Highest photocatalytic activity observed for nanocrystalline anatase-titania having lowest crystallinity

Manu Jose 1, Jatish Kumar 2,3, and Satyajit Shukla 1,a

1 Functional Materials Section (FMS), Materials Science and Technology Division (MSTD), National Institute for Interdisciplinary Science and Technology (NIIST), Council of Scientific and Industrial Research (CSIR), Industrial Estate P.O., Pappanammal Thiruvananthapuram – 695019, Kerala, India
2 Chemical Sciences and Technology Division (CSTD), NIIST-CSIR, Thiruvananthapuram – 695019, Kerala, India
3 Photonic Molecular Science Laboratory, Graduate School of Material Science, Nara Institute of Science and Technology (NAIST), Nara, Japan

Corresponding author: satyajit_shukla@niist.res.in, Phone: +91-471-2515385, Fax: +91-471-2491712

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ABSTRACT: The nanocrystalline anatase-TiO₂, a well-known photocatalyst, has been synthesized via the conventional sol-gel method involving an alkoxide-precursor. The nanocrystalline anatase-TiO₂ has also been processed via the modified sol-gel technique involving the phosphoric acid (H₃PO₄) as an acid-catalyst. The different samples have been characterized using the various analytical techniques such as the transmission electron microscope (TEM), selected-area electron diffraction (SAED), energy dispersive X-ray (EDX), X-ray diffraction (XRD), and Fourier Transform Infrared (FTIR) spectroscop. The relative concentrations of free-hydroxyl radicals (OH⁻) generated by these samples, under the ultraviolet (UV)-radiation exposure, has been qualitatively measured via the OH⁻-trapping experiments using the photoluminescence (PL) spectrophotometer. The photocatalytic activity of different samples has been measured under the UV-radiation exposure using the methylene blue (MB) as a model catalytic dye-agent. The maximum photocatalytic activity has been exhibited by the nanocrystalline anatase-TiO₂ processed via the modified-sol-gel method, which has the lowest crystallinity among all the investigated samples. This has been primarily attributed to the presence of PO₄³⁻ anions on the surface, which help adsorb relatively large amount of MB dye in the dark-condition and subsequently take part in the generation of superoxide ions (O₂⁻), which along with the OH⁻ produced, attack and degrade the surface-adsorbed MB dye. © Global Scientific Publishers 2013

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1. Introduction

The nanocrystalline anatase-titania (TiO₂) is a well-known wide band-gap n-type semiconductor oxide used as a photocatalyst for the removal of organic synthetic-dyes present in the aqueous solutions via the photocatalysis mechanism [1]. The latter process involves suspending the photocatalyst nanoparticles in an aqueous dye-solution and exposing the resulting suspension to the external-radiation such the ultraviolet (UV), visible, or solar which results in the generation of photo-induced electron (e⁻)-hole (h⁺) pairs within the particle, which in turn migrate to the particle-surface to take part in the redox-reactions, generating the hydroxyl-radicals (OH⁻) responsible for the decomposition of surface-adsorbed organic synthetic-dyes.

It has been well established that the various material parameters such as the powder morphology [2], specific surface-area [3-5], average pore size, pore volume and its distribution [3-5], average nanocrystallite size [6], amount of rutile-phase [7], amount and nature of surface-deposited metal / metal oxide nanoparticles [8], and amount and nature of dopants [9] significantly affect the photocatalytic activity of nanocrystalline anatase-TiO₂. In addition to these parameters, the crystallinity of nanocrystalline anatase-TiO₂ is also considered to be one of the most important factors in controlling its photocatalytic activity [3, 4, 10, 11]. In general, the higher the crystallinity of nanocrystalline anatase-TiO₂, the higher the photocatalytic activity, and vice versa. Presently, there is no report in the literature which has shown higher photocatalytic activity for the nanocrystalline anatase-TiO₂ having lower crystallinity. The techniques to enhance the photocatalytic activity of nanocrystalline anatase-TiO₂ having lower crystallinity, which may even surpass that of highly crystalline anatase-TiO₂, are presently unknown.

