Efficient and rapid degradation of Congo red dye with TiO$_2$ based nano-photocatalysts

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Abstract. Degradation of Congo red (CR) dye with TiO$_2$ based nano-photocatalyst (NPC) loaded with Nd$^{3+}$ and Er$^{3+}$ ions is reported. The chemical route of synthesis through co-precipitation/hydrolysis (CPH) was employed to produce NPCs with general composition TiO$_2$[$R_2O_3$]$_x$, {x = 0.1, 0.2; R ≡ Nd, Er} and particle size within 12–16 nm. Photocatalytic degradation under visible light was measured in terms of the percent degradation of CR in 180 min ($C'_{180}$), time taken to degrade to half of the initial CR concentration ($t_{1/2}$) and apparent rate constant ($k_{app}$). For both doping types, values of $C'_{180}$ close to 100% were obtained with $x = 0.2$ NPCs, indicating complete removal of the dye. For the same NPCs, very high values of $k_{app}$ were found; 2.91 × 10$^{-2}$ min$^{-1}$ and 2.36 × 10$^{-2}$ min$^{-1}$, for Nd$^{3+}$ and Er$^{3+}$ loaded NPCs, respectively, suggesting very rapid degradation. Other NPCs with $x = 0.1$, also showed reasonably good and fast degradation of CR. The observations may be attributed to the small particle size of the NPCs. Moreover, from the DRS results it is observed that the addition of Nd$^{3+}$ and Er$^{3+}$ ions apparently introduces intermediate energy levels within the band gap of TiO$_2$. Such new levels seem to support photocatalysis because they act as electron traps leading to effective suppression of the undesired e$^-$/h$^+$ recombination. To some meaningful extent they also facilitate the absorption of visible irradiances required in the process.

1. Introduction
Heterogeneous photocatalysis has been an attractive method since 1970s to treat several pollutants. Titanium oxide (TiO$_2$) has been identified as one of the most effective photocatalyst for the purpose of degradation of pollutants from wastewater. However, it requires expensive UV irradiation for photocatalysis to take place. Utilization of visible light in TiO$_2$ based photocatalysis can make the process of treatment more cost-effective.

Photocatalysis can involve two fundamental processes: photo-excitation and photosensitization. In the first process the electrons from valence band (VB) need to be excited and promoted to the conduction band (CB), thus producing pairs of negative-electron and positive-holes (e$^-$/h$^+$ pairs). Here the energy-gap plays a vital role because it determines the energy required for the process to start. In the second process, an adsorbed pollutant (e.g., dye) molecule gets photo-excited initially leading to an interaction with the catalyst. As a result, electrons of adsorbed molecule are subsequently transferred to the catalyst particle. In this process, the particle-size becomes important because smaller size can offer larger specific area for adsorption. Nevertheless, in both processes the creation of e$^-$/h$^+$ pairs is...
critical, because these particles individually participate in the production of highly active species that eventually destruct the pollutants chemically. Due to the same reason, the recombination of e-/h+ pairs, which depletes significant portion of the electrons and holes produced, needs to be controlled for better photocatalytic efficiency [1-3].

In order to make photocatalysis possible with pure TiO$_2$ under visible light, the 3.2 eV band gap (i.e., cutoff wavelength, $\lambda_{\text{cutoff}} \sim$ 390 nm) needs to be narrowed down. On the other hand, specific surface area of the catalyst, to facilitate enhanced degradation, can be increased through synthesis of smaller particles. However, it should be noted that particles with less than about 10 nm size may impede the degradation, because at this size, (i) the detrimental e-/h+ recombination may become substantially high owing to smaller mean-free-path, and (ii) the band gaps may become wider due to quantum confinement. Both of these effects would result in undesirable blue-shift of $\lambda_{\text{cutoff}}$ away from the visible regions [2,3]. We have found that the most appropriate range of particle size is 10 – 20 nm [2,3].

Our recent investigations have shown that narrowing of band-gap may be of lesser importance than the reduced particle size of the photocatalyst. Moreover, effective control of the unwanted e-/h+ recombination through appropriate doping or mixing may be the key to additional improvement of degradation. In this direction, we have already noted that rare-earth ions could be the most suitable choice as dopants [2] because of their ability to efficiently suppress e-/h+ recombination. Further, because to their unique electronic structure, the rare-earths can possibly modify the band-gap of TiO$_2$ also, such that visible light photocatalysis through photo-excitation is supported. Along these lines, we report in this paper about the photocatalytic activity of TiO$_2$ based nanocomposites loaded with Nd$^{3+}$ and Er$^{3+}$ ions. Some of these materials have produced very rapid degradation of the dye Congo red (CR) with close to 100% removal of the dye.

