JMMS

Journal of Material and Metamaterial Sciences

Vol. 1, No. 1, January 2025, pp. 7-12, DOI: 10.59190/jmms.v1i1.293

PUBLISHED BY

LSPRAR

Nano rod-shaped core-shell TiO_2-SiO_2 coating exhibiting superior self-cleaning capabilities under visible light: A review

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ABSTRACT

Titanium dioxide (TiO_2) is a photocatalytic material widely used in self-cleaning applications due to its ability to decompose organic compounds with free radicals under UV irradiation. However, its limitations in stability and efficiency make it necessary to combine with other materials such as silicon dioxide (SiO_2). This combination forms a core-shell structure where TiO_2 becomes the active core, while SiO_2 acts as a shell that improves stability, extends the absorption spectrum to visible light, and reduces particle agglomeration. This study examines the synthesis and characterization of rod-shaped TiO_2-SiO_2 core-shell nanoparticles that have superior self-cleaning ability under visible light. The synthesis was carried out using a modified hydrothermal method. Structure analysis using SEM showed uniform particle distribution, while XRD analysis confirmed the presence of anatase phase in TiO_2. Self-cleaning evaluation was performed through methylene blue degradation and water contact angle measurement. Results show that this core-shell layer has better photocatalytic activity and hydrophilic properties than pure TiO_2. With these characteristics, this material has great potential to be applied in environmental purification, waste treatment, and renewable energy technologies.

ARTICLE INFO

Article history:

Received Nov 8, 2024
Revised Dec 11, 2024
Accepted Jan 14, 2025

Keywords:

Core-Shell
Photocatalytic
Self-Cleaning
TiO_2-SiO_2
Visible Light

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1. INTRODUCTION

Self-cleaning materials are crucial in numerous applications, particularly for surfaces susceptible to contamination, including building glass, mirrors, solar panels, and optical devices. Titanium dioxide (TiO_2) is a substance extensively utilised in self-cleaning technology due to its superior photocatalytic properties. TiO_2 exposed to ultraviolet (UV) radiation generates free radicals capable of decomposing organic molecules, rendering it an efficient material for self-cleaning applications. Nonetheless, the performance of TiO_2 requires enhancement, particularly regarding stability and efficiency [1].

A technique to enhance the self-cleaning efficacy of TiO_2 is to amalgamate it with silicon dioxide (SiO_2). This combination may exhibit a synergistic impact, with SiO_2 functioning as a support framework that enhances the stability of the TiO_2 structure, diminishes particle agglomeration, and enlarges the active surface area. Furthermore, the incorporation of SiO_2 can enhance pore distribution and particle size, directly influencing the photocatalytic activity and hydrophobic characteristics of the material. The combination of TiO_2 with silicon dioxide (SiO_2) produces a core-shell structure. Analysis by SEM and XRD reveals that rod-shaped TiO_2 possesses a thin, skin-like layer when combined with SiO_2 [1].

Core-shell nanoparticles, especially those based on TiO_2-SiO_2, have garnered attention in materials research for their potential in photocatalytic and optoelectronic applications. In core-shell systems, TiO_2 generally functions as the photocatalytically active core, whereas the SiO_2 layer serves as a shell that confers stability and improved surface characteristics. This core-shell architecture not only prolongs the photocatalyst's lifespan but also facilitates enhanced activity under more ecologically benign illumination, such as visible light [2].

The distinctive characteristics of the SiO_2 layer on the TiO_2 surface facilitate less electron-hole recombination and enhanced light absorption efficiency within the visible light spectrum. Recent research indicates that this core-shell structure can yield photocatalysts that exhibit enhanced stability, activity, and resistance to decomposition during the photocatalytic cycle, rendering them a promising choice for applications in water purification, waste treatment, and renewable energy conversion [2].

2. THEORITICAL REVIEW

2.1. Core-Shell Structure

Core-shell materials consist of a central material (core) enveloped by an exterior layer (shell) that is either physically or chemically distinct. This shape has multiple distinct benefits, including as enhanced stability, favourable surface functionality, and improved reactivity control. Core-shell materials are extensively utilised in self-cleaning technology to enhance photocatalytic, superhydrophobic, and durability characteristics, essential for maintaining surfaces free from dirt and contaminants. The core-shell structure often characterises the surface of catalyst particles composed of Pt and can be categorised into three forms: Pt shell, Pt monolayer, and nanoporous framework. A core-shell structure consists of a spherical core composed of a specific compound encased by an outer layer of a different component [3].

