

Enhanced Solar-Radiation Induced Photocatalytic Activity of Surface-Modified Nanocrystalline Anatase-Titania

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Abstract Sol-gel derived pure nanocrystalline (~ 20 – 30 nm) anatase-titania has been surface-modified by depositing silver(I) oxide and silver (predominantly the former) via UV-reduction process. The pure and surface-modified nanocrystalline anatase-titania have been characterized using different analytical techniques for determining the average nanocrystallite size, phase-contents, surface-chemistry, as well as the absorption and photoluminescence characteristics. It is demonstrated that, the latter exhibits an enhanced solar-radiation induced photocatalytic activity as compared to that of the former as a result of the absorption in the visible-region and enhanced photo-induced e^-/h^+ life-time, both caused by the surface-deposition of silver(I) oxide and silver.

Keywords Nanocrystalline · Photocatalysis · Silver · Sol-gel · Titania · UV-reduction

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1 Introduction

Nanocrystalline titania (TiO_2) is a well-known wide band-gap semiconductor oxide used for the photocatalytic application. In the photocatalysis process, the nanocrystalline TiO_2 particles are exposed to radiation having energy comparable with the band-gap to generate the photo-induced electron/hole (e^-/h^+) pairs, which migrate to the particle surface producing the surface-radicals such as the oxygen atoms, super-oxide ions, and hydroxyls ($\text{OH}^\bullet$). The surface-radicals then successively attack and degrade the surface-adsorbed organic molecules into different cations, anions, and gases [1–4].

The nanocrystalline TiO_2 generally shows the photocatalytic activity under the ultraviolet (UV) radiation exposure due to its higher band-gap value of 3.0–3.2 eV [5, 6]. The photocatalytic activity under the UV-radiation has been demonstrated to enhance by depositing the metal/metal oxide clusters on the surface of nanocrystalline TiO_2 , typically silver (Ag)/silver oxide (Ag_2O) clusters as investigated here and demonstrated earlier by others [7–15]. On the other hand, the nanocrystalline TiO_2 doped with nitrogen and sulfur is known to exhibit the photocatalytic activity under the visible-radiation due to the reduction in the band-gap as a result of doping [16, 17].

Interestingly, the visible-radiation induced photocatalytic activity of the nanocrystalline TiO_2 , which is surface-deposited with the metal/metal oxides, is hardly reported in the literature. Moreover, since the solar-radiation contains both the UV and visible-radiations and is cheaply available, it would be of significance to investigate the photocatalytic activity of nanocrystalline TiO_2 under the solar-radiation. Such investigation for the metal/metal oxide deposited nanocrystalline TiO_2 is currently not available in the literature. From this point of view, in this report, we

synthesize and investigate the solar-radiation induced photo-catalytic activity of nanocrystalline anatase-TiO₂, which is surface-modified with Ag₂O and Ag⁰ (predominantly Ag₂O).

2 Experimental

2.1 Chemicals

Titanium(IV) isopropoxide (Ti[OC₃H₇]₄) and anhydrous 2-propanol were purchased from Aldrich, India; silver nitrate (AgNO₃) from S.D. Fine-CHEM Limited, India; Ammonium hydroxide (aqueous NH₄OH, Assay 25–28 wt%) from Merk Limited, India; and methylene blue (MB) (AR Grade) from Glaxo Laboratories Ltd., India. All chemicals were used as received without any further purification.

2.2 Sol-Gel Processing of Pure Nanocrystalline Anatase-TiO₂

Pure nanocrystalline anatase-TiO₂ was synthesized via conventional sol-gel involving the hydrolysis and condensation of Ti[OC₃H₇]₄ in an anhydrous 2-propanol [5, 6]. For this purpose, a measured quantity of water was first mixed with 125 mL of anhydrous 2-propanol. A second solution was prepared in which 0.1 M (final concentration) of Ti[OC₃H₇]₄ was dissolved completely in 125 mL of anhydrous 2-propanol. Both the solutions were sealed immediately and stirred rapidly using the magnetic stirrer to obtain the homogeneous solutions. The solutions were prepared with the *R* (ratio of molar concentration of water to that of the alkoxide-precursor) value of 90. The water-part of the solution was then added drop-wise to the alkoxide-part under the continuous magnetic stirring. As a result of the hydrolysis and condensation of Ti[OC₃H₇]₄ due to the reaction with water, the color of the solution changed from transparent to white. After the complete addition of water-part of the solution to that of the alkoxide-part, the resulting suspension was stirred overnight before drying in the oven at 80 °C for the complete removal of the solvent and residual water. The dried powder was then calcined at 600 °C for 2 h to transform the amorphous-TiO₂ completely into nanocrystalline anatase-TiO₂.

