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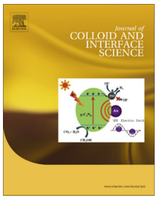

Interactions of titania based nanoparticles with silica and green-tea: Photo-degradation and -luminescence

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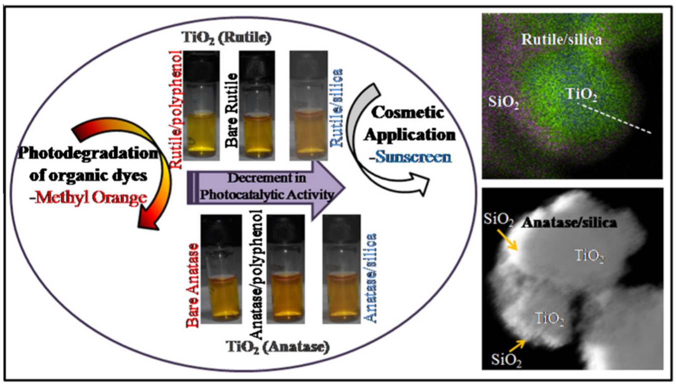
GRAPHICAL ABSTRACT

Anatase and rutile nanoparticles (40–100 nm) were coated with ultra-thin layers of green-tea and silica, as confirmed by XRD, FTIR and TEM. Anatase_silica showed lowest whereas, rutile_polyphenol demonstrated highest photocatalytic activity among their corresponding forms when methyl orange dye was used as a model. Results were found to be in agreement with photoluminescence spectra.



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ABSTRACT

An effective way to modify the photocatalytic activity of both anatase and rutile TiO_2 nanoparticles by coating the surface with either an inorganic (SiO_2/silica) or organic (green-tea) layer using a chemical approach is demonstrated. Tetraethyl orthosilicate (TEOS) was used to cover the surface of TiO_2 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 TiO_2. 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 TiO_2 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.

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1. Introduction

TiO_2 (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 TiO_2 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 behavior is undesirable. It is reported that irradiation of UV light on TiO_2 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 SiO_2, Al_2O_3, ZrO_2, WO_3, MoO_3 [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, it is used for "green" synthesis of nanoparticles [25]. Green tea also is antimutagenic, anti-inflammatory, antibacterial, antiproliferative and has strong natural antioxidant properties that are known to protect the skin from UV damage and prevent cellular damage caused by ROS generation [26,27]. Green tea is characterized by high content of catechins, a sub-class of flavan-3-ol (a flavonoid), having 20 times more potent antioxidant property than vitamin C in the lipoprotein oxidation model [28]. In general, the main constituent of green tea extract is polyphenols, predominantly the catechins [29–31]. The four major catechins are: (i) epicatechin (EC) (ii) epicatechin gallate (ECG) (iii) epigallocatechin (EGC) and (iv) epigallocatechin gallate (EGCG). Of the catechins, the main component found in green tea is EGCG [32]. EGCG contributes to the overall protection of cell integrity and immune function and also suppresses the growth of cancerous cells [24,33]. EGCG is not only the good antioxidant but it also promotes anti-aging, anti-acne and anti-inflammatory effects, so it is an attractive component for use in cosmetics [34]. Green tea extract enhances the activity of enzyme superoxide dismutase (SOD) which helps to quench the excess superoxide radicals, peroxyl radicals, singlet oxygen and thus helps inhibiting the premature aging [35,36]. It is approximately 99% water, so it helps to maintain hydration, makes an important contribution to daily fluid requirement and thus helpful to remove the waste product from the body [37]. Also, the antioxidant action of polyphenols, found in green tea, is known to increase the antioxidant capacity of blood [38]. Thus, green tea extract was expected to be an attractive material for modifying the surface of photocatalysts [25,39].

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

2. Experimental section

2.1. Chemicals used

The chemicals used in the synthesis of TiO_2 nanoparticles were titanium tetra isopropoxide (TTIP, $Ti(OCH(CH_3)_2)_4$, LR, 98%, Spectrochem Pvt. Ltd., India), Absolute ethanol (C_2H_6O, AR, 99.9%, S D Fine-Chem Ltd., India), Methanol (CH_3OH, HPLC grade, AR, 99.8%, Rankem, India).

For coating with silica, polyvinyl alcohol (PVA, LR, 75%, Central Drug House Pvt. Ltd., India), ammonia solution (NH_3, LR, 25%, Rankem, India), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, 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.

2.1.1. 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 TiO_2. The produced white product was characterized by various characterization techniques.

2.1.2. Synthesis of titania_silica nanoparticles

0.5 g of obtained TiO_2 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 TiO_2 nanoparticles. The obtained PVA coated nano-sized TiO_2 (1 g) were dispersed in 5 ml ethanol and 1.5 ml ammonia solution. Then the solution