2. Experimental

2.1. Materials synthesis

Titanium oxide nanocomposites loaded with Nd$^{3+}$ and Er$^{3+}$ ions, i.e., with general formula TiO$_2$[R$_2$O$_3$]$_x$ {x = 0.1, 0.2; R = Nd, Er} were synthesized through the method of co-precipitation/hydrolysis (CPH). The details about sample preparation are reported elsewhere [2,3]. Chemicals used in the process of synthesis were neodymium nitrate (99.9% metal basis), erbium nitrate (99.9% metal basis), isopropanol and titanium(IV)-butoxide [Ti(OBu)$_4$] (97% reagent grade), supplied by Aldrich Chemical Corporations. Ammonium hydroxide was obtained from Shalom Laboratory Supplies and Congo red was procured from E. Merck Co. (Darmstadt, Germany).

2.2. Measurements

Powder X-ray diffraction (XRD) patterns were recorded with Shimadzu D6000 diffractometer (from Shimadzu, Japan) using CuK$\alpha$ radiation ($\lambda = 1.5406$ Å) and transmission electron microscopy (TEM) was carried out on a Philips CM200 TEM instrument (from FEI Co.). Fourier transform infra-red spectroscopy (FTIR) and Raman spectroscopy were carried out on Jasco FTIR 4100 set up (from Jasco) and on inVia Raman microscope (from Renishaw) units, respectively. A source wavelength of 514 nm was used in Raman analysis. The diffused reflectance spectroscopy (DRS) was carried out to record the absorption spectra of the samples using a Varian CARY 5000 UV-VIS-NIR absorption spectrometer (from TNLabs).

Visible-light photocatalytic degradation of CR was carried out on a locally fabricated cost-effective photoreactor. A series of control experiments were performed prior to the actual investigations in order to observe separately the effects of both the photocatalyst and the visible light. First, the absorbance of an experimental solution without any NPC under light irradiation, and then in the dark but with a solution that contained the NPC, were recorded. It was noticed that the catalyst and light alone could not produce any meaningful degradation. Apart from this, the amounts of photocatalyst...
and CR in the experimental solution were also optimized for best results. The step-by-step details about these measurements are already reported elsewhere [3].

Results and Discussion

The XRD results for the NPC samples of TiO$_2$[R$_2$O$_3$]$_x$, \( x = 0.1, 0.2; R \equiv \text{Nd, Er} \) show that most of

Figure 1: XRD plots of the Nd$^{3+}$ and Er$^{3+}$ loaded TiO$_2$ NPC samples.

Figure 2: Typical TEM images of the NPCs: (a) Nd$^{3+}$ and (b) Er$^{3+}$ loaded TiO$_2$ samples (The scale shown is equivalent to 20 nm), and (c) particle-size distribution of all samples.
the peaks are highly broadened [Figure 1], because of the smaller crystallite size of the samples. Nevertheless, the dominating TiO$_2$ phase in all the samples, is confirmed by the presence of the most prominent peak around $2\theta = 25.2^\circ$, which corresponds to the (101) reflection of anatase. Compared to the XRD data for pure anatase however, the slightly shifted peaks of NPC indicate that the rare-earth ions probably occupy the lattice sites. Further, the presence of cubic Er$_2$O$_3$ and hexagonal Nd$_2$O$_3$ phase in the composites is also confirmed. The XRD results also established that overall homogeneity of the composites was maintained and no new phase was formed.

The XRD data was also used to roughly estimate the particle- (crystallite-) size $z$, through Debye-Scherrer equation $[2,3]$:

$$z = \frac{k\lambda}{\beta \cos \theta},$$

where, the shape-factor $k$ was taken as 0.9, assuming spherically symmetric crystallites in the NPCs. For the Nd$^{3+}$ loaded samples, estimated particle size were around 13 and 15 nm, respectively, for $x = 0.1$ and 0.2. The same were estimated for $x = 0.1$ and 0.2, Er$^{3+}$ loaded samples, as 16 and 12 nm, respectively.