2.2. Autocleaning Capability

Self-cleaning refers to a surface or material's capacity to autonomously eliminate dirt, dust, or other particulates without human intervention. This method is utilised on materials including glass, fabrics, paints, and ceramics. The self-cleaning feature is extensively utilised in daily life as it diminishes the necessity for manual cleaning and enhances maintenance efficiency. The self-cleaning functionality operates through the physical and chemical features of the materials employed, relying on two fundamental principles: the lotus effect and photocatalysis [4].

2.3. TiO_2-SiO_2 Composite

TiO_2 is a white pigment chemical utilised as a dye additive, semiconductor, and photocatalyst. TiO_2 can be utilised to mitigate waste through the photodegradation process employing UV radiation and visible light. TiO_2 is acidic, insoluble in water, robust to high temperatures, and has excellent light scattering properties. Despite its excellent stability, TiO_2 possesses a relatively low electrical value and limited energy storage capacity, leading to its frequent combination with other chemicals.

SiO_2 is a chemical compound consisting of silicon and oxygen. In microsystems, SiO_2 serves as a dielectric in capacitors and transistors, functioning as an insulator to separate electronic components. SiO_2 occurs naturally as a prevalent form of crystalline silica, utilised primarily as the fundamental material for glass production due to its clarity and durability. In the crystalline state, atoms are systematically organised in a three-dimensional configuration, whereas in the amorphous state, they are grouped haphazardly [5].

The TiO_2-SiO_2 composite integrates TiO_2 and SiO_2 materials to harness the advantageous features of each. This union can yield photocatalytic capabilities that are superior and more stable than those of TiO_2 alone. The photocatalytic capabilities of this composite are highly effective in degrading pollutants, as it may eliminate hazardous compounds or microbes in water and air when exposed to UV radiation, thereby purifying the environment. An anti-contaminant surface coating applicable to glass or ceramics.

This TiO_2-SiO_2 combination generates rod-shaped nanostructures and exhibits a core-shell configuration, demonstrating superior self-cleaning capabilities under visible light. Rod-shaped TiO_2-SiO_2 nanoparticles exhibit significant photocatalytic activity under UV and visible light [5].

3. RESEARCH METHODS

3.1. Scanning Electron Microscopy Examination

Scanning electron microscopy (SEM) is an analytical method employed to examine the surface morphology of materials with high resolution. SEM is a multivariate statistical analysis technique. SEM can enhance data processing through statistical analysis utilising various methods or software. SEM can generate images with exceptional resolution (up to 1 nm), enabling the observation of surface details and the analysis of the sample's elemental composition. SEM operates through repeated scans, allowing it to produce a three-dimensional representation of the sample surface, which is invaluable for examining surface morphology and structure. SEM is an analytical method that integrates factor analysis, structural modelling, and path analysis techniques. In SEM, three activities occur concurrently: verifying the instrument's validity and reliability (confirmatory factor analysis), examining the relational model between variables (path analysis), and deriving a model suitable for prediction (structural model and regression analysis) [6, 2]. SEM operates by directing a high-energy electron beam onto the sample's surface. Upon collision with the surface, the electrons generate secondary and backscattered electrons, which are subsequently detected. In the investigation of nano rod-shaped TiO_2-SiO_2 core-shell layers, SEM was employed to ascertain the morphology of the core-shell layer and to verify the distribution of the carving and nano-rods, assessing the quality and uniformity of the TiO_2-SiO_2 coating [2].

In the investigation of nano rod-shaped TiO_2-SiO_2 core-shell coatings, SEM was employed to ascertain the morphology of the core-shell structure, verify the distribution of the carving, delineate the shape of the nano rod, and assess the uniformity of the TiO_2-SiO_2 coating quality [7].

3.2. X-Ray Diffraction Analysis

X-ray diffraction (XRD) is an analytical technique that determines the structure of both crystalline and non-crystalline materials. Advanced XRD offers insights into strain, roughness, crystal symmetry, and electron density. When radiation interacts with a solid, coherent scattering by dispersed atoms generates a scattering beam that creates the speckle pattern characteristic of a polycrystalline sample. The operational principle of the XRD instrument is based on the Bragg principle, which posits that the variation in the path of the XRD beam must be an integer multiple of the wavelength, expressed by the formula $n\lambda = d\sin\theta$, where n represents an integer, λ denotes the X-ray wavelength, d signifies the interplanar distance, and θ indicates the diffraction angle [5].