2.3 Processing of Surface-Modified Nanocrystalline Anatase-TiO₂

The sol-gel derived pure nanocrystalline anatase-TiO₂ was then utilized to deposit Ag on the surface using the UV-reduction method. In this technique, 3 g of sol-gel derived pure nanocrystalline anatase-TiO₂ was dispersed in

250 mL aqueous AgNO₃ solution under continuous magnetic stirring with Ag/Ti ratio of 10⁻¹, which corresponds to the Ag-concentration of ~10 mol%. The pH of the solution was then adjusted to ~10–12 by slowly adding NH₄OH solution to an aqueous AgNO₃ solution containing the pure nanocrystalline anatase-TiO₂. The resulting suspension was then exposed to the UV-radiation for 5 h in a Rayonet Photoreactor (The Netherlands) containing 15 W tubes (Philips G15 T8) as the UV-source [12], which emitted the UV-radiation having the wavelength within the range of 200–400 nm (corresponding to the photon energy range of 3.07–6.14 eV), which peaked at 360 nm. The Ag-deposited nanocrystalline anatase-TiO₂ was then separated using a centrifuge (R23, Remi Instruments India Ltd.) and dried in an oven at 80 °C overnight.

2.4 Characterization of Pure and Surface-Modified Nanocrystalline Anatase-TiO₂

The transmission electron microscope (TEM, Tecnai G², FEI, Netherlands) images of pure nanocrystalline anatase-TiO₂ were taken at 300 kV to obtain the average nanocrystallite size and its distribution. Selected-area electron diffraction (SAED) pattern was obtained to confirm the nano-crystallinity and nature of phases involved. The crystalline phases present in the pure and surface-modified nanocrystalline anatase-TiO₂ were determined using the X-ray diffraction (XRD, Rigaku, Japan).

The surface-chemistry of the sol-gel derived pure and surface-modified nanocrystalline anatase-TiO₂ was revealed via X-ray photoelectron spectroscopy (XPS, VG Micro Tech ESCA 3000, United Kingdom) analysis at the base pressure of 10⁻⁹ Torr using the Mg K α X-radiation (1253.6 eV, linewidth 0.7 eV) generated at the power of 200 W. Both the survey and high-resolution narrow-scan spectra were recorded with the electron pass energy of 50 eV and take-off angle of 55° to achieve the maximum spectral resolution. The narrow scans were typically conducted for Ag 3d_{5/2} to determine the oxidation states of deposited-Ag under the given processing conditions. The narrow-scan Ag 3d_{5/2} spectrum was deconvoluted using the peak-fit software (XPSPEAK 41) to reveal the presence of different Ag-species on the surface of nanocrystalline anatase-TiO₂. The binding energy (BE) of Au 4f_{7/2} at 84.0 ± 0.1 eV was used to calibrate the BE scale of the spectrometer. Any charging shifts produced by the samples were carefully removed using a BE scale referred to C (1 s) BE of the hydrocarbon part of the adventitious carbon line at 284.6 eV [18]. The non-linear least-square curve-fitting was performed using a Gaussian/Lorentzian peak-shape after the background removal.

The absorption spectra of the pure and surface-modified nanocrystalline anatase-TiO₂ were obtained using the

UV-visible (UV-vis) spectrophotometer (UV-2401 PC, Shimadzu, Japan), operated in the diffuse reflectance (DR) mode, for the wavelength within the range of 200–800 nm. The PL spectra, obtained at the excitation wavelength of 327 nm, were recorded on a Spex-Fluorolog FL22 spectrofluorometer equipped with a double grating 0.22 m Spex 1680 monochromator and a 450 W Xe Lamp as the excitation source operating in the front face mode.

