Interactions of titania based nanoparticles with silica and green-tea: photo -degradation and -luminescence

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Abstract: An effective way to modify the photocatalytic activity of both anatase and rutile TiO₂ nanoparticles by coating the surface with either an inorganic (SiO₂/silica) or organic (green-tea) layer using a chemical approach is demonstrated. Tetraethyl orthosilicate (TEOS) was used to cover the surface of TiO₂ with silica which facilitates the inhibition of photocatalytic activity, ensuring its application in sunscreens by blocking the reactive oxygen species (ROS). Green- tea extract, rich in epigallocatechin gallate (EGCG), was used to coat/stabilize nano-sized TiO₂. The morphology of these coatings was revealed by transmission electron microscopy (TEM) and by energy dispersive spectroscopy (EDS) mapping. These studies showed good coverage for both types of coating, but with somewhat better uniformity of the coating layer on rutile TiO₂ compared to anatase due to its more uniform particle geometry. The effectiveness of each coating was evaluated by photodegradation of an organic dye (methyl orange). These studies showed rutile_{polyphenol} exhibits the highest photocatalytic activity among rutile forms which validates its feasibility to be used in photodegradation.

Keywords: TiO₂ nanoparticles, silica, green-tea, photocatalytic activity, electron microscopy.

Introduction:

TiO₂ (titania) is attractive as a photocatalyst because of its high surface area, high absorption capability, slow rate of charge carrier recombination and biocompatibility [1]. As a result, a range of applications that rely on TiO₂ have been developed including dye-sensitized solar cells (DSSCs) [2-3], effective photocatalytic activity [4-7] by the photodegradation of organic dyes [8-9], water purification [10], biological applications [11-12], antimicrobial activities [13, 14] and cosmetics [15, 16]. Photodegradation of organic dyes is an application in which fast separation and spatial control of exciton pair is highly beneficial but for cosmetic application this behaviour is undesirable. It is reported that irradiation of UV light on TiO₂ nanoparticles leads to the production of reactive oxygen species (ROS) which includes: (i) superoxide radical, (ii) hydroxyl radical and (iii) singlet oxygen, causing an adverse affect to all the types of organic biomolecules, including carbohydrates, proteins, nucleic acids, lipids and DNA [17-18]. Thus, the ability to manipulate the surface property is an extremely critical factor to optimize different phases of titania nanoparticles, anatase and rutile, for both these photo-related phenomena.

Surface modification of these materials has traditionally been achieved by coating the photocatalyst surface with ceramic and other oxide materials such as SiO₂, Al₂O₃, ZrO₂, WO₃, MoO₃ [19-20]. Utilization of organic materials for surface modification has typically involved bulk admixtures, which has been exploited successfully in the pigment industry [21-22] or the addition of antioxidants such as vitamin A, E, or C. Even though success has been achieved in both titania-based cosmetic applications and photocatalyst applications, a comparative study and understanding of the balance between these processes is yet to be fully realized.

For example, the intrinsic photocatalyst behavior may change when bulk admixtures are introduced. Organic surface coatings can be utilized to circumvent this effect. In addition, organic coatings offer other advantages compared to inorganic coatings. Surface modification of nanoparticles by organic coating provides good biocompatibility and biodegradability of the functional organic materials. It has also been reported that organic moiety provides various functional groups such as hydroxyl group, aldehydic group, carboxyl group and many others. These groups can be used to enhance chemical interactions to various biosubstances [23]. In addition, organic species are cheaper and naturally abundant as compared to inorganic species.

In the present work, we compared the effectiveness of a traditional inorganic coating, silica, to that of an organic coating derived from green tea (*camellia sinensis*). Green tea is a popular beverage because of health promoting effects and a pleasant aroma [24]. Owing to its low toxicity, biocompatibility and environmental friendly nature,

1 it is used for “green” synthesis of nanoparticles [25]. Green tea also is antimutagenic, anti-inflammatory,
2 antibacterial, antiproliferative and has strong natural antioxidant properties that are known to protect the skin
3 from UV damage and prevent cellular damage caused by ROS generation [26-27] .Green tea is characterised by
4 high content of catechins, a sub-class of flavan-3-ol (a flavonoid), having 20 times more potent antioxidant
5 property than vitamin C in the lipoprotein oxidation model [28]. In general, the main constituent of green tea
6 extract is polyphenols, predominantly the catechins [29-31]. The four major catechins are: (i) epicatechin (EC)
7 (ii) epicatechin gallate (ECG) (iii) epigallocatechin (EGC) and (iv) epigallocatechin gallate (EGCG). Of the
8 catechins, the main component found in green tea is EGCG [32]. EGCG contributes to the overall protection of
9 cell integrity and immune function and also suppresses the growth of cancerous cells [24, 33]. EGCG is not only
10 the good antioxidant but it also promotes anti-aging, anti-acne and anti-inflammatory effects, so it is an
11 attractive component for use in cosmetics [34]. Green tea extract enhances the activity of enzyme superoxide
12 dismutase (SOD) which helps to quench the excess superoxide radicals, peroxy radicals, singlet oxygen and
13 thus helps inhibiting the premature aging [35-36]. It is approximately 99% water, so it helps to maintain
14 hydration, makes an important contribution to daily fluid requirement and thus helpful to remove the waste
15 product from the body [37]. Also, the antioxidant action of polyphenols, found in green tea, is known to increase
16 the antioxidant capacity of blood [38]. Thus, green tea extract was expected to be an attractive material for
17 modifying the surface of photocatalysts [25, 39].