XRD occurs when X-rays interact with a crystalline sample, resulting in the reflection and diffraction of some X-rays by the atomic layers inside the crystal structure. The resultant diffraction pattern is contingent upon the interlayer distance within the crystal, known as the crystal plane spacing (d-spacing). The pattern is subsequently measured, and the acquired data is utilised to ascertain the crystal structure of the substance. Bragg's Law governs this process, asserting that diffraction transpires when the X-ray wavelength (λ) fulfils the equation: $n\lambda=2d\sin(\theta)$ [5]. In the investigation of nano rod-shaped TiO_2-SiO_2 core-shell layers, XRD serves to ascertain the crystalline phases of TiO_2 (anatase, rutile, or brookite) and SiO_2 (amorphous or crystalline) while assessing the interaction between the TiO_2 and SiO_2 layers inside the core-shell architecture [7].

3.3. Synthesis of Core-shell TiO_2-SiO_2 Nanoparticles

Core-shell rod-shaped TiO_2-SiO_2 nanoparticles were synthesised using a modified low-temperature hydrothermal technique in an aqueous solution. The researchers synthesised TiO_2-SiO_2 nanoparticles by combining $TiCl_4$ with ice water and stirring for several minutes to guarantee complete hydrolysis of $TiCl_4$. The pH of the system was subsequently adjusted to 8-9 using aqueous ammonia. This procedure will eliminate Cl- through washing with distilled water; the resulting precipitate is suspended in water, and H_2O_2 is introduced under agitation to yield a peroxotitanium acid solution. The produced peroxotitanium solution was placed in a flask, followed by the addition of SiO_2 and TEOS to the ethanol and H_2O combination while stirring, and heated to 50°C for 2 hours. A specified quantity of KBr was introduced and heated at 100°C for two hours one day. The rod-like TiO_2 nanorods-nanoparticles core-shell SiO_2 were obtained using centrifugal separation, subsequently rinsed five times with deionised water, and then re-dispersed in ultrapure water to create a suspension of core-shell TiO_2-SiO_2 nanoparticles [7].

3.4. Self-Cleaning Evaluation of TiO_2-SiO_2 Nanoparticles under Visible Illumination

The self-cleaning characteristics were evaluated using the photocatalytic degradation of methylene blue (MB) in an aqueous solution and methyl stearate (MS) on the coated surface under visible light. A fragment of a quartz crucible containing glass covered with rod-like TiO_2-SiO_2 nanoparticles was subjected to irradiation with visible light of wavelength (λ) > 400nm produced by a lamp 400 W metal with a cut-off filter. The degradation of MB by the coating was assessed by recording the UV-Vis spectra of the MB solution at the highest absorbance of 665 nm. The surface of the coating was modified for methyl stearate, which was subsequently dissolved in n-hexane and applied to the rod-like TiO_2-SiO_2 nanoparticle coating using the dip coating method. Contaminant samples were exposed to visible light at a specific wavelength (λ) on the glass surface at consistent intervals until a stable contact angle was attained. This procedure is laborious due to the gradual degradation rate. The contact angle of the water droplet is assessed at five distinct locations on the sample [7].

3.5. Examination of TiO_2-SiO_2 Nanoparticles by SEM

SEM was conducted using a Hitachi S-4300 scanning electron microscope at an operating voltage of 10 kV. For SEM examination, samples were prepared by depositing a drop of dispersion onto a carbon-coated Cu grid and permitting it to air dry. Rod-shaped TiO_2-SiO_2 nanoparticles were synthesised using the hydrolysis of $TiCl_4$ and TEOS. SEM of coatings formulated from rod-shaped TiO_2-SiO_2 nanoparticles (nanorods) was conducted following the implementation of the cross-cutting test. The rod-shaped nanoparticles (nanorods) can be uniformly spread on the substrate surface [7].