Figure 2 (a) and (b) depict the TEM images of the NPCs [shown only for $x = 0.1$ loaded samples], which facilitated the analysis of the crystallinity and morphology of the samples. Mostly spherical and ellipsoidal particles seem to agglomerate into bigger particles forming bulk of the NPCs. Particle size was also measured directly from TEM images using the ImageJ software. Typical distributions of particle size obtained from these pictures are shown in figure 2 (c). Clearly, majority of the NPC particles, i.e., close to 80% or more, have the size within 10 – 15 nm. The size varies from around 8 to 16 nm for Nd$^{3+}$ loaded, and from around 9 to 17 nm for Er$^{3+}$ loaded samples. The mean particle size of around 12 nm and 14 nm for both $x = 0.1$ NPCs was measured respectively for Nd$^{3+}$ and Er$^{3+}$ loaded samples. Similarly, for the $x = 0.2$ doped samples, the average size were found to be nearly 15 and 12 nm, respectively. These values were in good agreement with the size estimated from XRD data. All the estimated and measured particle size are listed in Table 1.

Figures 3 and 4 show the typical Raman and FTIR spectra for the NPCs, respectively. In general, five characteristic peaks around 144, 197, 399, 513 and 639 cm$^{-1}$ are clearly visible in the Raman

![Figure 3: Raman spectra of Nd$^{3+}$ and Er$^{3+}$ loaded TiO$_2$ samples ($x = 0.1$).](image1)

![Figure 4: FTIR spectra of Nd$^{3+}$ and Er$^{3+}$ loaded TiO$_2$ samples ($x = 0.1$).](image2)
profiles obtained with our samples, which may be associated with the anatase TiO$_2$. Usually, the presence of anatase is identified through five distinct Raman peaks at about 151, 196, 409, 515 and 633 cm$^{-1}$, assigned to the $E_g$, $E_g$, $A_1g$ or $B_1g$ and $E_g$ modes, respectively [4,5]. However, the peaks corresponding to $E_g$ and $B_1g$ modes in our Raman spectra are apparently red-shifted to around 144 and 399 cm$^{-1}$, respectively. Such red-shifts may be explained on the basis of a phonon confinement model, and are associated with reduced particle size of the material under consideration [2,4]. This observation is in agreement with the XRD results for all the NPCs. Further, Raman spectroscopy results also indicate suppression of the Ti–O bonds due to loading of rare-earth ions. The FTIR spectra (Figure 4) of pure TiO$_2$, in general, shows multiple peaks in the region 420 cm$^{-1}$ to 550 cm$^{-1}$, which are usually associated with the various characteristic vibrational modes of Ti–O bonds [5]. For loaded NPC samples however, the intense peaks at wavenumber 492 cm$^{-1}$ and 434 cm$^{-1}$ are missing and overall peak intensity is reduced in the FTIR spectra, which indicates that the dopant ions have suppressed the Ti–O bonds. This observation was supported also by Raman spectroscopy results as mentioned earlier. The absence of characteristic vibration modes for Nd and Er and their oxides Nd$_2$O$_3$ and Er$_2$O$_3$ in the Raman and FTIR spectra suggests that there was no segregation of these elements or the oxides in TiO$_2$ matrix. It confirms the homogeneity of the NPC samples. Moreover, both the Raman and FTIR results do not show any new peak corresponding to either R–O or Ti–O bonds.

The UV-vis absorption data obtained from diffused reflectance spectroscopy (DRS), plotted in figure 5 (a), were used to estimate the band-gaps of all the NPC samples using the Tauc’s equation, $\alpha h\nu = A(h\nu - E_g)^n$, with $n = 1/2$, for direct allowed transitions [6]. Figure 5 (b) shows the plots of $(\alpha h\nu)^2$ against $h\nu$. From these plots, the intersection of the tangent to the most linear part of the curve, with energy axis gives the value of energy-gap. Interestingly, the band-gap for all the NPCs loaded with Nd$^{3+}$ and Er$^{3+}$ ions was determined to be 3.35 eV. On the other hand, the band-gap for pure anatase (not shown), following the same method, was estimated to be 3.2 eV. Clearly, the loading of TiO$_2$ with rare-earth ions seems to widen the band-gap, which is opposite to what was initially desired. Widening of band-gap is expected to push the absorption-edge, $\lambda_{\text{cutoff}}$ more towards the shorter

![Figure 5: DRS spectra (a) and the Tauc’s plots obtained from DRS spectra (b) for the TiO$_2$ NPCs loaded with Nd$^{3+}$ and Er$^{3+}$.](image)
wavelengths (UV region) instead of bringing it inside the visible range to facilitate photocatalysis under visible light. However, a careful examination of the original absorption (DRS) spectra [figure 5 (a)] shows some absorption peaks in the visible regions. Among these, the peak at 587 nm for Nd³⁺ doped NCs, and the one at 522 nm for Er³⁺ doped NCs cannot be ignored. The 528 and 587 nm absorption peaks have already been reported and their appearance has been attributed to the formation of intermediate energy levels between the VB and CB of TiO₂ due to the 4f shells of Nd³⁺ ions [7-9]. In the same line, the absorption peaks at 489, 522 and 654 nm observed with Er³⁺ doped NCs may also be associated with the formation of similar energy levels in these composites. Expectedly, these new energy levels in the band-gap of TiO₂ should facilitate both the suppression of e⁻/h⁺ recombination through trapping of electrons, and absorption of visible radiations through effective narrowing of band-gap.