18 Herein, we studied coatings on two forms of TiO_2 - anatase and rutile. The TiO_2 nanoparticles can be produced
19 by simple, efficient wet chemical method and then annealed at different temperatures. The products were then
20 coated with either silica or by polyphenol from green tea extract. The effectiveness of each coating was
21 evaluated by photodegradation of an organic dye (methyl orange). The samples were analyzed by various
22 characterization techniques including XRD, FTIR, SEM/EDX, high resolution transmission electron microscopy
23 (HR-TEM), high- angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and
24 UV-Vis. We propose a mechanism for the chemical interaction at the surface of the titania particles and
25 compare the photoluminescence spectra and photocatalytic capability of bare-, silica coated- and polyphenol
26 coated- TiO_2 nanoparticles at various time intervals.

27 **2. Experimental Section**

28 *2.1 Chemicals used*

The chemicals used in the synthesis of TiO₂ nanoparticles were titanium tetra isopropoxide (TTIP, Ti(OCH(CH₃)₂)₄, LR, 98%, Spectrochem Pvt. Ltd., India), Absolute ethanol (C₂H₆O, AR, 99.9%, S D Fine-Chem Ltd., India), Methanol (CH₃OH, HPLC grade, AR, 99.8%, Rankem, India).

For coating with silica, polyvinyl alcohol (PVA, LR, 75%, Central Drug House Pvt. Ltd., India), ammonia solution (NH₃, LR, 25%, Rankem, India), tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄, LR, 98%, Otto, India) were used.

For coating with polyphenol, Lipton green tea was used. Millipore water (18 MΩ) was used during the synthesis process and further characterizations.

2.2.1 Synthesis of Titania Nanoparticles

The different phases of titania were synthesized by wet chemical method using TTIP as titania precursor. 6 ml of TTIP precursor was added to 2 ml of ethanol. The resulting mixture was magnetically stirred at 55 °C. Now, 2 ml of methanol and 60 ml of millipore water was also added dropwise for the completion of chemical reaction. The precipitate obtained was collected, filtered and washed with hot water, ethanol and methanol. The precipitate was dried at 130 °C/12 h in oven and annealed at 550 and 730 °C/10 h in a muffle furnace to get two different phases of TiO₂. The produced white product was characterized by various characterization techniques.

2.2.2 Synthesis of Titania_silica Nanoparticles

0.5 g of obtained TiO₂ nanoparticles were dispersed in 15 ml of ethanol followed by magnetic stirring, say solution A. On the other hand, same amount of PVA was dispersed in 15 ml of water at 70 °C, say solution B. Now solution B was added to solution A dropwise. It was then dried at 70 °C/2 h in oven. The purpose of coating PVA over nanoparticles before silica coating was that due to the adhesive nature of PVA, it will bind properly over TiO₂ nanoparticles. The obtained PVA coated nano-sized TiO₂ (1 g) were dispersed in 5 ml ethanol and 1.5 ml ammonia solution. Then the solution was magnetically stirred followed by the dropwise addition of 6 ml TEOS. The obtained product was naturally dried and then utilized for various characterizations.

2.2.3 Synthesis of Titania_polyphenol Nanoparticles

During the preparation of bare phases of titania nanoparticles, 5 ml of green tea extract was added before the precipitate formation. All the conditions were kept same.

2.3 Materials Characterization

The information about crystallinity and purity of the samples were procured by X-ray diffraction (XRD) pattern using a Rigaku bench top X-ray diffractometer equipped with a monochromatic Cu-K α radiation ($\lambda = 1.541 \text{ \AA}$) as X-ray source and scanning in 2θ range from 10 to 80° . All FTIR spectra were recorded with a single beam Perkin Elmer instrument (Spectrum BX-500) FTIR Model spectrophotometer. The morphology and the size of powder particles were analyzed by a Scanning Electron Microscope (Zeiss EVO MA-10 SEM operating at 10 keV) equipped with an energy dispersive spectrometer (EDS; OXFORD INCA ENERGY 250). The TEM was performed using a FEI Tecnai G2 F30 STWIN operating at 300 kV and a JEOL 2100F operating at 200 kV . The UV-Vis absorption spectra of the products were recorded using a UV-Vis spectrometer (UV-2401 PC, Shimadzu Corporation Japan). The room temperature Photoluminescence (PL) spectroscopy was done on FL-1039 HORIBA JOBIN YVON, USA.

2.4 Photocatalysis Reaction

The photocatalytic degradation of MO (Methyl Orange) was examined using the different phases of TiO_2 as photocatalyst at various time intervals. The bare and core_shell nanoparticles of anatase and rutile were used as photocatalyst. A 0.01 g of the photocatalyst was suspended in a 50 ml MO aqueous solution with an initial concentration of 0.153 mg l^{-1} in a sealed beaker. Prior to irradiation, the solution was magnetically stirred for an hour at ambient temperature in dark to establish the adsorption-desorption equilibrium. The optical system for the photocatalytic reaction was composed of 150 W lamp. One millilitre of the solution was drawn out and concentration of MO at $0, 30, 60$ and 120 min was calculated using absorption graph obtained from UV-Vis spectrophotometer. The distance between UV light and the sample was 20 cm that was kept constant throughout. The ability and comparison of photodegradation of MO solution by bare-, silica coated- and polyphenol coated- TiO_2 nanoparticles were scrutinized.