4. RESULTS AND DISCUSSIONS

4.1. Self-Cleaning Evaluation of TiO_2-SiO_2 Nanoparticles under Visible Illumination

The outcomes of the self-cleaning assessment are illustrated in Figure 1. Figure 1 (a) illustrates the absorption spectra within the wavelength range of 400-800 nm during the self-cleaning test process under visible light, observed throughout a time interval of 30 minutes to 6 hours. The peak at around 664 nm exhibits the distinctive peak of MB. The reduction in intensity of this peak signifies that MB is progressively degraded over the visible light irradiation period, indicating the efficacy of the photocatalytic mechanism responsible for the degradation of the MB solution. Figure 1 (b) illustrates the graph of the methylene blue (MB) concentration ratio (C/C0) with irradiation time, where C0 represents the beginning concentration of MB and C denotes the concentration of MB at a specific time. Two graphs represent the irradiation conditions of UV and visible light, illustrating an exponential decline in C/C0, which indicates that MB degrades more rapidly under UV irradiation compared to visible light. This signifies that the photocatalyst exhibits enhanced activity under UV light. Figure 1 (c) illustrates the variation in water contact angle on the TiO_2-SiO_2 nanoparticle layer's surface as a function of visible light irradiation duration. The reduction in contact angle from around 90° to almost 30° signifies the hydrophilic characteristics of the material surface post-irradiation. This suggests that the surface exhibits increased water-wettability due to photocatalytic alteration, maybe resulting from the elimination of organic pollutants or the development of hydrophilic groups on the surface [7].

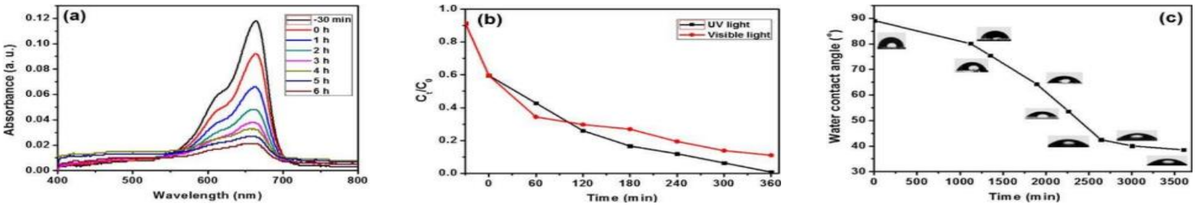

Figure 1. (a) time-dependent UV-vis absorption spectrum alterations of aqueous MbB and TiO_2-SiO_2 nanoparticle coating under visible light, (b) graph of C_t/C_0 versus irradiation duration, and (c) variation in water contact angle of the MS-coated rod-like TiO_2-SiO_2 nanoparticle coating versus visible light irradiation duration.

4.2. Outcomes of SEM Analysis of TiO2-SiO2 Nanoparticles

Figure 2. (a) illustrates that at a lower magnification, the overall distribution of nanoparticles reveals rod-shaped structures evenly dispersed across the surface. The scale of 200 nm confirms that these structures are at the nanometre scale, consistent with the characteristics of nanoscopic materials. In contrast, Figure 2 (b) presents a higher magnification view, where the rod structures are more distinctly visible, with a defined scale of 50 nm indicating that each rod possesses nano dimensions with specific length and diameter, highlighting the unique properties of the material post-annealing. Utilisation of self-cleaning in the uniformity of nanorods as a foundation for the fabrication of high-quality coatings. To enhance the transparency of the coating, the nanorod dimensions must be less than λ/4 of the incident light. The average diameters of the nanorods, as determined by the study of TEM images, are around 110 nm and 9.2 nm, respectively [7].

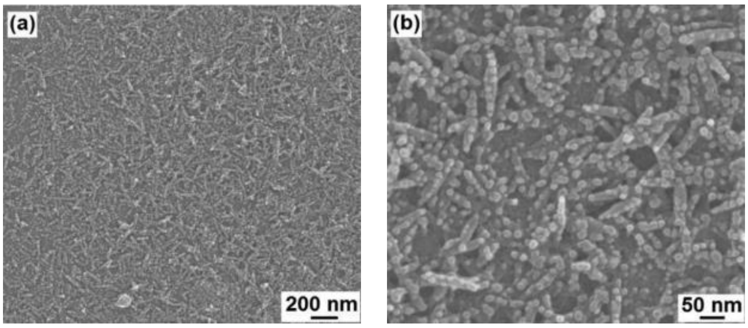

Figure 2. Present SEM images for (a) 200 nm and (b) 50 nm depicting a rod-like TiO_2-SiO_2 nanoparticle layer subsequent to heating at 200°C.

