Preparation, characterization and enhanced photocatalytic activity of Ni$^{2+}$ doped titania under solar light

L. Gomathi Devi*, Nagaraju Kottam, S. Girish Kumar, K. Eraiah Rajashekar

Department of Post Graduate Studies in Chemistry, Central College City Campus, Bangalore University, Bangalore 560001, INDIA

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Abstract: Anatase TiO$_2$ was prepared by sol-gel method through the hydrolysis of TiCl$_4$. Ni$^{2+}$ was doped into the TiO$_2$ matrix in the concentration range of 0.02 to 0.1 at.% and characterized by various analytical techniques. Powder X-ray diffraction revealed only anatase phase for all the samples, while diffuse reflectance spectral studies indicated a red shift in the band gap absorption to the visible region. The photocatalytic activities of these photocatalysts were probed for the degradation of methyl orange under natural solar light. The photocatalyst with optimum doping of 0.08 at.% Ni$^{2+}$, showed enhanced activity, which is attributed to: (i) effective separation of charge carriers and (ii) large red shift in the band gap to visible region. The influence of crystallite size and dopant concentration on the charge carrier trapping - recombination dynamics is investigated.

Keywords: Ni$^{2+}$ doping • Crystallite size • Solar light photocatalysis • Charge carrier trapping-recombination dynamics

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1. Introduction

Wastewater from dyeing processes contains a wide variety of water soluble chemical products that are unsuitable to treat by traditional methods like filtration, carbon adsorption and hypochlorite oxidation. Most of the dyes used in textile industry are highly stable, soluble in water, resistant to chemical oxidation and will have low bio-degradability. Over 100 000 different types of dyes are commercially available [1] and 700 000 tons are produced annually over the world [2]. Nearly 50% of these dyes belong to the azo-category. Azo dyes resist biodegradation by aerobic treatment. However, they can be decolorized by anaerobic treatment leads to the reduction of azo bonds to amines, which are much more carcinogenic than the parent molecule [3-4]. Advanced oxidation processes (AOPs) is widely used, which is based on in situ generation of hydroxyl radicals, a strong oxidizing agent and can oxidize almost all the organic pollutants and mineralize them to CO$_2$, H$_2$O and simple mineral acids. Among various AOPs, TiO$_2$ based photocatalysis is promising technique and extensively used for the degradation of these recalcitrant organic contaminants [5-10]. However, the large band gap of TiO$_2$ (~3.2eV) limits its efficiency under solar light. Further, the high degree of recombination between photogenerated charge carriers limits its overall photocatalytic efficiency. Doping with various transition metal ions is one of the most effective approaches for synthesizing visible light active photocatalysts [11-16]. It has been considered that the metal ions incorporated into TiO$_2$ crystal lattice can modify the electronic properties of TiO$_2$ and extending its light absorption ability to the visible light region. In this regard, the present research focuses on the doping of Ni$^{2+}$ ion into the TiO$_2$ crystal lattice (Ni$^{2+}$-TiO$_2$) and its photocatalytic activity was investigated by the degradation of methyl orange (MO) an azo dye under solar light. The photocatalytic mechanisms for Ni$^{2+}$-TiO$_2$ under solar light were discussed in detail.

* E-mail: gomatidevi_naik@yahoo.co.in
2. Experimental procedure

2.1. Catalyst preparation
Anatase TiO$_2$ is prepared by sol-gel method through the hydrolysis of TiCl$_4$ as mentioned earlier [17]. 25 mL of diluted TiCl$_4$ was taken along with one mL of concentrated H$_2$SO$_4$ and diluted to one liter using double distilled water. Liquor NH$_3$ was added to the solution so as to maintain the solution pH in the range of 7-8. The precipitate was filtered and washed free of chloride and ammonium ions. The precipitate is first oven dried at 100°C for 12 hours and ground in a mortar for about one hour. The powder was then calcined at 550°C for 4.5 hours to get pure anatase TiO$_2$. To the accurately weighed TiO$_2$, a known volume of stock solution of dihydrate NiC$_2$O$_4$ (1.8 g of NiC$_2$O$_4$•2H$_2$O dissolved in 100 mL of water) was added to get the dopant concentration in the range 0.02, 0.06, 0.08, 0.1 at.% and labeled as Ni-1, Ni-2, Ni-3 and Ni-4, respectively, while undoped TiO$_2$ was labeled as Ni-0. For instance, to get dopant concentration of 0.1 at.% - 1 mL of the stock solution was added to 0.624 g of TiO$_2$. The dopant solution and TiO$_2$ mixture was ground in the mortar and oven dried at 120°C for one hour. The process was repeated 3-4 times and the sample was finally calcined at 550°C for 4.5 hours.