3. Results and Discussion

3.1 Crystallographic Phase Transition and Phase Identification

The phase and phase purity of TiO_2 particles prepared at various annealing temperatures of 550 and 730°C were determined by XRD as shown in figure 1. X-ray diffraction patterns of the sample annealed at 550°C , figure 1(a1), (a2) and (a3), can be indexed to the tetragonal anatase structure (JCPDF-ICDD card no.-

84-1286). The intensity of the diffraction peaks of anatase_silica and anatase_polyphenol are much lower than those for the bare anatase, but in all three cases the peaks are located at $2\theta = 25.60, 37.9, 48.28, 54.24, 55.18, 62.86, 69, 70.48, 75.2$. The peak centred at 25.60 with FWHM (Full width at half maximum, obtained by gauss fit) 0.36 was used to obtain the crystallite size of anatase by Debye-Scherrer equation. The obtained crystallite size was 23 nm. An interesting finding scrutinized that the crystallite size was found to be decreased when anatase was coated with silica [40] and polyphenol and also hints the existence of core-shell nanostructures. The crystallite size of anatase_silica and anatase_polyphenol was calculated as 19.1 and 17.8 nm, respectively. The peaks in case of anatase_polyphenol were found to be sharper which may be attributed to its high crystallinity. The diffraction peaks of the sample annealed at 730°C , figure 1(b1), (b2) and (b3), were found to be correlated with the documented tetragonal rutile phase (JCPDF-ICDD card no.- 88-1172), the peak

Figure 1. XRD pattern of (a) anatase and (b) rutile phases of TiO_2 , where (a1, b1), (a2, b2) and (a3, b3) represent corresponding bare-, silica coated-, and polyphenol coated- TiO_2 , respectively. (c) crystallographic ball-and-stick model and (d) crystal shape of tetragonal anatase; color code: blue (small) balls indicate titanium (Ti) atoms and grey (large) balls signify oxygen (O) atoms, green square represents $[101]$ plane, blue, green and pink illustrate $(0 -1 3)$, $(0 -1 1)$ and $(-1 0 -1)$ face, respectively, (e) provides the repeating unit of anatase.

1.5 column image, 500 dpi, image width 140 mm

centred at 27.8 with FWHM (obtained by gauss fit) 0.23 calculates the crystallite size to be 36 nm by using Debye- Scherrer equation. The diffraction peaks of rutile_silica decrease sharply only in intensity keeping the position same. The crystallite size was obtained to be 35.7 nm. The peaks observed for rutile_polyphenol were sharp and an increase in crystallite size, 48.2 nm, was observed proving its more crystalline nature. Even, the diffraction peaks of rutile_polyphenol were narrower than its corresponding anatase phase also. No extra peaks were observed apart from the two phases of TiO_2 showing the absence of any remnant and also it is because of low content of silica, polyphenol and amorphous phase of silica [41]. The crystallographic ball-and-stick model of tetragonal anatase, figure 1(c), represents the two kind of bonding of titanium with oxygen atom. The axial Ti-O bond length was found to be 1.97 Å and the equatorial Ti-O bond length was calculated as 1.93 Å. Axial bond length was found to be longer and thus weaker than the equatorial Ti-O bond length. The angle Ti-O-Ti was observed as 102°. The various faces of the crystal shape of anatase have been shown in figure 1(d). The repeating unit of TiO_2 is octahedral in nature where the two axial and four equatorial Ti-O bonds are easily distinguishable as depicted in figure 1(e).

3.2 FTIR Spectroscopy

FTIR spectroscopy was performed to further investigate the nature of chemical bonding present in bare- and coated- TiO_2 nanoparticles. The bands in the region 800-400 cm^{-1} correspond to Ti-O and Ti-O-Ti bonds as shown in figure 2. Thus the peaks at 745, 488, 770, 463, 790 and 513 cm^{-1} can be associated with $\nu(\text{Ti-O})$ vibration. Bands at 1431, 1451, 1444, 1648, 1655 and 1641 cm^{-1} can be attributed to O-H bending mode. Also, broad band in the region 3650-3000 cm^{-1} can be assigned for physically adsorbed water [42-44]. In case of silica coated phases of TiO_2 , the amorphous silica absorbs in 1200-1000 cm^{-1} as shown in the figure 2(a2), (b2). So, the peak at 1076 cm^{-1} corresponds to $\nu(\text{Si-O-Si})$ and the two peaks at 1096 and 1180 cm^{-1} are associated with Si-O-Ti bond [45-46]. The peak at 953 cm^{-1} corresponds to Si-OH peak and the carbonyl group peak can be assigned at 1716 cm^{-1} . The peak at 2384 cm^{-1} substantiates to the absorption of atmospheric CO_2 [47-48]. Rutile provides evidence of some extra peaks at around 1028 and 1165 cm^{-1} that can be substantiated to carbonate ions and their presence can be due to the dissolution of CO_2 from air [49-50]. The two bands at 2514 and 2922 cm^{-1} represent the combination bands [51]. After that the pure phases of titania products are compared with their corresponding polyphenol coated phases. Interestingly, Ti-O bands were found to be bathochromic (red) shifted from 745 to 488 cm^{-1} (in case of anatase) and from

Figure 2. FTIR spectra of (a) anatase and (b) rutile phase of TiO_2 , where (a1, b1), (a2, b2) and (a3, b3) represent corresponding bare-, silica coated-, and polyphenol coated- TiO_2 , respectively.