From this point of view, in the present investigation, we process the nanocrystalline anatase-TiO₂ having both higher and lower crystallinity via the conventional and modified sol-gel methods, and demonstrate for the first time that under the given processing conditions, the photocatalytic activity of nanocrystalline anatase-TiO₂ having lower crystallinity can be higher than that of its highly crystalline form.
2. Experimental Details

Titanium(IV)-isopropanoxide (Ti(OC3H7)4, 97 %), phosphoric acid (H3PO4, 85 wt.%, 99.99 %), and terephthalic acid (TA, 98 %) were purchased from Sigma-Aldrich Chemicals, Bengaluru, India; 2-propanol (99.5 %, ACS reagent), sodium hydroxide (NaOH, Assay 97 %), methylene blue (MB, 96 %) from S.D. Fine-Chem Ltd., Mumbai, India; and nanocrystalline TiO2 (Degussa-P25) having the mixed anatase and rutile phases from Evonik, Mumbai, India. All chemicals and powders were used as received without any further purification and/or modification.

The nanocrystalline anatase-TiO2 powders were synthesized via the conventional sol-gel method involving the hydrolysis and condensation of Ti(OC3H7)4 in 2-propanol. First, measured quantity of water was dissolved in 125 ml of 2-propanol. A second solution was then prepared in which 0.12 M (final concentration) of Ti(OC3H7)4 was dissolved completely in 125 ml of 2-propanol. The ratio of final molar concentrations of water to that of alkoxide-precursor (R) was 90. Both the solutions were sealed immediately and stirred rapidly using a magnetic stirrer (C MAG HS 7, IKA, Germany) to obtain the homogeneous solutions. The water-part of solution was then added drop-wise to the alkoxide-part under the continuous magnetic stirring. After the complete addition of water-part of solution to that of alkoxide-part, the initial solution-pH (Hanna HI 2210 Bench pH Meter, Sigma-Aldrich Labware, Bengaluru, India) was measured to be 7.8. As a result of the hydrolysis and condensation reactions of Ti(OC3H7)4 due to its reaction with water under the continuous magnetic stirring, the color of solution gradually changed from colorless to white. After the complete addition of water-part of solution to that of alkoxide-part, the resulting suspension was stirred overnight before drying in an oven at 80 °C for the complete removal of solvent and residual-water. The dried powders were then calcined at 300, 350, 400 °C for 1 h and 600 °C for 2 h, with the heating rate of 3 °C•min⁻¹, for the crystallization of amorphous-TiO2 powders.

The conventional sol-gel process, as described above, was modified in order to process the nanocrystalline anatase-TiO2 powder using the H3PO4 as an acid-catalyst. For this purpose, the H3PO4 was added to the water-part of solution with the ratio of molar concentration of acid-catalyst to that of alkoxide-precursor equal to 0.11. After the complete addition of water-part of solution to that of alkoxide-part, the initial solution-pH was measured to be 5.9. After obtaining the dried-powder, it was calcined at 600 °C for 2 h, with the heating rate of 3 °C•min⁻¹, for the crystallization of amorphous-TiO2.

The morphology and average nanocrystallite size of different samples were determined using the transmission electron microscope (TEM, Tecnai G², FEI, The Netherlands) operated at 300 kV. The chemical constituents and crystalline nature of different samples were confirmed using the energy dispersive X-ray (EDX) and selected-area electron diffraction (SAED) techniques. The crystalline phases present were determined using the X-ray diffraction (XRD, PW1710 Phillips, The Netherlands). The broad-scan analysis was typically conducted within the 2θ range of 10-80° using the Cu Ka (λKa=1.542 Å) X-radiation. The obtained XRD patterns were then utilized to determine the weight-fraction of anatase-TiO2 (XA) using the equation [1],

\[ X_A = \left[ 1+1.26 \frac{(I_R)}{(I_A)} \right] \]

where, IA and IR represent the linear-intensities of main-peaks of anatase-TiO2 (101)A and rutile-TiO2 (110)R. The surface-chemistry of different samples was analyzed using the Fourier Transform Infrared (FTIR, IRPrestige-21 Shimadzu, Japan) spectroscopy within the frequency range of 4000-400 cm⁻¹ using the powders dispersed in the potassium bromide (KBr) pellets.