2.5 Measurement of Photocatalytic Activity of Pure and Surface-Modified Nanocrystalline Anatase-TiO₂ Under Solar-Radiation

The photocatalytic activity of the pure and surface-modified nanocrystalline anatase-TiO₂ was studied by monitoring the degradation of MB dye in an aqueous suspension under the solar-radiation exposure with the continuous magnetic stirring. Although the intensity of solar-radiation could not be measured, in order to eliminate its effect during comparison, the experiments were conducted for both the powders at the same time (10:00–11:00 am) on a sunny day (March 31, 2008; Monday) in an open atmosphere.

Two 75 mL of aqueous suspensions were prepared by completely dissolving 0.0072 $\mu\text{mol L}^{-1}$ of MB dye and then dispersing separately 0.4 g L^{-1} of the pure and surface-modified nanocrystalline anatase-TiO₂. The resulting suspensions were equilibrated by stirring in the dark (without the solar-radiation exposure) for 1 h to stabilize the adsorption of MB over the powder surface.

The stable aqueous suspensions, with the continuous magnetic stirring, were then exposed to the continuous solar-radiation. About 3 mL of samples were taken from the respective suspensions after each 5 min interval until the solution became colorless. The nanocrystalline anatase-TiO₂ was then filtered out from both the sample suspensions using a centrifuge and the filtered solutions were examined using a UV-vis spectrophotometer to study the degradation of MB dye. The absorption spectra of MB dye solutions were recorded within the range of 200–800 nm as a function of the solar-radiation exposure time. The intensity of the main absorbance-peak (*A*) of MB dye solution, located at 656 nm, was taken as a measure of residual MB dye concentration (*C*). The UV-vis absorption spectrum of MB solution, without the addition of photocatalyst powder, was also recorded as a reference spectrum corresponding to the initial MB concentration (*C*₀). The normalized residual MB concentration was calculated using the relationship of the form,

$$\left(\frac{C}{C_0}\right)_{\text{MB}} = \left(\frac{A_{\text{time}=t}}{A_{\text{time}=0}}\right)_{656\text{nm}} \quad (1)$$

A photocatalysis experiment was performed in the absence of nanocrystalline anatase-TiO₂ photocatalyst to confirm

the stability of MB in an aqueous solution under the continuous solar-radiation exposure. Under this condition, the initial MB concentration (*C*₀) remained unchanged even after irradiating the solution for total 1.5 h.

3 Results and Discussion

The TEM images of sol-gel derived pure nanocrystalline anatase-TiO₂ have been presented in Fig. 1. The powder consists of an agglomeration of strong aggregates (~ 100 –200 nm), Fig. 1a, of nanocrystallites of TiO₂ having the size distribution of ~ 12 –40 nm, Fig. 1b. The SAED pattern, shown as an inset in Fig. 1b, reveals the continuous ring pattern suggesting the nanocrystalline nature of the powder. The corresponding XRD pattern is presented in

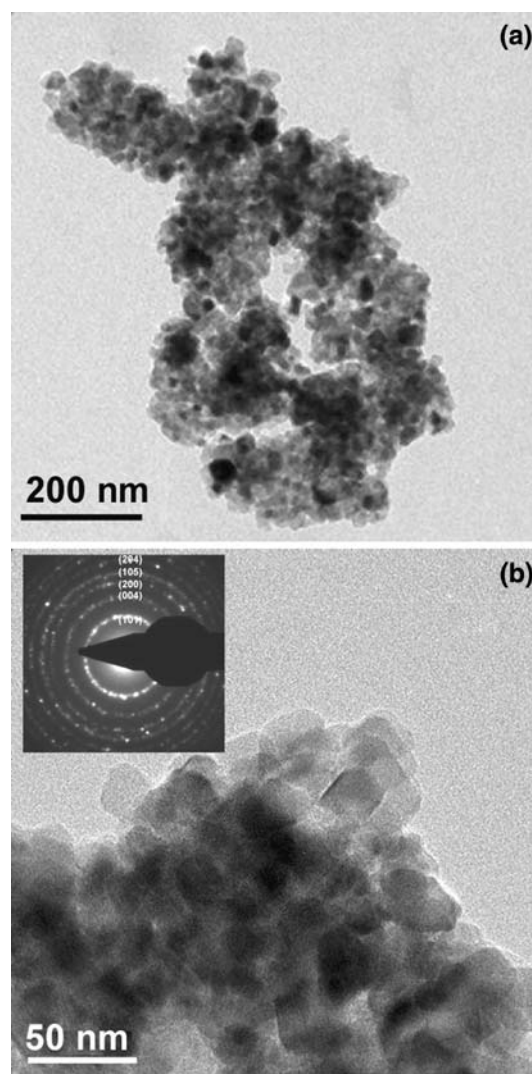


Fig. 1 Typical TEM images of sol-gel derived pure nanocrystalline anatase-TiO₂ at lower (a) and higher (b) magnifications. Inset in (b) shows the corresponding SAED pattern