Figure 6 shows the degradation of CR in terms of the relative percentage \( (C/C_0) \times 100 \) with time up to 180 min. One can immediately observe from this figure that in less than about 25 min, all the NPCPs degrade the dye to half of the starting concentration or even more. It clearly indicates that the NPCPs are very fast catalysts. In comparison, the as-received anatase powder (particle size around 57 nm) seems to take more than three hours to reach maximum achievable degradation of CR under the same experimental conditions.

For all the NPCP samples, the rate of degradation was found to be of first order. From a least-square regression of \( \ln(C/C_0) \) vs time data, the apparent rate constant \( k_{obs} \) was estimated. The best

| Sample                          | \( x \) | Particle-size | \( k_{obs} \) | \( t_{1/2} \) | \( C'_{180} \) |
|---------------------------------|--------|--------------|--------------|--------------|--------------|
| CPH TiO₂[Nd₂O₃]x                | 0.1    | 13           | 2.01 (3.58)  | 18           | 97           |
| CPH TiO₂[Er₂O₃]x                | 0.2    | 15           | 2.91 (2.91)  | 16           | 100          |
| CPH TiO₂[Nd₂O₃]x                | 0.1    | 16           | 1.03 (1.70)  | 20           | 90           |
| CPH TiO₂[Er₂O₃]x                | 0.2    | 12           | 2.36 (3.88)  | 11           | 99           |

* The quantities in the brackets in \( k_{obs} \) column are the initial values for apparent rate constants calculated using the first four points (i.e., up to 90 min of degradation).
performing sample in terms of degradation after 180 min \( (C'_{180}) \) was Nd\(^{3+} \) \( (x = 0.2) \) loaded TiO\(_2\) NPC, which degraded close to 100% of the dye \( (C'_{180} = 100\%, k_{obs} = 2.91 \times 10^{-2} \text{ min}^{-1}) \). This performance was only marginally better than the Er\(^{3+} \) \( (x = 0.2) \) loaded TiO\(_2\) NPC for which \( C'_{180} = 99\% \) at \( k_{obs} = 2.36 \times 10^{-2} \text{ min}^{-1} \). The initial rate of degradation (calculated using the first four points only in the graph) however, for this NPC was much higher at 3.88 \( \times \) 10\(^{-2} \) \text{ min}^{-1} \). Because of such high initial rate, this NPC degraded more than half of the initial CR concentration in just about 11 min \( (t_{1/2}) \), and nearly 98% in just one hour. For the \( x = 0.1 \) Nd\(^{3+}\) and Er\(^{3+}\) loaded NPCs, \( C'_{180} \) was found to be 97 and 90%, respectively. For the pure anatase powder, on the other hand, \( C'_{180} \) was only about 80%. The relatively poor performance of the as-received anatase powder may be directly related to the larger average particle size of about 57 nm. However, for the NPCs loaded with Nd\(^{3+}\) and Er\(^{3+}\) ions, not just the smaller size, but a number of other factors too, contribute to the better degradation efficiency. The importance of loading of rare-earth ions and its exclusive contribution to degradation has been critically discussed in some of our earlier reports \[2,3\].