4.3. Analysis Results of TiO_2-SiO_2 Nanoparticles by XRD

The crystallinity of the lattice fringe of TiO_2-SiO_2 nanorods was assessed using HRTEM and XRD. The periphery of TiO_2 nanorods was examined using chosen area electron diffraction patterns, confirming that TiO_2 is crystalline. The indexed diffraction peaks correspond to the anatase phase of TiO_2, demonstrating its anatase composition. The presence of SiO_2 does not inhibit the growth of rod-shaped TiO_2, resulting in the formation of both crystalline and anatase phases [7].

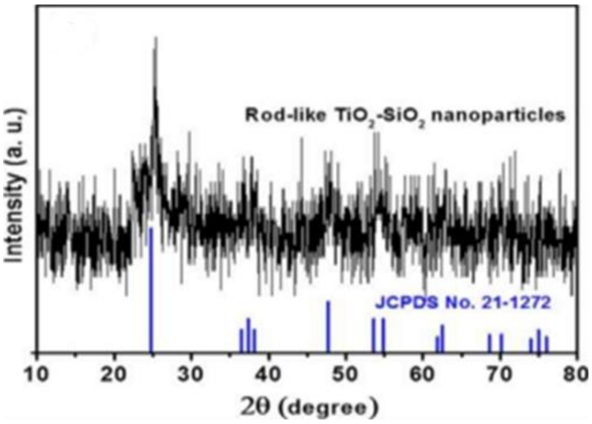

Figure 3. Results of XRD pattern analysis for synthesised rod-like TiO_2-SiO_2 nanoparticles.

Figure 3 above illustrates the XRD pattern and bar-shaped TiO_2-SiO_2 nanoparticles. The pronounced peaks observed in the graph signify that the material possesses crystallinity characteristics known as diffraction peaks. The diffraction peaks in this XRD pattern corresponded with JCPDS reference No. 21-1272, confirming that the predominant phase is anatase for TiO_2. The XRD pattern indicates a fusion of TiO_2 and SiO_2. Typically, amorphous SiO_2 does not exhibit distinct peaks in X-ray diffraction, whereas crystalline (anatase) TiO_2 does, as evidenced by this pattern. The breadth of the diffraction peaks signifies the diameter of the nanorods. Reduced diameters of nanorods will result in broader peaks as a consequence of the Scherrer effect. This signifies that the resultant nanoparticles are diminutive in size. This crystalline structure is significant for catalytic applications, particularly in photocatalysis, due to anatase TiO_2's elevated photocatalytic activity. The location of the diffraction peaks signifies particular crystal planes within the material's crystal structure. The peak at around 1100 cm-1 is attributed to Su-O and Ti-O stretching vibrations. The heating method of TiO_2-SiO_2 nanoparticles involved raising the temperature to 200° under air pressure using KBr. This influences the structural morphology of the rod-shaped TiO_2-SiO_2 nanoparticles and the index peak, which exhibits a width of approximately 3430 cm^{-1}, attributable to Si-OH, Ti-OH, and H-OH. A substantial quantity of -OH groups on the surface is crucial for the hydrophilicity of the self-cleaning coating [7].

The rod-shaped TiO_2-SiO_2 nanoparticle coating exhibits elevated optical transmittance in the ultraviolet and visible light spectra, achieving a maximum transmittance of 94% within the 400 – 800 nm range, whereas pure glass and the rod-like TiO_2 nanoparticle coating demonstrate transmittance levels of merely 90% and 87%, respectively, in the same spectrum. The TiO_2-SiO_2 nanoparticle-coated glass exhibits a 4% enhancement in anti-reflective properties compared to pure glass. The hardness of adhesion quality is classified using a numerical scale from 0 to 5. SEM and microscopy observations reveal that the edge of the smooth specimen lacks disconnected lattice boxes (classified 0), signifying that the TiO_2-SiO_2 nanoparticles are securely affixed to the glass surface. The results indicate that rod-shaped TiO_2-SiO_2 nanoparticles have superior performance under visible light, as demonstrated by their optical, mechanical, and photocatalytic, making them highly applicable in daily life [7].

5. CONCLUSION

The amalgamation of TiO_2 and SiO_2 produces core-shell rod-shaped TiO_2-SiO_2 nanoparticles exhibiting superior self-cleaning characteristics and higher photocatalytic efficacy under visible light. The SiO_2 shell covering on the TiO_2 core broadens the absorption range in the visible light spectrum, allowing these nanoparticles to harness visible light energy more effectively than pure TiO_2. The interaction between TiO_2 and SiO_2 underscores the promise of core-shell nanoparticles for applications necessitating efficient photocatalysis under visible light.

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