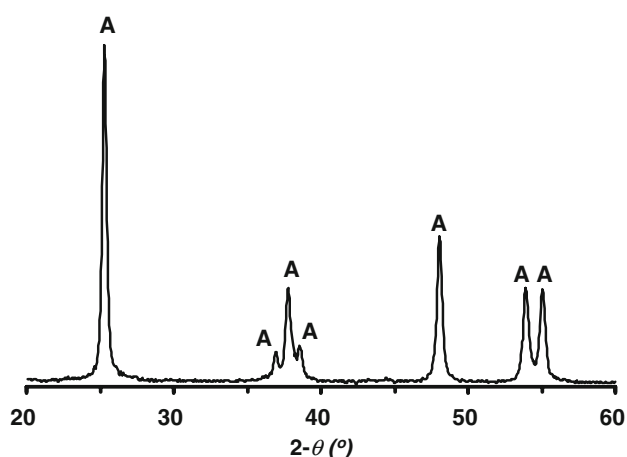
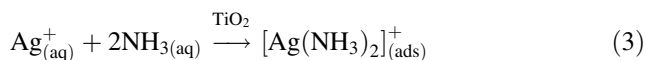
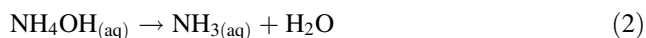


Fig. 2 Typical broad-scan XRD pattern of the sol-gel derived pure nanocrystalline anatase-TiO₂. 'A' represents the anatase-phase

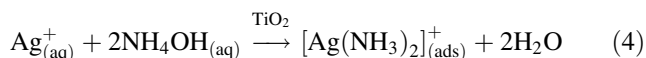
Fig. 2, where the peaks are identified as those of anatase-TiO₂ by comparison with the JCPDF card no. 21-1272. Hence, the metastable anatase-phase is stabilized at room temperature as a result of the size-effect and aggregate formation tendency of TiO₂ nanocrystallites [5]. The XRD pattern corresponding to the surface-modified nanocrystalline anatase-TiO₂ was similar to that shown in Fig. 2 and no additional peaks related to Ag⁰ and Ag₂O could be detected.

The XPS broad-scan analyses of the pure and surface-modified nanocrystalline anatase-TiO₂ are presented in Fig. 3. In Fig. 3a, the presence of Ti and O on the surface of pure nanocrystalline anatase-TiO₂ has been detected. An additional presence of Ag is noted for the surface-modified nanocrystalline anatase-TiO₂, Fig. 3b. Thus, the XPS analysis shows the successful Ag-deposition on the surface of sol-gel derived nanocrystalline anatase-TiO₂ via UV-reduction method.

In this method of Ag-deposition, the addition of ammonium hydroxide to an aqueous AgNO₃ solution results in the formation of silver-ammonia complex-ions via following reactions [19],



The net reaction can be written as,



The addition of nanocrystalline anatase-TiO₂ to the above solution results in the surface-adsorption of silver-ammonia complex-ions. When the suspension is illuminated with the UV-radiation, the e⁻/h⁺ pairs are effectively created within the nanocrystalline anatase-TiO₂. The photo-