2.2. Characterization
Powder X-ray diffraction (PXRD) patterns were obtained for the samples using Philips powder diffractometer PW / 1050 / 70 / 76. The diffraction patterns were recorded at room temperature using CuKα radiation with Ni filter in the 2θ range 5°-60° at a scan rate of 2° per min. To study the light absorption characteristics of the photocatalyst, the Diffuse Reflectance Spectra (DRS) were recorded in the range 200–800 nm. The baseline correction was done using a calibrated sample of BaSO$_4$. The band gap values of photo catalysts were indexed to anatase phase as shown in the Fig. 1. The ionic radius of Ni$^{2+}$ (0.72 Å) is almost similar to that of Ti$^{4+}$ (0.68 Å). Hence, the Ni$^{2+}$ ion can easily substitute Ti$^{4+}$ ion in TiO$_2$ lattice without distorting the phase structure of TiO$_2$. The average crystallite size (D) was calculated in accordance with Scherrer’s formula using full width at half maximum (FWHM) data

\[ D = \frac{k\lambda}{\beta\cos\theta} \]  

where k is the constant (shape factor, about 0.9), λ is the X-ray wavelength (0.15418 nm), β is the full width at half maximum (FWHM) of the diffraction line and θ is the diffraction angle. The values of β and θ are taken for the crystal plane (101) of anatase phase. The crystallite sizes for the Ni$^{2+}$-TiO$_2$ catalysts were found to be 26.3, 23.8, 20.1, 18.9 and 15.1 nm for a dopant concentration of 0.0, 0.02, 0.06, 0.08 and 0.1 at.%, respectively. This result suggests that the Ni$^{2+}$ doping into the TiO$_2$ lattice effectively inhibits the anatase grain growth by providing dissimilar boundaries. The decrease in grain growth can also be attributed to the formation of Ni-O-Ti bond in the photocatalyst.

3. Results and discussion
The PXRD patterns, of all the photocatalysts, were indexed to anatase phase as shown in the Fig. 1. The ionic radius of Ni$^{2+}$ (0.72 Å) is almost similar to that of Ti$^{4+}$ (0.68 Å). Hence, the Ni$^{2+}$ ion can easily substitute Ti$^{4+}$ ion in TiO$_2$ lattice without distorting the phase structure of TiO$_2$. The average crystallite size (D) was calculated in accordance with Scherrer’s formula using full width at half maximum (FWHM) data

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![Figure 1. PXRD pattern of Ni$^{2+}$-TiO$_2$ photocatalysts](image-url)
doped samples, which inhibits the growth of the crystal grains [18,19]. Further, the reduction in crystallite size is proposed to be due to the segregation of dopant cations at the grain boundary. These dopant Ni$^{2+}$ ions can inhibit the grain growth by restricting the direct contact of the grains. The X-ray diffraction peaks of crystal plane (101), (200) and (004) of anatase were selected to determine the lattice parameter of Ni$^{2+}$-TiO$_2$. The lattice parameters are obtained by using the following equations:

\[ d_{(hkl)} = \frac{\lambda}{2\sin \theta} \]  

(2)

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]  

