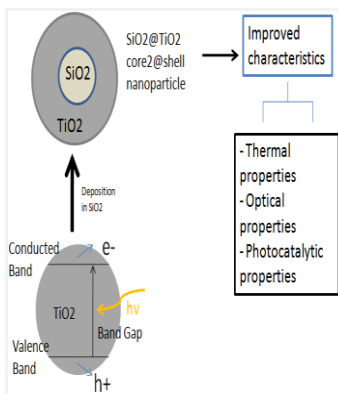


SiO₂@TiO₂ Core@Shell Photocatalytic Nanoparticles: Review on Fundamentals, Properties And Applications

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In heterogeneous photocatalysis, titanium dioxide has stood out for its high photocatalytic capacity. However, in an attempt to improve this process, TiO₂ is incorporated into other materials, such as SiO₂, in the form of layers in a structure known as core@shell. This structure improves the thermal, optical and photocatalytic properties of titania due to its incorporation into silica. In this work, we will present the fundamentals and the main synthetic routes for SiO₂@TiO₂core@shell nanoparticles, discuss their physicochemical properties and present some applications for this type of material.

Introduction

Heterogeneous photocatalysis is a set of photo-driven electrochemical reactions based on interactions between a photocatalyst, usually a semiconductor, and the fluid containing the reactants. The interaction between the photocatalyst and the light energy generates a series of physicochemical processes that lead to the formation of electron/hole pairs (e⁻/h⁺) that participate in redox reactions at the surface of the photocatalyst. The light energy received by the material is only effective in the photoexcitation process if it is at least equal to the bandgap (BG) energy of the semiconductor. Other factors such as light absorption capacity, crystallinity and particle morphology are fundamental to the efficiency of the material as a photocatalyst [1].

Titanium dioxide (TiO₂) is a prominent photocatalyst due to the photochemical stability and high photocatalytic efficiency. However, problems such as agglomeration of nanometric particles and heat treatments that reduce the surface area and cause crystalline phase transformation make it difficult to apply this material [2].

To overcome this problem, TiO₂ is combined in layers with other thermally stable materials with high surface area, such as silicon dioxide (SiO₂), in structures called core@shell [3]. In this work, we will discuss the fundamentals and synthesis strategies of SiO₂@TiO₂ core@shell structures, describe their properties, and present applications for this type of material.

Fundamentals of SiO₂@TiO₂ Core@Shell Particles

SiO₂@TiO₂Core@Shell nanoparticles are particles composed of an SiO₂corecoatedwith a TiO₂ shell.

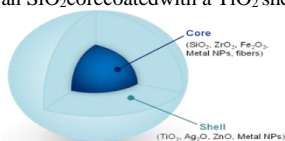


Figure 1. Core@shellparticle representation (Adapted from reference [4]).

SiO₂ is an excellent material for use as a core in core@shell systems due to several factors such as ease of synthesis and control of size and porosity, optical transparency at UV-vis wavelength, thermal and mechanical stability, and non-toxicity [1]. This combination improves the physicochemical properties of titania and consequently the photocatalytic effect of the particles.

The main methods for synthesizing SiO₂@TiO₂ particles include sol-gel processing of titanium alkoxides, thermolysis of titanium chloride salts, and liquid-phase deposition of titanium fluoride salts. In the first case, Si and Ti precursors are hydrolyzed to form oxides. SiO₂ particles are formed and then TiO₂ is deposited from its precursor. It is possible to control the kinetics, nucleation and deposition of materials by controlling the reaction parameters [1]. In the thermolysis technique, titanium (IV) chloride, a tetrahedral precursor that is highly hydrolyzable in the presence of water, forms octahedral monomeric species ([Ti(OH)₂(OH)₂]²⁺ or [TiO(OH)₃]²⁺) which, after thermohydrolysis (80-100 °C) or hydrothermal treatment (100-300 °C), leads to the nucleation of TiO₂ by oxolation or ololation in silica nanoparticles [5]. In liquid phase deposition, oxides or hydroxides are formed from metal fluoride salts hydrolyzed in the presence of boric acid, which is used to alter the equilibrium and accelerate the reaction, and are converted to TiO₂ by calcination [6].

Properties of SiO₂@TiO₂ Nanoparticles

The combination of SiO₂ with TiO₂ in the core@shell nanoparticle configuration improves the thermodynamic stability of titania, increases the size and surface area of the material, leads to better light scattering, and increases the photocatalytic effect of the particles.

Calcination at temperatures above 500°C in the preparation of TiO₂ nanoparticles is challenging because

the more photoactive anatase phase is rapidly and irreversibly converted to the less photoactive rutile [7]. However, when deposited on SiO₂, there is an increase in the thermal stability of anatase due to the combination of the SiO₂ induced formation of smaller, thermodynamically stable and better dispersed anatase nanocrystals, the restricted mobility on the SiO₂ surface due to the formation of interfacial Ti-O-Si bonds, and the interdiffusion of ions (Ti⁴⁺ and Si⁴⁺) between the TiO₂ and SiO₂ networks stabilizing the interface [8].

In terms of optical properties, the core@shell structure, consisting of a low refractive index core ($n_{\text{SiO}_2}=1.47$ at 385 nm) and a high refractive index shell ($n_{\text{TiO}_2}=2.49$), results in multiple scattering at the core/shell interface. This increases the optical path length and confines the light within the SiO₂@TiO₂ particles. This process leads to greater absorption of UV-vis radiation, which can be applied in the development of advanced photoactive materials and optical devices [4].

In terms of material size, TiO₂ nanoparticles are difficult to recover after use in aqueous media due to their small size, which makes separation by centrifugation inefficient. The use of SiO₂@TiO₂ particles improves this by increasing the size, surface area and adsorption capacity of the material, which facilitates removal after centrifugation and increases contact with the substances in solution [9]. These characteristics, in turn, increase the photocatalytic effect of the particles by ensuring a more photoactive crystalline phase of titania, improving the absorption and scattering of light, better photoexcitation of the

Conclusions

Studies show the superiority of SiO₂@TiO₂ nanoparticles photocatalytic and structural properties compared to unsupported silica nanoparticles. This superiority is due to the interfacial interactions between TiO₂ and SiO₂, in particular the formation of Ti-O-Si bonds, which improve the thermal and optical properties and, consequently, the photocatalytic activity, opening up various applications for the material.

Acknowledgments

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photocatalyst and more contact with the reagent to be degraded. This makes this type of material useful for a variety of applications.

Applications SiO₂@TiO₂ Nanoparticles

SiO₂@TiO₂ nanoparticles can be used for photocatalytic degradation of organic pollutants. Studies with dyes have shown the superiority of core@shell structures over pure TiO₂. Their ease of recovery and recyclability provide additional economic and environmental benefits [1]. Studies show the almost total photodegradation of crystal violet dye by SiO₂@TiO₂ nanoparticles and showed its recyclability by at least 4 times without affecting efficiency [8].

The improved light-harvesting and light-scattering capacity is also attractive for use in dye-sensitized solar cells. SiO₂@TiO₂ is used to improve the performance of the solar cell due to the internal reflections caused by the different refractive indices of the material, avoiding the recombination of pairs (e⁻/h⁺) and increasing the interaction between the dye and the light [4].

Its improved thermal stability, which reduces the phase transformation of titania, combined with its photocatalytic activity, makes these nanoparticles useful in the development of self-cleaning ceramics, which must withstand high temperatures (>800°C) for their manufacture. For instance, SiO₂@TiO₂-coated tiles degraded 90% of crystal violet dye, whereas tiles coated with commercial TiO₂ degraded around 30% of the dye [10].