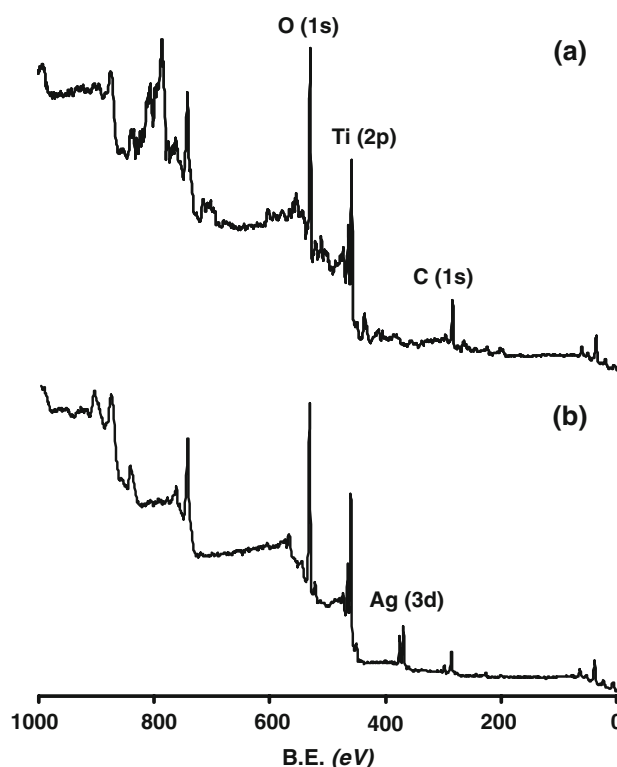
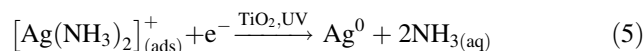
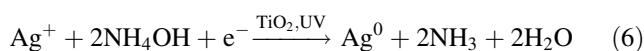


Fig. 3 Typical broad-scan XPS spectra obtained from the pure (a) and surface-modified (b) nanocrystalline anatase-TiO₂

induced electrons then reduce the surface-adsorbed silver-ammonia complex-ions to Ag⁰.



The overall reaction for the Ag⁰-deposition on the surface of nanocrystalline anatase-TiO₂ via UV-reduction method can be written as,



The XPS narrow-scan analysis for the deposited-Ag is presented in Fig. 4. The deconvolution of the obtained spectrum reveals the presence of two sub-peaks located at the BE positions of 367.7 and 368.7 eV, which are assigned to Ag₂O and Ag⁰ species [7, 10, 11]. Considering the peak-heights of two sub-peaks, the fractions of deposited-Ag present on the modified-surface of nanocrystalline anatase-TiO₂ as Ag⁰ and Ag₂O have been estimated to be 9 and 91 mol% suggesting immediate oxidation of Ag⁰-Ag₂O following the surface-deposition. Thus, in the present investigation, the surface of sol-gel derived nanocrystalline anatase-TiO₂ has been successfully modified by depositing both Ag₂O and Ag⁰ (predominantly Ag₂O) via UV-reduction method.

The absorption spectra obtained for the pure and surface-modified nanocrystalline anatase-TiO₂ have been presented in Fig. 5. The pure nanocrystalline anatase-TiO₂

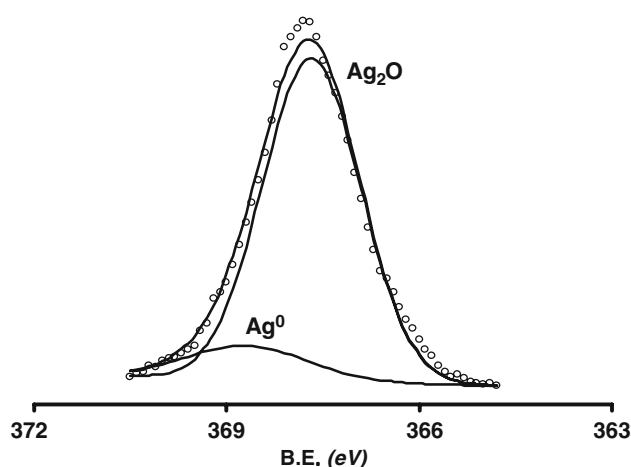


Fig. 4 Typical narrow-scan XPS Ag 3d_{5/2} spectrum obtained from the surface-modified nanocrystalline anatase-TiO₂

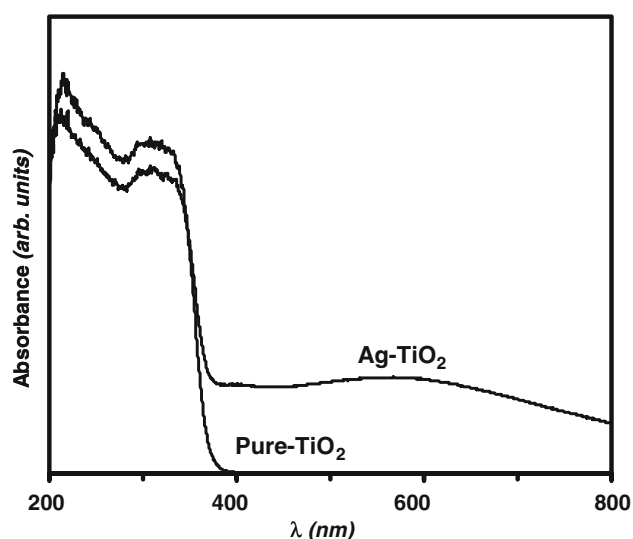


Fig. 5 UV-vis absorption spectra obtained from the pure and surface-modified nanocrystalline anatase-TiO₂