(3)

where \(d_{(hkl)}\) is the distance between crystal planes of (hkl), \(\lambda\) is the wavelength of X-ray used, hkl is the crystal plane indices and \(a\), \(b\), and \(c\) are lattice parameters (in the anatase phase \(a = b \neq c\)). The lattice parameters and the unit cell volume of all the samples are shown in Table 1. Burns et al. reported that Nd$^{3+}$ dopant acts as a substitutional or interstitial impurity by the changes observed in the variation along the c-axis [20]. The author suggested that Nd$^{3+}$ can act as substitutional impurity up to the dopant concentration of 0.1 mol%, for which maximum elongation in the c-axis was observed. For higher dopant concentration (>0.1 mol%), the elongation in c-axis remained almost constant suggesting the incorporation of excess Nd$^{3+}$ ions at the interstitial sites. In the present study, gradual elongation of c-axis with increase in the Ni$^{2+}$ concentration was observed over the entire range of dopant concentration (Fig. 2). This confirms the possibility of incorporation of Ni$^{2+}$ ion substitutionally at Ti$^{4+}$ lattice sites. Since only c-axis is changing, while \(a (= b)\) remains almost constant for the entire range of dopant concentration, it is speculated that Ni$^{2+}$ substitutes Ti$^{4+}$ ion preferentially on the body centered and face centered lattice sites in the anatase structure. The unit cell volume for Ni$^{2+}$-TiO$_2$ samples were almost similar to that of undoped TiO$_2$ owing to the similarity in the ionic sizes of Ni$^{2+}$ with that of Ti$^{4+}$, which inhibits the lattice expansion.

To investigate the optical absorption properties of catalysts, we examined the DRS of TiO$_2$ and Ni$^{2+}$-TiO$_2$ and the band gaps were calculated by Kubelka-Munk plot (Fig. 3 and Table 1). Undoped TiO$_2$ has a strong absorption in the UV-region while Ni$^{2+}$-TiO$_2$ photocatalysts showed significant shift in the band gap absorption to the longer wavelength due to the Ni$^{2+}$ substitution. The electronic transition in the undoped TiO$_2$ arises from the 2p level of oxygen (valence band) to 3d level of titanium (conduction band). In the case of Ni$^{2+}$-TiO$_2$, interband transition arises from the valence band to \(t_{2g}\) level of Ni (3d), since 3d level of Ni is located at the bottom of conduction band (Fig. 4A). The shift in the band gap absorption increased with increase in Ni$^{2+}$ concentration up to 0.08 at.% (468 nm) and a slight decrease was observed for higher dopant concentration ~0.1% (457 nm). It has been proved that transition metal ions present in a suitable oxidation state can additionally introduce d-d transitions in the UV-vis spectra [21]. Hence, the absorption of Ni$^{2+}$-TiO$_2$ catalysts in the visible region is partially attributed to the d-d transition of Ni, similar to that of Fe [22]. SEM analysis showed almost similar morphology for both doped and undoped

### Table 1. Detailed characterization of Ni$^{2+}$ doped titania

| Photocatalyst | Crystallite size (nm) | Lattice parameters (Å$^3$) | Unit cell volume (Å$^3$) | \(\lambda_{\text{max}}\) (nm) | \(E_g\) (eV) | Surface area (m$^2$ g$^{-1}$) |
|---------------|-----------------------|---------------------------|-------------------------|-----------------------------|---------|-----------------------------|
| Ni-0          | 26.3                  | \(a = b = 3.7628\) \(c = 9.5023\) | 135.97                  | 380                         | 3.2     | 18                          |
| Ni-1          | 23.8                  | \(a = b = 3.7632\) \(c = 9.5069\) | 136.06                  | 426                         | 2.9     | 25                          |
| Ni-2          | 20.1                  | \(a = b = 3.7624\) \(c = 9.5131\) | 136.09                  | 454                         | 2.7     | 32                          |
| Ni-3          | 18.9                  | \(a = b = 3.7800\) \(c = 9.5189\) | 136.00                  | 468                         | 2.6     | 40                          |
| Ni-4          | 15.1                  | \(a = b = 3.7800\) \(c = 9.5228\) | 136.06                  | 457                         | 2.7     | 36                          |
samples (Fig. 5) while EDX confirmed the presence of dopant in the TiO$_2$ matrix. The specific surface areas of the doped catalysts were higher than that of undoped TiO$_2$ due to crystallite size and also due to the introduction of additional nucleation sites by the dopant (Table 1).