Single column image, 500 dpi, image width 90 mm

770 to 513 cm^{-1} (in case of rutile) due to the weakening or elongation of Ti-O bond [52]. The peaks shown in figure 2(a3), (b3) are accredited at 1671 and 1658 cm^{-1} in polyphenol coated phases of titania nanoparticles can be attributed to C=C ring stretching in polyphenol [32, 39].

3.3 Topography and Morphological Characteristics

The morphology and microstructures were characterized by SEM and TEM. The SEM micrographs of bare- and coated- TiO_2 project the morphological evolution as shown in figure 3. The micrographs reveal the size of the nanoparticles and provide information about their agglomeration. It was found that the particle size decreases and agglomeration increases in bare forms of TiO_2 with the increase in annealing temperature from 550 to 730 $^{\circ}\text{C}$ as shown in figure 3(a1, b1). As TiO_2 nanoparticles are

found to agglomerate strongly, thus zeta-potential measurement can help in stability study [53]. The increase in particle size due to coating with silica is evident in figure 3(a2, b2). In the case of polyphenol coating, the monodispersity of nanoparticles is noticeable as revealed by figure 3(a3, b3). The anatase_polyphenol represents refined and highly compact structure wherein no open surfaces are found. In contrast, the rutile_polyphenol microstructures provide evidence of porosity. To unravel the elemental composition, energy dispersive X-ray spectroscopy (EDS) was conducted that reveal the presence of Si in the silica coated samples as shown in figure 3(c2), with little evidence of carbon as depicted in figure 3(c3), along with Ti and O atoms in polyphenol coated products.

High-resolution TEM was performed to evaluate coating uniformity and coating roughness [54], as illustrated in figure 4. A typical bright field TEM image at high magnification shows the bare anatase nanoparticles with sizes ranging from 40-100 nm. The crystal structure analysis of titania nanoparticles are confirmed based on lattice fringe image as displayed in the inset of figure 4(a). The TEM images show well organised lattice fringes of

Figure 3. SEM micrographs of anatase and rutile phase of TiO_2 where, (a1, b1), (a2, b2) and (a3, b3) represent corresponding bare-, silica coated-, and polyphenol coated- TiO_2 , respectively. EDS spectra of corresponding (c2) silica coated- and (c3) polyphenol coated- rutile phase of TiO_2 . Scale bar= 1 μm .

Single column image, 500 dpi, image width 90 mm

spacing $d = 0.34 \text{ nm}$ that represents the d - spacing between (101) planes of TiO_2 , anatase phase. The stacking of (101) is atomically clean without any imperfections at the lattice scale within the grain. Figure 4(b) shows a

bright field image of anatase nanoparticle clusters coated with silica. The diameters of two anatase clusters visible in Figures 4b and 4c are about 800 and 350 nm. The lattice fringe d-spacing of 0.34 nm is consistent with the (101) plane of anatase phase, inset of figure 4(b), further confirming the nature of TiO_2 particles. In high resolution HAADF-STEM (Z-contrast) images the anatase nanoclusters appear dark and silica coating appears bright as shown in figure 4(c). EDS mapping in figure 4(d) also substantiates the formation of core_shell

Figure 4. TEM images of bare and silica coated anatase. (a) low magnification micrograph of anatase, (b) Bright field image of two NPs showing core_shell-like structure in case of anatase_silica, (c) corresponding HAADF- STEM image of anatase_silica, (d) EDS mapping supporting core_shell structure of anatase_silica, (e) EDS line scan indicates core_shell structure (80 nm extra silica), (f) Image of anatase_silica, and (g-i) corresponding EDS elemental mapping images of (g) Si element (h) O element (i) Ti element. Insets in (a) and (b) represent HR-TEM images showing the lattice spacing. White dotted circle B in (b) reveals the overlapped grain boundaries.

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structure. The thickness of the silica shell on this particle as determined by an EDS line scan was found to be 80 nm as shown in figure 4(e). The average coating thickness statistically measured from 10 different particles was found to be 100 nm. The EDS elemental mapping also indicates uniform coating as shown in figure 4(f) and the presence of Si, O, Ti elements as revealed in figure 4(g-i). The rutile nanoparticle clusters are typically 150-200 nm in diameter, and the silica coating thickness was found to be 20 nm as shown in bright field image, figure 5(a). The silica coating on rutile nanoparticle clusters is typically more uniform and the interface between core and shell is more distinct than for the case of anatase particles (figure 5a). This is likely due to the more