shows the absorption in the UV-region below 400 nm. However, the absorption spectrum of the surface-modified nanocrystalline anatase-TiO₂ is different than that of the former and shows a broad absorption in the visible-region as well, which peaks at 575 nm. In the literature, the absorption in the visible-region for the Ag-deposited nanocrystalline TiO₂ has been attributed to the surface plasmon absorption due to the spatially confined electrons in the Ag⁰ nanoparticles [7, 10, 11, 20]. Since, the band-gap of Ag₂O is 1.3–1.5 eV, the absorption in the visible-region ($\lambda = 400$ –800 nm) is also likely to be contributed by Ag₂O. Moreover, in the literature, more intense and broader absorbance-peak in the visible-region have been ascribed to relatively larger average-size and broader size-distribution of Ag⁰ nanoparticles, high refractive index of

TiO₂, and the interaction between Ag⁰ and TiO₂ [20]. Hence, from the absorption spectrum obtained for the surface-modified nanocrystalline anatase-TiO₂ processed via UV-reduction method, it is inferred that the average nanoparticle size, size-distribution, and surface-coverage by Ag⁰ and Ag₂O are relatively larger under the given processing conditions.

The PL spectra obtained from the pure and surface-modified nanocrystalline anatase-TiO₂ have been presented in Fig. 6. A broad PL spectrum in the visible-region peaking at 433 nm has been observed for the pure nanocrystalline anatase-TiO₂. This is an excitonic PL, which suggests the presence of large concentration of oxygen-ion vacancies, which mediate the recombination of photo-induced e⁻/h⁺ pairs [21]. Comparison shows that, the PL from the surface-modified nanocrystalline anatase-TiO₂ is considerably quenched. Such PL quenching has been attributed to the enhanced e⁻/h⁺ life-time caused by the effective trapping of the photo-induced electrons by the deposited Ag₂O and Ag⁰ [11, 21]. As a result, the photo-induced e⁻/h⁺ life-time appears to be larger for the surface-modified nanocrystalline anatase-TiO₂ relative to that of pure nanocrystalline anatase-TiO₂. Thus, the DR and PL analyses suggest that, the surface-modified nanocrystalline anatase-TiO₂ not only absorbs the visible-radiation but also exhibits higher photo-induced e⁻/h⁺ life-time compared with the pure nanocrystalline anatase-TiO₂. Both of these factors have a strong effect on the photocatalytic activity under the solar-radiation.

The variation in the normalized residual MB concentration as a function of solar-radiation exposure time, for the pure and surface-modified nanocrystalline anatase-TiO₂, is presented in Fig. 7a; while the corresponding plots

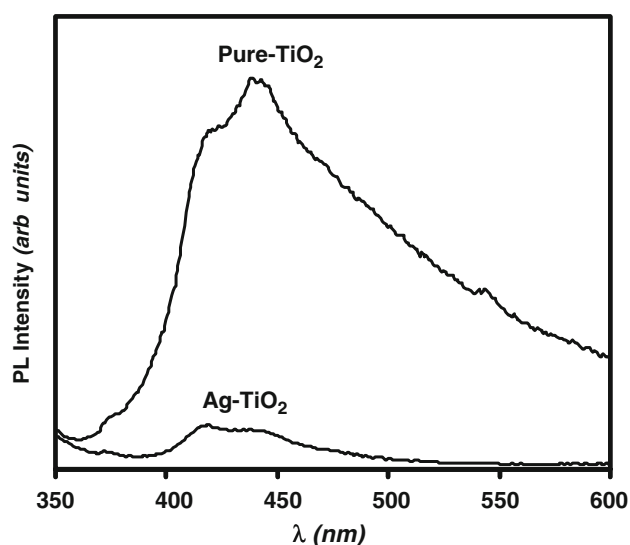


Fig. 6 PL spectra obtained from the pure and surface-modified nanocrystalline anatase-TiO₂. The excitation wavelength is 327 nm