The photocatalytic activity was studied by monitoring the degradation of MB dye in an aqueous suspension containing the photocatalyst particles under the continuous ultraviolet (UV)-radiation exposure. A 125 ml of aqueous suspension was prepared by completely dissolving 7.5 μM of MB dye and then dispersing 0.4 g•l⁻¹ of photocatalyst particles under the continuous magnetic stirring. The resulting suspension was equilibrated via stirring in the dark for 1 h to stabilize the adsorption of MB dye over the surface of photocatalyst particles. The stable aqueous suspension was then irradiated with the UV-light, under the continuous magnetic stirring, using a Photoreactor (Luzchem Inc., Canada) containing 16 UVA tubes as the UV-source having the illuminance of 255 lm•m⁻² (lux) and emitting the radiation having the peak-wavelength at ~350 nm. Following the UV-radiation exposure, 8 ml of aqueous suspension was taken out of the UV-chamber after the specific time interval for total 1 h for obtaining the absorption spectra. The photocatalyst particles were separated from the sample suspension using a centrifuge (Hettich EBA 20, Sigma-Aldrich, India) and the filtered solution was then examined using a UV-visible absorption spectrophotometer (UV-2401 PC, Shimadzu, Japan) to study the degradation kinetics of MB dye. The absorption spectra of MB dye solution were obtained within the range of 200-800 nm as a function of UV-radiation exposure time. The intensity of main absorption peak (Aa) of MB dye solution, located at 656 nm, was taken as the measure of residual MB dye concentration (C). The UV-visible absorption spectrum of MB dye solution obtained after stirring the suspension for 1 h in dark was regarded as a reference spectrum corresponding to the initial MB dye concentration, C0, and initial absorbance of A0. The normalized residual concentration of
MB dye was calculated using the relationship of the form,

\[
\left( \frac{C_t}{C_0} \right)_{MB} = \left( \frac{A_t}{A_0} \right)_{656nm}
\]  

(2)

The amount of MB dye adsorbed on the surface of photocatalyst particles after stirring in dark for 1 h was calculated using the relationship of the form,

\[
\left( \frac{C_{60} - C_0}{C_{60}} \right)_{MB} = \left( \frac{A_{60} - A_0}{A_{60}} \right)_{656nm}
\]  

(3)

The experiments for trapping the free hydroxyl-radicals (OH\(^{-}\)), produced under the continuous UV-radiation exposure of photocatalyst particles in an aqueous solution, were performed using the TA. These experiments were similar to the one described above for the photocatalytic measurements except that the MB dye was replaced with 5×10\(^{-4}\) M of TA and 2×10\(^{-3}\) M NaOH [12, 13]. The trapping of free-OH\(^{-}\) by TA results in the formation of 2-hydroxyterephthalic acid, which exhibits a characteristic photoluminescence (PL) peak located at ~423 nm. The PL spectra of 2-hydroxyterephthalic acid, obtained at an excitation wavelength of ~315 nm, were recorded as a function of UV-radiation exposure time using the UV–visible absorption spectrofluorometer. The intensity of PL peak is regarded as the measure of concentration of free-OH\(^{-}\) produced by the photocatalyst particles at a given time under the UV-radiation exposure. The different nanocrystalline anatase-TiO\(_2\) samples processed via the conventional and modified sol-gel methods were tested via the free-OH\(^{-}\) trapping experiments.