uniform, round shape of the rutile particles. High resolution HAADF-STEM image represented in figure 5(b), and EDS mapping as shown in figure 5(c), also discern the core-shell moiety. The EDS line scan along the dotted line in figure 5d shows the thickness of that silica shell on the rutile particle to be 20 nm. The TEM micrographs affirm that the coating is uniform over mostly all the nanoparticles, and the average coating thickness over 15 clusters is ~25 nm. However, modified Stober method is used to control shell thickness and particle shape [55]. Convincing proof of the polyphenol coating is evident from TEM micrographs as depicted in figure 6. The low magnification images represented in figure 6(a,b), clearly manifest that polyphenol acts as the capping agent which stabilizes the nanocrystals of titania [25] because of the presence of 3 nm coating over the surface of anatase-polyphenol core as already represented in the inset of figure 6(a). The planes obtained by relating the corresponding d-spacing with JCPDF data have been marked on the selected area electron diffraction (SAED) pattern, figure 6(c). High contrast between the surface of the nanoparticles and coating confirm the thick polyphenol cover over the anatase surface, figure 6(d). The crystalline characteristic was investigated by HR-TEM through exploring the atomic scale image and revealing the d-spacing of 0.34 nm, corresponding atomic plane hkl: 101, figure 6(e,f). In case of polyphenol coated anatase core, the coating was observed on single core of nanoparticle, unlike silica coating on nanocluster.

Figure 5. Images revealing core-shell structure of rutile-silica nanoparticles. (a) Bright field image of a nanoparticle cluster showing silica thickness 20 nm., (b) corresponding HAADF-STEM image, (c) EDS mapping, (d) EDS line scan reflecting the shell structure, revealing 20 nm extra silica.

Single column image, 500 dpi, image width 90 mm

Figure 6. TEM images of polyphenol coated anatase phase. (a), (b) represent the low magnification images, (c) SAED pattern, (d), (e), and (f) illustrate HRTEM images showing lattice fringes. Inset in (a) reveal the thickness of coating. White dotted circle in (e), (f) illustrate the size of a particle and the multiple grain boundary formation due to overlapping of crystallites, respectively. White arrows in (d) elucidate the polyphenol coating.

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3.4 Mechanism of the interaction of Silica and polyphenol with TiO_2 phases

3.4.1 Silica interaction with TiO_2 Nanoparticles

There can be two ways of the interaction of silica with TiO_2 phases, either Si can interact with TiO_2 at its

Scheme 1. Schematic representation of the mechanism of Si interacted at the surface of anatase nanoparticles.

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surface or it can get incorporated into the crystal structure of TiO_2 as shown in Scheme 1. There occurs the formation of Ti-O-Si bond at the surface of titania nanocrystals as confirmed by FTIR spectroscopy. If Si gets

incorporated into the crystal structure of TiO_2 , then there can be two mechanisms; (i) One of them consist of the incorporation of Si into the TiO_2 crystal interstitially, (ii) The second possibility may be Si incorporation into the crystal structure of TiO_2 substitutionally and thereby altering the lattice parameters. Ti^{4+} has an ionic radius of 0.68 Å while the ionic radius of Si^{4+} is 0.42 Å. Thus it is very small enough to enter into the interstices of TiO_2 crystal [56]. There are two vacant interstitial sites in which the extra cation could be accommodated in the rutile structure: (0 0.5 0) octahedral positions and (0 0.5 0.25) tetrahedral sites [57]. The incorporation of Si atom in octahedral positions is represented in Scheme 2(b), where the inset clearly reveals the coordination state of Ti-atom. The incorporated Si atoms in tetrahedral position of rutile are ascribed in the Scheme 2(c). When Si^{4+} replaces Ti^{4+} into the anatase crystal structure substitutionally and randomly, the lattice parameters and unit cell volume decrease slightly. The parameter a decreases only slightly from 0.3782 to 0.3781 nm, and c decreases from 0.952 to 0.9405 nm [58]. Scheme 2(d) represents the Si atom incorporation substitutionally at some random places into the anatase crystal.

Scheme 2. Pictorial representation of Si incorporation in the crystal structure of titania phases. Ball and stick model of (a) rutile, Si- atom incorporation in (b) octahedral positions, (c) tetrahedral positions of rutile. (d) Substitution of Ti atom by Si atom in some positions of anatase. Insets clearly represent the coordination state of titanium atom when Si is incorporated.

Single column image, 500 dpi, image width 90 mm

3.4.2 Polyphenol interaction with TiO_2 Nanoparticles

The main constituent of green tea is polyphenols, predominantly the catechins. Out of catechins, EGCG is the main polyphenolic component found which interacts via its hydroxyl group with TiO_2 surface [29-31]. It is also evidenced by FTIR data, figure 2(a3, b3), where the peak of metal oxide bond was found to be shifted towards lower wavenumber that points to the weakening of Ti-O bond of TiO_2 nanostructure. This weakening of bond clearly illustrates that Ti-O bond in TiO_2 gets elongates/weakens up presumably due to some chemical interaction with hydroxyl groups of the green tea component. EGCG is found to interact with those hydroxyl groups which are less bulky and are present at meta position to each other, as shown in Scheme 3.

Scheme 3. Pictorial representation of the chemical interaction between EGCG, a polyphenol and TiO_2 surface.