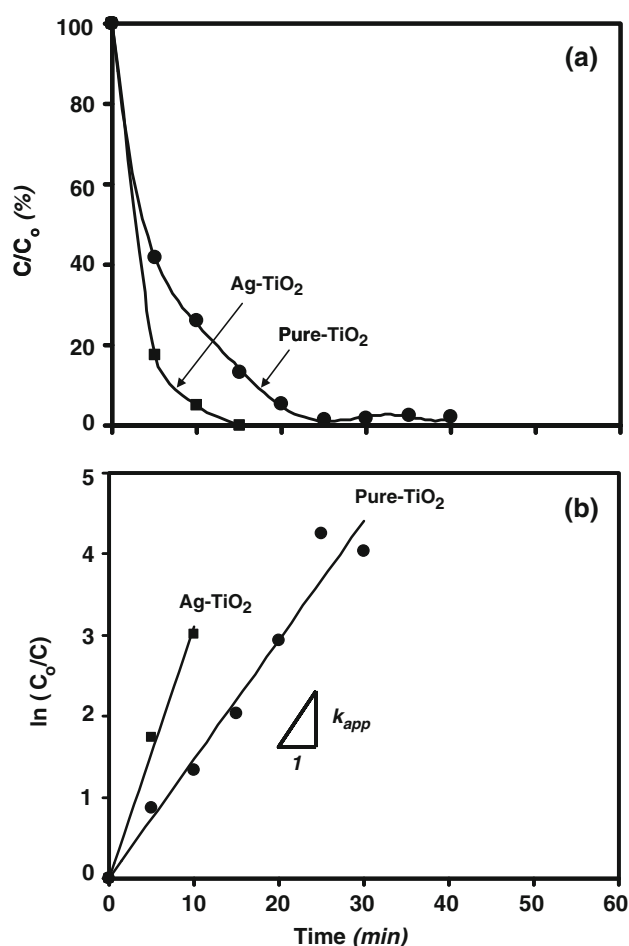


Fig. 7 Variation in the normalized residual MB concentration as a function of solar-radiation exposure time (a) and the corresponding plots for determining the k_{app} values

for obtaining the apparent first-order reaction rate-constant (k_{app}) have been presented in Fig. 7b. The k_{app} values for the pure and surface-modified nanocrystalline anatase-TiO₂ have been estimated to be 0.147 min^{-1} and 0.310 min^{-1} . Thus, the surface-deposition of Ag₂O and Ag⁰ (predominantly Ag₂O) is observed to enhance the photocatalytic activity of the nanocrystalline anatase-TiO₂ under the solar-radiation by the factor of 2. Since the solar-radiation contains both the UV and visible-radiations, this enhanced solar-radiation induced photocatalytic has been attributed to the absorption of the visible-radiation and higher lifetime of the photo-induced e^-/h^+ pairs, caused by the presence of Ag₂O and Ag⁰ (predominantly Ag₂O) on the surface-modified nanocrystalline anatase-TiO₂.

Lastly, it is necessary to mention that, the surface of nanocrystalline anatase-TiO₂ may also be modified using other noble metals (such as gold (Au) and platinum (Pt)), foreign oxides (such as tin oxide (SnO₂) and ceria (CeO₂)), and sulfides (such as cadmium sulfide (CdS) and zinc

sulfide (ZnS)) for better utilization of the photocatalyst under solar-radiation. However, in order to determine the most effective candidate material, in comparison with Ag₂O and Ag⁰, further detail investigation would be necessary.

4 Conclusions

Pure nanocrystalline anatase-TiO₂ has been synthesized via sol-gel and subsequently surface-modified by depositing Ag₂O and Ag⁰ (predominantly Ag₂O) via UV-reduction process. The photocatalytic activity of surface-modified nanocrystalline anatase-TiO₂, under solar-radiation, is observed to be twice as high as that of pure nanocrystalline anatase-TiO₂. This has been attributed to the absorption of visible-radiation and enhanced photo-induced e^-/h^+ lifetime caused by the presence of surface-deposited Ag₂O and Ag⁰ (predominantly Ag₂O).

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