3. Results and Discussion

The TEM images of nanocrystalline anatase-TiO\(_2\) processed via the conventional and modified sol-gel methods are presented in Fig. 1. The corresponding SAED patterns are presented as insets, which show the concentric ring patterns indicating the nanocrystalline nature of all samples, which consist of aggregated nanocrystallites having the different size-distribution. Typically, the average nanocrystallite size is noted to be ~10 nm and ~20 nm for the nanocrystalline anatase-TiO\(_2\) processed via the conventional sol-gel method, Fig. 1a,b; while, it is ~7 nm for that processed via the modified sol-gel method, Fig. 1c. The EDX spectra obtained for these samples are presented in Fig. 2, which show the presence of Ti and O as the major elements in all the samples. In addition to these elements, large amount of C is detected in Fig. 1a, which is absent in Fig. 1b,c. This is attributed to lower calcination temperature (300 °C) which could not burn-off the residual alkoxide-groups present in the sample. The nanocrystalline anatase-TiO\(_2\) processed via the modified sol-gel method show an additional peak of P, which suggests the presence of PO\(_4^{3-}\) anions on its surface. Very fine and porous morphology, Fig. 1c, is typically observed for the nanocrystalline anatase-TiO\(_2\) processed via the modified sol-gel method. This is attributed to the negative surface-potential provided by the PO\(_4^{3-}\) anions which create the repulsive forces between the adjacent nanocrystallites, which in turn results in their less aggregation, and hence, the porous morphology [14].

![Figure 1. TEM images of nanocrystalline anatase-TiO\(_2\) processed via the conventional (a,b) and modified (c) sol-gel methods. In (a), the sample is calcined at 300 °C for 1 h, and in (b) and (c), the samples are calcined at 600 °C for 2 h. The insets show the corresponding SAED patterns.](image-url)
Figure 2. EDX spectra obtained using the nanocrystalline anatase-TiO$_2$ processed via the conventional (a,b) and modified (c) sol-gel methods. In (a), the sample is calcined at 300 °C for 1 h, and in (b) and (c), the samples are calcined at 600 °C for 2 h.

The XRD patterns of different powder samples are presented in Fig. 3. All samples are noted to crystallize predominantly into the anatase-TiO$_2$ after the calcination treatment. For the nanocrystalline-TiO$_2$ processed via the conventional sol-gel method, Fig. 3a-d, the intensity of main anatase-peak is observed to increase with the calcination temperature. Moreover, the crystallinity of sample calcined at 600 °C for 2 h is observed to be the maximum with the presence of small amount (15 wt.%) of rutile-TiO$_2$, Fig. 3a. Comparison further shows that the intensity of main anatase-peak is the lowest for the nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method, Fig. 3e, and it is comparable with that processed via the conventional sol-gel method which is calcined at 300 °C for 1 h, Fig. 3d.

The FTIR spectra obtained using the different samples are presented in Fig. 4. For all the samples, the absorbance peaks within the frequency range of 3134-3400 cm$^{-1}$ have been attributed to the stretching vibrations of surface-adsorbed hydroxyl (–OH) groups; while, those within the frequency range of 1632-1651 cm$^{-1}$ have been attributed to the bending vibrations of surface-adsorbed H$_2$O [14,15]. The absorbance peak in lower frequency region, 400-800 cm$^{-1}$, is related to Ti-O-Ti bonds. For the nanocrystalline anatase-TiO$_2$ processed via the conventional sol-gel method, obtained after the calcination treatment in lower temperature range (300-400 °C), the small absorbance peaks located at 1440, 1533, and 1560 cm$^{-1}$ are observed, Fig. 4b-d, which are related to the residual organics such as –CH$_2$/CH$_3$.
functional groups suggesting the deposition of carbon-residue as a surface-contamination due to the incomplete decomposition and/or oxidation of unhydrolyzed alkoxide \((C_3H_7O)\)-groups [16]. This is also supported by the EDX analysis presented in Fig. 1a where large amount of residual C is detected. No organic-residue has been detected on the surface of nanocrystalline anatase-TiO\(_2\) which is obtained typically after the calcination treatment at 600 °C (Figs. 2b,c and 4a,e). For the nanocrystalline anatase-TiO\(_2\) processed via the modified sol-gel method, Fig. 4e, an additional absorbance peak located at 1051 cm\(^{-1}\) is noted which corresponds to the stretching vibrations of PO\(_4^{3-}\) anions on the surface [14]. Compared with the other samples, this sample exhibits the presence of relatively large amount of OH-groups and moisture adsorbed on the surface possibly via the hydrogen bonding with the PO\(_4^{3-}\) anions.

The variation in the normalized residual MB dye concentration as a function of UV-radiation exposure time, and the corresponding plots for determining the apparent first-order-reaction rate-constants \((k_{app})\), as obtained for the different samples are presented in Fig. 5a and b.