Single column image, 500 dpi, image width 90 mm

3.5 Optical Property Determination

Figure 7 represent the UV-Vis spectra of coated (with silica and polyphenol) and bare TiO_2 phases prepared at the two annealing temperatures. In figure 7(a), all the three forms of anatase i.e. bare, silica coated and polyphenol coated, show an absorbance at 251 nm, whereas in coated forms blue shift is also noticed at 224 nm

for silica and at 221 nm for polyphenol that may be accounted for the variation in the particle size. In case of anatase_polyphenol, the absorbance at 221 nm depicts higher blue shift as compared to the absorbance at 224 nm in anatase_silica. Figure 7(b) portrays the UV-Vis absorbance spectra of all the three forms of rutile i.e. bare, silica coated and polyphenol coated. All of three forms show the peak at 256 nm which is found to be red shifted as compared to corresponding anatase forms, figure 7(a), because of increase in particle size at higher annealing temperature. The silica coated rutile validates absorbance at 287 nm which is red shifted as compared to bare rutile and polyphenol coated show the absorbance at 221 nm which is blue shifted. Obviously, the red shifted peak is because of increase in the size of rutile_silica. The similar peak at 251 nm in case of both bare and coated forms of anatase and at 256 nm in bare and coated rutile form clearly indicate no change in optical property which is found to be in agreement with the result obtained by Gass et.al. [17].

Figure 7. UV-Vis spectra of (a) anatase phase, (b) rutile phase, (c) fresh polyphenol solution, (d) oxidised polyphenol solution.

Single column image, 500 dpi, image width 90 mm

Absorbance peak at 275 nm as shown in figure 7(c) may correspond to $\pi \rightarrow \pi^*$ transition in case of freshly prepared polyphenol solution. Though, another peak at 334 nm can also be noticed when polyphenol solution undergoes oxidation. The reddish colour of this oxidised solution contributes to the formation of thearubigin, figure 7(d).

3.6 Photo-catalytic and -luminescence study of Anatase

3.6.1 Bare Anatase

The photocatalytic activity of anatase nanoparticles was assessed by analyzing the photo-degradation of MO solution & then confirmed by PL spectra. Figure 8(a₁₀) illustrates spectrum of MO degradation with anatase phase as photocatalyst under UV light irradiation at various time intervals. The UV-Vis absorption spectrum of MO solution with initial concentration 0.153 mg l⁻¹, shows a broad band at 464 nm which corresponds to $\pi \rightarrow \pi^*$ transition [59]. In PL spectrum, the three peaks are observed at 334, 394 and 524 nm in case of bare MO solution as represented in the inset of figure 8(a₂₁). Upon UV exposure for 30 min, electrons and holes get separated out and are available at the surface of catalyst to carry out degradation. At this time interval, PL emission spectrum shows no sharp peak supporting complete photodegradation and negligible exciton recombination as illustrated in Fig. 8(a₁₁). As we know that when a photocatalyst is illuminated by UV light with energy equal to or greater than the band gap energy, the valence band (VB) electrons can be excited to conduction band (CB), leaving positive holes into the VB and electrons to the CB which then helps to degrade the methyl orange dye solution and thus the negligible number of excitons are undergoing recombination resulting in the minimum PL intensity. At 60 min of UV irradiation, the characteristic absorption peak intensity decreases. This decrease was not accompanied by the existence of new peaks or any shift in the spectral location of peaks. The PL emission also shows peak however with moderate intensity indicating that phenomenon, PL and photodegradation, occur simultaneously. Here, excitons are separated out resulting in photodegradation, at the same time exciton recombination also occurs. But the trend seems peculiar after 60 min or second exposure. The photocatalytic activity, instead of increasing, deteriorates at 120 min that is because of deactivation of catalyst. The catalyst deactivation may occur to some extent due to the formation of number of degraded fragments of MO at the catalyst surface that block the active site of catalyst and also that solution become concentrated which scatters the UV light instead of transmitting through the solution [60]. It causes hindrance for further photodegradation [61]. So, in this case photodegradation is reduced whereas PL emission shows

Figure 8. Photo-catalytic and -luminescence spectra of anatase nanoparticles. UV-Vis spectra of photodegradation of methyl orange dye by anatase (a_{10}), anatase_silica (a_{20}), anatase_polyphenol (a_{30}) at various time durations. PL spectra of these samples have also been depicted. (a_{11}), (a_{21}) and (a_{31}) showing the PL characteristics of anatase, anatase_silica and anatase_polyphenol, respectively. Inset in (a_{21}) represents the PL spectrum of methyl orange at $\lambda_{ex} = 300$ nm. Y-axes are same in all PL spectra showing PL intensity.

1.5 column image, 500 dpi, image width 140 mm

highest peak corresponding to the recombination of generated excitons. Also, blue shift was noticed in PL from 404 nm (at 60 min) to 394 nm (at 120 min).

3.6.2 Anatase_silica

The photocatalytic degradation of MO dye by anatase_silica shows a sharp decrease in absorbance at 0 min as compared to pristine MO solution that may be because of inter/intra chain interactions [62] of the catalyst with MO. As UV exposure is applied, the overlapping absorbance curves can be observed

with various time irradiations which clearly reveal that the silica coating is uniform which helps to inhibit the photocatalytic activity of the catalyst. Silica is good radical scavenger and also its amorphous coating not only engulfs all the radicals produced by TiO_2 but also prevents its interaction with the surroundings. However, the degree of degradation is found to be less in all the cases as compared to bare anatase due to coating. So, the photocatalytic activity of TiO_2 remains almost same with increment in time as shown in the figure 8(a₂₀). To understand the fate of photogenerated charge carriers, PL spectrum has been employed at excitation wavelength of 300 nm which illustrated decreasing trend with increasing irradiation time indicating the electrons and holes generated are solely engaged in degradation and not in exciton generation leading to drop in PL emission as shown in figure 8(a₂₁).

