyzed by checking absorbance at 664 nm with a UV–Vis spectrophotometer (Perkin Elmer Lambda 25).

3. Results and discussion

3.1. Structural characterization

Fig. 1A represents low angle X-ray diffraction patterns of the calcined MCM-41(a) and prepared nanocomposite samples of NTM-1(b), NTM-2(c) and NTM-3(d). While the wide angle X-ray patterns for the prepared NTM-1(b), NTM-2(c) and NTM-3(d) nanocomposites are shown in Fig. 1B. The very intense peak appeared at low angle ($2\theta = 2.55$) on the Fig. 1A(a) is assigned to reflections at (100) and two other additional picks with low intensities at (110) and (200) reflections indicate to the regular pore structure of MCM-41, and can be attributed to quasi-two-dimensional hexagonal lattice of MCM-41 [21]. On dispersing NiTiO₃ over MCM-41, a decrease in the peak intensity of the characteristic (100) plan is predominant while, at the higher NiTiO₃ loadings samples, the peaks of (110) and (200) planes tend to merge with the base line. Decrease in the intensity can be attributed to the pores filling effects that reduce the scattering contrast between the pores and the framework of MCM-41 sample. The wide angle X-ray diffraction patterns ($2\theta = 20-70$), Fig. 1B, show the characteristic peaks appeared at $2\theta = 33.10$, $2\theta = 35.68$ and $2\theta = 53.86$ and confirm the presence of NiTiO₃ loadings indicate agglomeration of the particles at higher loadings. The average grain sizes were determined from X-ray diffraction patterns according to Scherrer's equation [22]:

$D = k\lambda/\beta \cos\theta$

where *D* is the average grain size, *k* is a constant equal to 0.9, λ is the X-ray wavelength equal to 0.15406 nm and β is the half-peak width, It was found that the average grain sizes of MCM-41, NTM-1, NTM-2 and NTM-3 nanopowders determined from Scherrer's equation were 70, 74, 78 and 78 nm, respectively.

Fig. 2 shows the FT-IR spectra of MCM-41, NTM-1, NTM-2 and NTM-3 samples. In the spectrum of the raw MCM-41 (Fig. 2(a)), the broad intense double bands appeared at about 1000–1290 cm⁻¹ is due to asymmetric stretching vibrations of Si–O–Si bridges and the absorption bands observed at 467 and 812 cm⁻¹ is assigned to the asymmetric and symmetric Si–O stretching vibrations [23,24]. On dispersed NiTiO₃ over MCM-41 samples, a new absorption band appeared at about 947–961 cm⁻¹ in comparison with raw MCM-41 spectra can be ascribed to the stretching vibration of Ti–O–Si bridges in similarity to the results reported elsewhere [25,26].

Fig. 3 shows UHTEM images of as-prepared raw MCM-41 and NTM-1 nanoparticles. The ordered hexagonal pore arrangements of these two samples were clearly visible and the pore sizes were estimated in the range of 2.6–3 nm and a thick wall about 1 nm. These figures indicate that the hexagonal mesostructures of MCM-41 has not affected by loading NiTiO₃ nanoparticles. In accordance with these results, specific surface area and pore volume measurements (BET measurements) for all the samples show that the pore volumes of the host mesoporous material, which was 0.92 ml g⁻¹ for MCM-41 was decreased to 0.84, 0.80 and 0.75 ml g⁻¹ for NTM-1, NTM-2 and NTM-3 samples, respectively. Similarly, the specific surface areas of the composite materials were decreased from 815 m² g⁻¹ for MCM-41 to 741, 702 and 675 m² g⁻¹ for NTM-1, NTM-2 and NTM-3 samples, respectively. Decreasing of the volumes of the pores and the specific surface area of these mesoporous materials demonstrate that the guests are located in the channels.

Fig. 4 shows the diffuse reflectance of UV–Vis (DRUV-Vis) absorption spectra of (a) NiTiO₃, (b) NTM-3, (c) NTM-2 and (d) NTM-1. According to the result obtained, raw MCM-41 exhibits almost no absorption in the UV–Vis ranges. But, pure NiTiO₃ shows two absorption edge bands situated at about



Fig. 2. FT-IR spectra of: (a) pure MCM-41 (b) NTM-1 (c) NTM-2 (d) NTM-3.



Fig. 3. Ultra high resolution transmission electron microscopy (UHRTEM) images of (a) MCM-41 (b) NTM-1.

370 nm indicating the optical band gap attributed to the $O^{2-} \rightarrow Ti^{4+}$ charge-transfer interaction. Three other significantly broad absorption peaks appeared at about 420, 480 and 550 can be due to the crystal field splitting spectra of NiTiO₃ [27]. By increase of the loaded amount of NiTiO₃, the intensities of absorption bands increased, and the band edges shifted to the longer wavelength region and shifts towards bulk NiTiO₃ showing that the size quantization effect of the dispersed particles. These results are in accordance with the presence of NiTiO₃ in all the prepared samples.



Fig. 4. DRS UV–Vis spectra of: (a) NiTiO₃; (b) NTM-3; (c) NTM-2 and (d) NTM-1.