A combination of some crucial intrinsic properties of the composites determines the final degradation results. Most important among these are the particle size and the ability to control \( e^-/h^+ \) recombination. Apart from these two, the sensitivity of the NPCs to visible light also plays a significant role if the loading modifies the band-gap for absorption of the latter. In the \( x = 0.2 \) Er\(^{3+}\) loaded NC, \( C'_{180} = 99\% \) may be due to the smaller average particle size of 12 nm. The \( x = 0.1 \) Er\(^{3+}\) loaded NPC, on the other hand, produced \( C'_{180} = 90\% \), apparently because it had a marginally bigger average particle size of 14 nm. Besides the smaller particle size of the NPC, the loading of Nd\(^{3+}\) and Er\(^{3+}\) ions was also critical because: (i) it helped efficient suppression of \( e^-/h^+ \) recombination; and (ii) it introduced intermediate energy states in the energy gap of the host TiO\(_2\), which may have enhanced the visible light sensitivity of the composites. Intermediate levels may be introduced in semiconductors through doping of rare-earths \[7-9\], which is confirmed from our DRS results as discussed earlier. These intermediate, rare-earth related energy levels may not only act as electron-traps, but they could also facilitate the absorption of visible radiations through indirect narrowing of the band-gap. Upon irradiation with visible light, the electrons produced in the molecules (pollutant) adsorbed on the TiO\(_2\) particles can be captured on these traps, and thus the holes would be left alone to freely participate in the chemical processes leading to degradation (suppression of \( e^-/h^+ \) recombination). Moreover, under the changed scenario, the electrons in the VB of TiO\(_2\) would require less excitation energy, which could possibly be supplied from visible light irradiation, to get transferred to the rare-earth related intermediate energy levels. Thus, the charge-separation necessary for the process may be supported and some additional photocatalytic degradation through photo-excitation may also take place.

Conclusions

We have reported the visible light photocatalytic activity of TiO\(_2\) base nano-photo-composites loaded with Nd\(^{3+}\) and Er\(^{3+}\) ions; TiO\(_2[\text{R}_2\text{O}_3]_x\), \( \{x = 0.1, 0.2; \text{R} = \text{Nd}, \text{Er}\} \), in the degradation of Congo red dye. Close to 100% degradation at a very rapid rate has been produced with both types of NPCs having \( x = 0.2 \). The other two compositions of NPCs with \( x = 0.1 \), also showed reasonably significant degradation of CR. The observations have been attributed to the smaller particle size \( (12 – 16 \text{ nm}) \) of the NPCs. It has been concluded that doping of rare-earth ions further supports photocatalysis through introducing intermediate energy levels in the energy gap of host TiO\(_2\), which may act like efficient electron traps for suppression of the unwanted \( e^-/h^+ \) recombination. At the same time, these energy levels may also narrow down the energy gap indirectly, so that visible light induced photocatalysis through photo-excitation also becomes possible to some extent.
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References

[1] K. Hashimoto, H. Irie, and A. Fujishima, “TiO2 photocatalysis: A historical overview and future prospects,” Jap. J. Appl. Phys., vol. 44 (12), pp. 8269-8285, 2005.
[2] H. Narayan, H. Alemu, L. Macheli, M. Thakurdesai, and T. K. Gundu Rao, “Synthesis and characterization of Y3+-doped TiO2 nanocomposites for photocatalytic applications,” Nanotechnology, vol. 20, 255601 (8 pp), 2009.
[3] H. Narayan, H. Alemu, L. Macheli, M. Sekota, M. Thakurdesai, and T. K. Gundu Rao, “Role of particle size in visible light photocatalysis of Congo red using TiO2[ZnFe2O4]x nanocomposites,” Bull. Mater. Sci., vol. 32 (5), pp.499-506, 2009.
[4] W. F. Zhang, Y. L. He, M. S. Zhang, Z. Yin, Q. Chen, “Raman scattering study on anatase TiO2 nanocrystals,” J. Phys. D: Appl. Phys., vol. 33, pp. 912-916, 2000.
[5] M. J. Šćepanović, M. Grujić-Brojčin, Z. D. Dohčević-Mitrović, Z. V. Popović, “Characterization of anatase TiO2 nanopowder by variable-temperature Raman spectroscopy,” Sci. Sintering, vol. 41, pp. 67-73, 2009.
[6] Anil Tumuluri, K. Lakshun Naidu, K. C. James Raju, “Band gap determination using Tauc’s plot for LiNbO3thin films,” Int. J. Chem. Tech. Res., vol. 6 (6), pp. 3353-3356, 2014.
[7] X. Su, J. Zhao, Y. Li, Y. Zhu, X. Ma, F. Sunb, and Z. Wang, “SolutionSynthesis of Cu2O/TiO2 Core-Shell nanocomposites,” Colloids Surf.-A, vol. 349, 151-155, 2009.
[8] W. F. Zhang, Y. L. He, M. S. Zhang, Z. Yin, and Q. Chen, “Raman scattering study on anatase TiO2 nanocrystals,” J. Phys. D: Appl. Phys., vol. 33, pp. 912-916, 2000.
[9] M. A. J. Klik, T. Gregorkiewicz, I. V. Bradley, and J. P. R. Wells, “Optically induced deexcitation of rare-earth ions in a semiconductor matrix,” Phys. Rev. Lett., vol. 89 (22), 227401 (4 pp), 2002.