3.6.3 Anatase_polyphenol

The photocatalytic degradation of MO dye by anatase_polyphenol represents no change when catalyst is added in the MO solution at 0 min (without UV irradiation) instead it traces the absorbance path of MO solution as represented in Figure 8(a₃₀). After that the trend was found peculiar. The absorbance suddenly increases on 30 min exposure of UV rays corresponds to least photocatalytic activity that is found to be in agreement with highly compact and refined morphology of these nanoparticles (as indicated in figure 3(a₃)) which does not allow the photodegradation. However, in case of PL (figure 8(a₃₁)), the peak position was same but the peak intensity decrease which is not in agreement with the photodegradation result. The reduction in both, PL intensity and photocatalytic activity, can be explained by the repelling/suppression of photoexcited electrons from polyphenol species to anatase domains because of electron donating tendency of polyphenols that results in charge separated state [32, 63]. At 60 min of UV exposure the absorbance decreases and thus helps in photocatalytic degradation. This shows that prolonged UV irradiation time (around 60 min) is required to enhance the photocatalytic activity of anatase_polyphenol due to its compact morphology. However in the PL peak, the peak intensity becomes highest keeping its position same which shows that there is definitely some change in the electronic structure of catalyst [64] which leads to exciton recombination. It is expected that after 60 min of exposure, surplus excitons are generated which due to accumulation supports photocatalysis as well as recombination. Although at 120 min of UV exposure, the absorbance rises and photodegradation diminishes that may be because of non availability of the catalyst surface owing to the degraded fragments of dye. The PL results are in agreement with the photodegradation result that the excitons are utilised to produce radicals instead of getting recombined

in 120 min of UV exposure. Here, blue shifting is noticed. In all the cases, it is also noticed that the absorbance peaks are narrower and even sharper than bare- and silica coated- anatase due to compact morphology leading to surface modification, as evident from the microstructures, figure 3(a3).

3.7 Photo-catalytic and -luminescence study of Rutile

3.7.1 Bare Rutile

In case of bare rutile, the trend is quite reasonable. Till 30 min exposure of UV-light, the absorbance

Figure 9. Photo-catalytic and -luminescence spectra of rutile nanoparticles. UV-Vis photocatalytic degradation of MO dye by bare rutile (b₁₀), rutile_silica (b₂₀) and rutile_polyphenol (b₃₀) at various time irradiation. PL spectra at the excitation wavelength of 300 nm are elucidated in (b₁₁), (b₂₁) and (b₃₁) by bare, silica coated and polyphenol coated rutile, respectively. The inset represented in (b₂₁) shows the PL spectrum of MO dye.

1 peak decreases with time, as shown in figure 9(b₁₀) which is quite expected. Whereas the PL emission
2 peaks, as depicted in figure 9(b₁₁), are also found to decrease till 30 min of UV exposure showing that
3 the photocatalytic activity favours in that interval of time. Whereas, after 30 min the absorbance peak
4 increases that can be explained as with prolonged interval of time the degradation of MO becomes
5 lower leading to the blocked active surfaces of catalyst due to degraded fragments and thus there occurs
6 no significant photocatalytic activity. In this case, the absorbance peaks other than the peak in pristine
7 MO peak, are quite overlapped and quite diminished. However, the absorbance peak decrease very
8 sharply as catalyst is added to the pristine MO solution without UV illumination as represented in figure
9 9(b₂₀). But PL emission peaks show enhanced intensity after 30 min leading to the recombination of
10 excitons generated. The peak intensity varies but the peak positions remain same, at 400 nm. However,
11 the absorbance of pristine MO when catalyst is added under no UV light is found higher in case of bare
12 rutile than its corresponding anatase phase which is obvious as anatase has higher photocatalytic
13 activity than rutile.
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27 *3.7.2 Rutile_silica*

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30 In this case, the absorbance peaks other than the peak in pristine MO peak, are quite overlapped and
31 quite diminished. However, the absorbance peak decrease very sharply as catalyst is added to the
32 pristine MO solution, Fig. 9(b₂₀), without UV illumination. This decrease in the absorbance was found
33 to be more prominent in this case in contrast to the its corresponding anatase phase. Here, it is observed
34 that the PL spectrum peaks indicate the rate of recombination is higher than the rate of
35 photodegradation that is because of coated surface of rutile, figure 9(b₂₁). Our result of reducing the
36 photodegradation of MO dye by coating the rutile form with silica is in correlation with the already
37 reported results in literature [65].
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47 *3.7.3 Rutile_polyphenol*

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50 The increment in photodegradation of MO with increase in UV irradiation till initial period of 60 min is clearly
51 noticed as depicted in figure 9(b₃₀). The absorbance peak decreases after 30 min of UV irradiation in
52 comparison to 0 min. The PL emission peak can also be noticed during this time interval indicating generation
53 of exciton that supports in e⁻-h⁺ separation (photocatalysis) as well as mild recombination. At 60 min of UV
54 exposure, it seems that exciton generation is reduced (in comparison to exposure at first 30 min) leading to less
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photodegradation as well as negligible PL. That may be because of excess fragments owing to the degradation of MO, scattering the exposed UV rays. Further, after prolonged UV irradiation (for 120 min), PL emission favours. The reason is the non availability of the active sites at the catalyst surface and simultaneously the electron donating ability of polyphenol, may suppress the photodegradation thereby enhancing photorecombination similar to anatase_polyphenols. Here, the porous surface morphology represented in figure 3(b3) provides enough active sites for easier photocatalytic reaction. Thus it can be inferred that improved textural properties and efficient electron hole separation are the factors that are responsible for enhanced light photocatalytic activities. Here, the porosity leads to higher surface area that can result in more active and exposed sites for efficient photocatalytic activity.