### 3.1. Influence of dopant concentration and crystallite size on the charge carrier trapping - recombination dynamics

Fig. 6 shows the plot of C/C$_0$ versus time for the degradation of MO using different photocatalysts under solar illumination. Only 5% of the MO was degraded in the presence of undoped TiO$_2$. The large band gap of TiO$_2$ makes it inefficient to absorb photons under solar light resulting in lower activity. Significant enhancement in the degradation rate was observed with Ni$^{2+}$-TiO$_2$ catalysts. The degradation rate increased with increase in the dopant concentration up to 0.08 at.% and a slight decrease was observed for the higher dopant concentration (Table 2). These results suggest that there exists an optimum dopant concentration of Ni$^{2+}$ in the TiO$_2$ lattice, which results in efficient separation of charge carriers. It is well known that the photogenerated hole reacts with surface water to produce hydroxyl radicals, which is a powerful oxidant for the degradation of organic pollutants. The yield of hydroxyl radicals depends upon the competition between oxidation of surface water by the holes and electron-hole recombination.

$$\text{TiO}_2 + h\nu \rightarrow e^- + h^+ \quad (4)$$

$$h^+ + \text{H}_2\text{O}_{ads} \rightarrow \text{OH}^-_{ads} \quad (5)$$

$$e^- + h^+ \rightarrow \text{recombination} \quad (6)$$

Thus, higher activity was observed in the case of Ni$^{2+}$ (0.08 at.%) - TiO$_2$ is attributed to the excess generation of hydroxyl radicals. This enhancement is possible due to the increased separation of charge carriers. At this optimum concentration (0.08 at.%) of Ni$^{2+}$, the surface barriers becomes higher and the space charge region gets extended leading to the efficient separation of electrons and holes due to the large electric field.
Preparation, characterization and enhanced photocatalytic activity of Ni$^{2+}$ doped titania under solar light

experienced by the charge carriers. For higher dopant concentration (0.1%), the space charge region becomes very narrow and the penetration depth of light into TiO$_2$ greatly exceeds the thickness of the space charge layer, which increases the recombination rate of electrons and holes [18]. Hence, there is an optimum concentration of dopant ions to make the thickness of the space charge layer substantially equal to the light penetration depth. The dopant inside the matrix can serve as an electron - hole trap by altering the electron-hole pair recombination through the following process:

\[
\begin{align*}
\text{M}^{n+} + e^{-} & \rightarrow \text{M}^{(n-1)+} \quad \text{electron trap} \quad (7) \\
\text{M}^{n+} + h^{+} & \rightarrow \text{M}^{(n+1)+} \quad \text{hole trap} \quad (8)
\end{align*}
\]

where the energy level of M$^{n+}$/M$^{(n-1)+}$ lies below the conduction band edge and the energy level of M$^{n+}$/M$^{(n+1)+}$ lies above the valence band edge of TiO$_2$ (Fig. 4B).

If Ni$^{2+}$ is assumed to trap an electron, it gets reduced to Ni$^{+}$. The trapped electron may be transferred to an oxygen molecule to form a superoxide radical.

\[
\begin{align*}
\text{Ni}^{2+} + e^{-} & \rightarrow \text{Ni}^{+} \quad (9) \\
\text{Ni}^{+} + \text{O}_2^{ads} & \rightarrow \text{Ni}^{2+} + \text{O}_2^{-} \quad (10)
\end{align*}
\]

Other possible mechanism is where Ni$^{+}$ can trap valence band holes and oxidize to Ni$^{2+}$.

\[
\begin{align*}
\text{Ni}^{+} + h^{+} & \rightarrow \text{Ni}^{2+} \quad (11)
\end{align*}
\]

Alternatively, if Ni$^{2+}$ ions are assumed to behave as the hole trap, they would be oxidized to Ni$^{3+}$. The trapped hole can be transferred to the hydroxyl anion, adsorbed on the surface, forming a hydroxyl radical or it can also be transferred to the adsorbed dye molecule to form a dye anion.

\[
\begin{align*}
\text{Ni}^{2+} + h^{+} & \rightarrow \text{Ni}^{3+} \quad (12) \\
\text{Ni}^{3+} + \text{OH}^{-} & \rightarrow \text{Ni}^{2+} + \text{OH}^{-} \quad (13)
\end{align*}
\]