3.2. Photoreduction of methylene blue

Without any photocatalysts, MB has been reported to be a photobleached and photodegradable material under visible light irradiation [28]. In order to clarify how the prepared NiTiO₃/MCM-41 nanocomposites behave as photocatalyst for the degradation of MB, the blue LED with the wavelength of 400–500 nm is adapted as the light source to evade the self-photobleaching of MB in the visible light region because, the MB molecules may be photosensitized by the visible light around 664 nm to reduce the intensity of the characteristic absorption peaks. Fig. 5(A) represents the degradation of MB concentration vs. irradiation time for different samples under blue LED light irradiation and Fig. 5(B) illustrates the change of absorption spectra of MB in aqueous solution, degraded by NTM-3 sample under blue LED light irradiation at the interval time of 30 min. It was found that the decolorization process of MB proceeds with the increasing irradiation time, and the normalized concentration of MB solution decreases. Fig. 6(A) shows the normalized degradation of MB concentration vs. irradiation time for different nanocomposites samples under UV light irradiation. The rapid decrease in the intensity of 664 nm in Fig. 6(B) suggests that the chromophore responsible for characteristic color of MB is breaking down as the irradiation time increases due to the degradation of MB. The small blue shift which could be observed can be attributed to the formation of the demethylated dyes, as were reported by Chihiro Yogi et al. [29]. We note that, the shoulder around 610 nm in the MB aqueous solution is well known to come from a vibrational component (at \sim 610 nm) of the MB monomer electronic band and an absorption peak (at \sim 605 nm) of the MB dimmer [30]. The intensity of this shoulder around 610 nm varies in resemblance to the maximum characteristic peak at 664 nm, and no blue shift was found under the blue LED light irradiation. It is means that only photodegradation of MB occurs under the blue LED light irradiation.

The results obtained from Figs. 5 and 6 show that the photoactivity of the $NiTiO_3/MCM-41$ nanocomposites are considerably depended on the Ni^{2+} doped amounts. The maximum amount of



Fig. 5. (A). The photoreduction of MB over the samples: (a) MCM-41 (b) NiTiO₃ (c) NTM-1 (d) NTM-2 (e) NTM-3 under visible light irradiation. (B) The photoreduction of MB on the NTM-3 nanocomposite under visible light irradiation in the variation of time.

the MB degradation is found for Ni²⁺ doping of 15% (NTM-3). This high photocatalytic activity, in the case can be rationalized by assuming Ni²⁺ dopant serving as shallow trapping sites, preferably for trapping holes in mesoporous MCM-41. Considering that the position of Ni²⁺ is near the valence bond of TiO₂ as calculated by Nishicawa [31]. In this condition Ni²⁺ will change to Ni³⁺ after trapping a hole, and quickly return to Ni²⁺ due to its instability. This kind of shallow trapping can separate the arrival time of e⁻/h⁺ pairs at the surface and greatly reduce their recombination on channel surface of the mesoporous photocatalyst. This can be the main reason for observed high photoreduction properties of the our prepared nanocomposites.

For getting the accurate kinetic data, kinetic experiment was also carried out to assure the absorption equilibrium was reached. It was well-known that photocatalytic oxidation of organic pollutants follows Langmuir–Hinshelwood kinetics [32,33]. This kind of reaction can be represented as follows:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = kt$$

it can be integrated as follows:

$$kt = \ln\left(\frac{C_0}{C}\right)$$



Fig. 6. (A) The photoreduction of MB over the samples: (a) MCM-41 (b) NiTiO₃ (c) NTM-1 (d) NTM-2 (e) NTM-3 under UV light irradiation. (B) The photoreduction of MB on the NTM-3 nanocomposite under UV light irradiation in the variation of time.

where C_0 is the initial concentration of the MB solution and k is the rate constant. The apparent rate constants for our prepared different photocatalysts were calculated and listed in Table 1. It can be clearly seen that the addition of NiTiO₃, significantly improve the photodegradation activity of the MCM-41 under UV and visible irradiations. The catalyst NTM-3, has the highest rate constant of 0.0452 min⁻¹ under UV irradiation. While the highest rate constant for the same NTM-3 catalyst under visible irradiation was 0.0881 h⁻¹. These observed values are much higher than that of NiTiO₃ to be 0.0071 min⁻¹ and 0.0192 h⁻¹ respectively under UV and visible irradiations. We also note that, 100% MCM-41 has the lowest rate constant of 0.0011 min⁻¹ and 0.046 h⁻¹ under UV and visible irradiation.

4. Conclusion

Nanosized NiTiO₃ loaded mesoporous MCM-41 nanoparticles with crystalline framework were prepared by using a simple solid-state dispersion (SSD) method. High angle X-ray diffraction pattern and diffuse reflectance UV–Vis (DRUV–Vis) absorption spectra showed the presence and growth of NiTiO₃ nanoparticles in mesoporous MCM-41. Formation of Ti–O–Si bonds has been proved by FTIR spectra. The photocatalytic activity study of the prepared nanocomposite samples show that the nanosized NiTiO₃ supported on the mesoporous MCM-41 samples comparing to raw NiTiO₃ and MCM-41 is a very active as photocatalyst for effectively degradation of methylene blue. We attributed high

Table 1

Catalyst	$k ({\rm min}^{-1}) { m UV}$	k (h ⁻¹) Visible light
MCM-41	0.0011	0.0046
NiTiO ₃	0.0071	0.0192
NTM-1	0.0189	0.0278
NTM-2	0.0340	0.0863
NTM-3	0.0452	0.0881

The rate constant for degradation of methylene blue over mesoporous MCM-41 nanocomposites loaded with different percent of NiTiO₃ nanoparticles under UV and visible light irradiation compared with MCM-41 and NiTiO₃ nanoparticle.

photoactivity of the prepared nanocomposite samples, beside of the high surface area of its supporting MCM-41, to the existence of Ni²⁺ dopant. Ni²⁺ ions in the NiTiO₃/MCM-41, served as a shallow trapping sites by greatly reducing surface recombination of e^-/h^+ pairs, which has been thought to be the main reason responsible for low activity mesoporous photocatalyst.

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