The obtained values of \(k_{app}\) and amount of MB dye adsorbed on the surface after 1 h stirring in the dark are presented in Fig. 6a and b. The corresponding variation in the concentration of free-OH\(^-\) produced as a function of UV-radiation exposure time, as obtained for the above samples, is presented in Fig. 7. For the nanocrystalline anatase-TiO\(_2\) processed via the conventional sol-gel method, both the \(k_{app}\) and amount of MB dye adsorbed on the surface in dark are noted to decrease with increasing calcination temperature within the range of 300-400 °C and then to increase at 600 °C, Fig. 6. For these samples,

Figure 4. FTIR spectra obtained using the nanocrystalline anatase-TiO\(_2\) processed via the conventional (a-d) and modified (e) sol-gel methods. The samples are calcined at 600 °C for 2 h (a,e), 400 °C for 1 h (b), 350 °C for 1 h (c), and 300 °C for 1 h (d).

![Figure 4](image_url)

Figure 5. (a) The variation in the normalized residual MB dye concentration as a function of UV-radiation exposure time, as obtained using the nanocrystalline anatase-TiO\(_2\) processed via the conventional (i-iv) and modified (v) sol-gel methods. (b) The corresponding plots for determining the \(k_{app}\) values. The samples are calcined at 300 °C for 1 h (i), 350 °C for 1 h (ii), 400 °C for 1 h (iii), and 600 °C for 2 h (iv,v).

![Figure 5](image_url)
the crystallinity (Fig. 3a-d) and the concentration of free-OH produced (Fig. 7a-d) are observed to increase with the calcination temperature. These latter trends are, however, conducive in enhancing the photocatalytic activity of nanocrystalline anatase-TiO$_2$ with the calcination temperature. On the other hand, the concentration of surface-OH groups is noted to decrease with increasing calcination temperature (Fig. 4a-d), which is likely to decrease the photocatalytic activity with increasing calcination temperature [17]. Moreover, it appears that the amount of MB dye adsorbed on the surface in dark is affected by the residual organics such as the –CH$_2$/-CH$_3$ functional groups remaining on the surface of photocatalyst particles after the calcination treatment conducted in a relatively lower temperature range, Fig. 4b-d. These groups have been reported to contaminate the surface of nanocrystalline anatase-TiO$_2$ resulting in a decrease in both the amount of MB dye adsorbed on the surface and $k_{app}$ [18]. Hence, within the calcination temperature range of 300-400 °C, the photocatalytic activity is predominantly governed by the variation in the concentration of surface-OH groups and that of surface-adsorbed MB dye. Among the different nanocrystalline anatase-TiO$_2$ processed via the conventional sol-gel method, the maximum $k_{app}$ value is exhibited by the sample calcined at 600 °C for 2 h which is contributed by the combination of its clean-surface (Figs. 2b and 4a), the highest crystallinity and the presence of small amount of rutile-TiO$_2$ providing the synergy effect (Fig. 3a), [7,19] the moderate amount of MB dye adsorbed on the surface in dark (Fig. 6b), and the largest concentration of free-OH produced under the UV-radiation exposure (Fig. 7d).

However, comparison with the nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method, Fig. 5, shows that the latter sample exhibits the highest $k_{app}$ value among all the samples investigated here, which is also comparable with that of Degussa-P25. Surprisingly, the crystallinity of this sample is the lowest, Fig. 3e. Moreover, this sample exhibits higher amount of MB dye adsorbed on the surface when compared with that related to the best sample processed via the conventional sol-gel method, Fig. 6b. However, the concentration of free-OH produced by this sample is relatively lower to exhibit...
very high MB dye degradation kinetics (compare Fig. 7d and e). These factors strongly suggest the contribution of some other mechanism responsible for higher MB dye degradation kinetics which is possibly not present in the case of nanocrystalline anatase-TiO$_2$ processed via the conventional sol-gel method. This is further supported by the comparison of nanocrystalline anatase-TiO$_2$ processed via the conventional sol-gel method (calcined at 300 °C for 1 h) with the sample processed via the modified sol-gel method (calcined at 600 °C for 2 h). Both of these samples have comparable values of average nanocrystallite size (Fig. 1a and c), crystallinity (Fig. 3d and e), amount of MB dye adsorbed on the surface in dark (Fig. 6b), and concentration of free-OH$^-$ produced under the UV-radiation exposure (Fig. 7a and e). In spite of these similarities, these two samples exhibit large difference in the $k_{app}$ value. This further supports the fact that some other mechanism, other than the formation and attack of free-OH$^-$, is also responsible for higher MB dye degradation kinetics which is possibly not present in the case of nanocrystalline anatase-TiO$_2$ processed via the conventional sol-gel method.