Figure 5. SEM images of photocatalysts
Ni\textsuperscript{3+} + dye\textsubscript{ads} \rightarrow Ni\textsuperscript{2+} + dye\textsuperscript{+} \hspace{1cm} (14)

Alternatively, Ni\textsuperscript{3+} can trap the conduction band electron and reduce to Ni\textsuperscript{2+}
Ni\textsuperscript{3+} + e\textsuperscript{-} \rightarrow Ni\textsuperscript{2+} \hspace{1cm} (15)

The above mentioned mechanism enhances the interfacial charge transfer process. The detrapped charge carriers efficiently facilitate the generation of highly oxidative free radicals like hydroxyl and super oxide radicals. Therefore, the pre-requisite condition for an effective dopant not only involves the charge carrier trapping but it should also detrap these charges to the surface of the catalyst more efficiently. Beyond the optimal concentration of the dopant (0.08 at.%), the impurity level of the dopant steadily acts as recombination center for photogenerated charge carriers evidently decreasing the photocatalytic activity [23]. As Ni\textsuperscript{2+} can serve as both electron and hole trap, the possibility of trapping both the charge carriers will be high at higher dopant concentration and trapped charges may recombine through quantum tunneling [24]. Moreover, at a high dopant concentration (≥ 0.1 at.%), the charge carriers may be trapped more than once on its way to the surface so that their mobility becomes extremely low and undergoes recombination before it can reach the surface.

Reduction in crystallite size leads to larger surface area that increases available surface active sites, which consequently results in higher photonic efficiency. Further, the smaller crystallite size of the sample reduces the diffusion path length for the charge carriers from the site where they are photogenerated, to the surface site where they react. Reduction in this diffusion path length results in a reduced recombination rate of photogenerated carriers and hence results in greater photocatalytic activity. Hence, enhanced photocatalytic activity is observed for Ni-3. At higher dopant concentration (Ni-4), the crystallite size becomes small (15.1 nm) and most of the charge carriers are generated sufficiently close to the surface. As a result, the photogenerated charge carriers may quickly reach the surface resulting in faster recombination. This is also due to the multiple trapping sites in the sample and lack of driving force to separate the charge carriers [25]. Therefore, there is a need for optimal dopant concentration in the TiO\textsubscript{2} matrix to get effective crystallite size for the highest photocatalytic efficiency. Beyond the optimum dopant concentration, the rate of recombination dominates in accordance with the Eq. 16

\[ K_{rr} \propto \text{exp}\left(-\frac{2R}{a_0}\right) \]  

where \( K_{rr} \) is the rate of recombination, \( R \) is the distance between the trap sites of photogenerated electron and hole pairs, \( a_0 \) is the hydrogenic radius of the wave function for the charge carrier [26]. From the above equation it is clear that beyond optimum concentration of the dopant and with the reduction of distance between trap sites, the rate of recombination increases exponentially leading to the decrease in photocatalytic activity, which is in consistent with the experimental observations.

4. Conclusion

Ni\textsuperscript{2+} ion was doped into TiO\textsubscript{2} matrix and characterized by various analytical techniques. PXRD pattern

Table 2. Rate constant and percentage degradation of MO under solar light using various photocatalysts

| Photocatalysts | \( k^* \) min\textsuperscript{-1} | Percentage degradation |
|---------------|---------------------------------|------------------------|
| Ni-0          | 0.009                           | 5                      |
| Ni-1          | 0.006                           | 30                     |
| Ni-2          | 0.014                           | 54                     |
| Ni-3          | 0.035                           | 100                    |
| Ni-4          | 0.018                           | 68                     |

* First order rate constant is calculated from the plot of –log \( C/C_0 \) versus time.

Figure 6. Plot of \( C/C_0 \) versus time for the degradation of MO using various photocatalysts under solar light.
revealed only anatase phase for all the samples, while DRS studies indicated a red shift in the absorption band gap to the visible region. Ni\textsuperscript{2+} (0.08 at.\%-TiO\textsubscript{2} showed enhanced activity for the degradation of MO under solar light, which is attributed to the effective separation of charge carriers and also to the large shift in the band gap to visible region. The influence of crystallite size and dopant concentration on the charge carrier trapping and recombination dynamics is investigated in detail.

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