3.7 A Comparison on photocatalytic performances of bare and coated-anatase & -rutile nanostructures

It can be discussed that in case of bare anatase, UV absorbance decreases at 30 min of UV illumination, which further decreases at 60 min of prolonged irradiation pointing to the higher photocatalytic activity at 60 min. But after that it exhibits negligible photocatalytic activity. This result is in agreement with PL results which shows highly intensified PL peak at 120 min that corresponds to higher recombination of photogenerated charge carriers, as shown in figure 8(a₁₁). Although, in case of its silica coated form, the absorbance peak decreases at 30 min and then increases at 60 min of UV irradiation which is clearly pointing towards the decrease in photodegradation of an organic dye. That may be due to the thick coating which helps to inhibit the ROS generation and thus photodegradation. This also correlates with PL spectrum that was found to be diminished as compared to its UV absorbance, figure 8(a₂₁), revealing the fact that silica coating not only prevent the radical generation but it also enhances the UV absorbance. Similarly in case of its corresponding polyphenol coated sample, the UV absorbance suddenly increases at 30 min and then sharply decreases at 60 min of prolonged irradiation. The photocatalytic activity increases at 60 min of time because of some structure modifications as already examined by SEM analysis (Figure 8(a₃₁)). But that increment is not that sharp. So, in case of 60 min of illumination, the increase in absorbance in silica coated form is not that significant than the decrease in absorbance peak in case of bare anatase as compared with 0 min of UV irradiation. It clearly reveals that anatase has higher ability to generate ROS as compared to its other coating forms. Comparing the photoactivities of silica and polyphenol coated anatase, polyphenol stabilized form shows higher photocatalytic activity than its silica coated form that may be accounted due to some

structural/morphological changes and also due to thick coating of silica as compared to ultra-thin coating of polyphenol. To summarize these results, absorbance versus time graph for both the phases of TiO₂ nanoparticles have been plotted in figure 10. Now, the degradation by rutile as photocatalyst was examined. In case of its bare form, the absorbance curve decreases at 30 min but it rises at 60 min of UV irradiation which is in agreement with PL results as depicted in Figure 9(b₂₁). In its silica coated form, the UV curve rises which then decreases at 60 min of the time duration evincing its higher photocatalytic activity but it is not that significant as compared to its corresponding absorbance peak at 0 min of UV light irradiation. Whereas, in its polyphenol stabilized form, the absorbance reduces which again decreases at 60 min of UV irradiation and thus a significant alter in the absorbance peak magnitude is observed when compared with its corresponding 0 min of light illumination.

Figure 10. Absorbance versus time graph for (a) anatase and (b) rutile phase of titania nanoparticles. Color code: Black (square) represents bare, red (circle) elucidates -silica coated, and blue (triangle) shows -polyphenol coated samples.

Also, as seen in the microstructure, figure 3(b3), its surface morphology points to its porosity which enhances its photocatalytic activity. To compare the photocatalytic activity of bare and silica coated rutile forms, bare rutile nanoparticles were found to demonstrate higher photodegradation activity because there occurs sharp increase in UV peak as compared to its silica coated form that evince no significant change in its UV absorbance curve when compared the graph at 0 and 60 min of UV illumination. So, rutile_polyphenol evinces highest photocatalytic activity among the rutile forms.

The obtained results are summarized in Scheme 4.

Scheme 4. Pictorial representation of the summarized results.

Single column image, 500 dpi, image width 90 mm

4. Conclusions

In this study, nano-sized anatase and rutile TiO_2 particles have been well synthesized by varying the post annealing temperatures and subsequently coated with inorganic (silica) and organic (green-tea) layer, separately by simple and efficient wet chemical method. Various characterization techniques affirm the formation of each of the phases of bare and core_shell (TiO_2 _silica/polyphenol) titania. The microscopy images confirm the thickness of coating with silica shell that was found to be about 80 and 20 nm over anatase and rutile nanocluster, respectively. The thickness of polyphenol shell was found to be 3 nm over anatase core. Surface modification of titania nanoparticles using organic moiety, green-tea, has various advantages including biocompatibility, most abundant and cheaper which has not been studied in previous literature. The plausible mechanism of chemical interaction takes place with silica

and polyphenol species on titania surface has been interpreted and correlated with FTIR spectroscopy. The photodegradation of methyl orange dye by nanoparticles was studied and compared with their corresponding PL spectra. The results ascribe that silica coated -anatase and -rutile was found to be least photocatalytically active, ensuring their cosmetic application in sunscreens, whereas rutile_polyphenol and bare anatase discerns highest photocatalytic activity among their corresponding forms explore a wide research area including photodegradation of various dyes.

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