It is to be noted that the nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method possesses large concentration of PO$_4^{3-}$ anions on the surface (Fig. 4e) which provide the negative surface-potential conducive for the adsorption of large amount of cationic MB dye. This negative surface-potential is also responsible for repelling the hydroxyl (OH$^-$) ions away from the surface in an aqueous solution; thus, reducing the concentration of free-OH$^-$ produced under the UV-radiation exposure, Fig. 7c. It is known that the PO$_4^{3-}$ anions interact readily with the photo-induced holes than with the photo-induced electrons [20, 21]. Such interaction may possibly lead to the decomposition of PO$_4^{3-}$ anions to the superoxide-ions (O$_2^-$). As demonstrated in Fig. 8 (compare this figure with Fig. 4e), the nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method shows decrease in the concentration of PO$_4^{3-}$ anions present on the surface after the photocatalytic process, which strongly supports the role of PO$_4^{3-}$ anions in the degradation of surface-adsorbed MB dye under the UV-radiation exposure. Nevertheless, the formation of O$_2^-$ ions should enhance the concentration of free-OH$^-$ produced under the UV-radiation exposure [6] which is not reflected here in the free-OH$^-$ trapping experiments (compare Fig. 7d and 7e). This suggests that the O$_2^-$ ions produced as a result of the decomposition of PO$_4^{3-}$ anions cannot enhance the concentration of free-OH$^-$; however, can degrade the MB dye through the direct attack under the UV-radiation exposure [22]. Consequently, due to the attack of both O$_2^-$ ions and free-OH$^-$ produced under the UV-radiation exposure, the maximum photocatalytic activity is obtained for the nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method which has the lowest crystallinity.

Figure 8. FTIR spectrum obtained using the nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method. The sample is calcined at 600 °C for 2 h. The FTIR spectrum is acquired after using the sample for the photocatalytic activity measurements under the UV-radiation exposure using 7.5 µM of MB dye solution.

Overall, the most striking observation made in this investigation is the largest photocatalytic activity of nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method, which has the lowest crystallinity of all the samples processed here. The effect of lower crystallinity on the photocatalytic activity appears to be nullified by the presence of PO$_4^{3-}$ anions on the surface, which help adsorb relatively larger amount of MB dye in the dark and subsequently also take part in the generation of O$_2^-$ ions under the UV-radiation exposure by the trapping of photo-induced holes, which along with the OH$^-$ produced, attack and degrade the surface-adsorbed MB dye. The obtained results strongly suggest that the mechanism of MB dye degradation as proposed above can lead to the highest photocatalytic activity under the UV-radiation exposure even when the crystallinity of anatase-TiO$_2$ is very low.

4. Conclusions

The nanocrystalline anatase-TiO$_2$ has been synthesized via the conventional and modified sol-gel methods. The maximum photocatalytic activity is exhibited by the nanocrystalline anatase-TiO$_2$ processed via the modified sol-gel method, which has the lowest crystallinity among all the samples processed here. This has been primarily attributed to the presence of PO$_4^{3-}$ anions on the surface, which help adsorb relatively large amount of MB dye in the dark and subsequently also take part in the generation of O$_2^-$ ions by the trapping of photo-induced holes under the UV-radiation exposure, which along with the OH$^-$ produced, attack and degrade the surface-adsorbed MB dye. Hence, under the UV-radiation exposure, the presence of PO$_4^{3-}$ anions on the surface is conducive for enhancing the photocatalytic activity of anatase-TiO$_2$ having lower crystallinity.
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