

Synthesis of Nanoparticles and Quantum Dots for Visible-Light Photocatalysis: TiO₂ and AgNPs

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ABSTRACT

Visible-light-driven photocatalysis has emerged as a promising and sustainable approach for addressing environmental pollution and energy challenges. Among various photocatalytic materials, titanium dioxide (TiO₂) nanoparticles and silver nanoparticles (AgNPs), including quantum dots, have gained significant attention due to their unique physicochemical properties, high stability, and strong catalytic potential. This review comprehensively summarizes recent advances in the synthesis of TiO₂ nanoparticles, AgNPs, and their corresponding quantum dots with a focus on strategies that enhance visible-light activity. Conventional chemical and physical synthesis routes are discussed alongside green and bio-mediated approaches that offer eco-friendly and cost-effective alternatives. The review further highlights band-gap engineering, metal and non-metal doping, surface modification, and heterojunction formation as key methods to improve light absorption and charge separation under visible-light irradiation. Applications of TiO₂- and AgNP-based photocatalysts in wastewater treatment, degradation of organic pollutants, antimicrobial activity, and renewable energy generation are critically analyzed. Finally, current challenges, limitations, and future perspectives are outlined to guide the rational design of efficient, stable, and environmentally benign photocatalysts for next-generation visible-light applications.

Keywords: TiO₂ Nanoparticles; Silver Nanoparticles; Quantum Dots; Visible-Light Photocatalysis; Green Synthesis; Band-Gap Engineering

INTRODUCTION

Photocatalysis under visible light has attracted considerable scientific interest as an environmentally sustainable technology for mitigating pollution and addressing global energy demands, particularly due to the abundance of solar irradiation in the visible region of the spectrum. Titanium dioxide (TiO₂) has long been recognized as a benchmark photocatalyst because of its chemical stability, non-toxicity, and low cost; however, its wide band gap restricts photoactivity mainly to the ultraviolet region, limiting overall solar utilization (Asahi et al., 2001). To overcome this limitation, extensive efforts have been devoted to band-gap engineering of TiO₂ through doping, surface modification, and coupling with noble metals. In this context, silver nanoparticles (AgNPs) and quantum dots have emerged as highly effective modifiers due to their surface plasmon resonance, efficient charge trapping ability, and enhanced visible-light absorption (Baker and Baker, 2010). Recent advances in nanotechnology have further enabled precise control over particle size, morphology, and electronic structure, leading to significant improvements in photocatalytic efficiency. This review therefore focuses on the synthesis of TiO₂ nanoparticles, AgNPs, and quantum dots, emphasizing visible-light-responsive strategies and their implications for environmental and energy-related photocatalytic applications.

Visible-light photocatalysis overview

Solar energy converted into clean fuels can effectively solve the energy and environmental crisis, such as, converting carbon dioxide (CO₂) into valuable fuel by photocatalysis reduction process could achieve the chemical store of solar energy. However, photocatalysis is difficult to be widely used due to the low utilization efficiency of sunlight and the rapid recombination of the photogenerated electrons and holes. Besides, the diversity of reduction products and the existence of competing hydrogen evolution during CO₂ reduction process lead to its low efficiency and poor product selectivity to target products, greatly limiting its industrial application. Therefore, it is meaningful to design photocatalysts with high selectivity to C-products for photocatalytic CO₂ reduction (Chen and Mao, 2007).

Semiconductor TiO₂, as one of the most common photocatalysts, shows photocatalytic CO₂ reduction performance. However, its wide band gap also prevents it from making full use of sunlight. Therefore, there are many strategies proposed to improve its photocatalytic activity, such as doping with heteroatoms, construction of the heterojunctions, the modification of cocatalysts the regulation of crystal faces and so on. Recent research has also found that the intrinsic defects of semiconductor TiO₂, i.e., low valance Ti species, oxygen vacancy and lattice distortion, play a positive role in photocatalytic process, which can reduce the band gap width, enhance the spectral utilization in the visible region, promote the adsorption and activation of reactants and improve carrier density and mobility (Fujishima et al., 2000). Additionally, the pore structure of catalyst is crucial because it can affect the adsorption, diffusion and accessibility of guest molecules. Generally, the larger and

interpenetrating mesopore is conducive to the transport of guest molecules, and the smaller mesopore can enlarge the Brunauer-Emmett-Teller (BET) specific surface areas which can provide more active sites for reactants adsorption and photocatalysis. More importantly, the multiple scattering of light in the mesopore will also lead to the improved light harvesting efficiency. Thus, it is concluded that the defects and typical pore structure in the semiconductor contribute to the improved photocatalytic activity. Moreover, modifying noble metal on/in the semiconductor is also a reasonable method for improving photocatalytic performance. On one hand, the loading of precious metals on the semiconductor surface can increase sunlight energy utilization efficiency due to the surface plasmon resonance effect (SPR). On the other hand, the Schottky junction can be formed at the interface by combining noble metals with semiconductors, and the formed Schottky barrier can capture photogenerated electrons and greatly improve the separation efficiency of photogenerated carriers and photocatalytic efficiency (Ganesh, 2014).

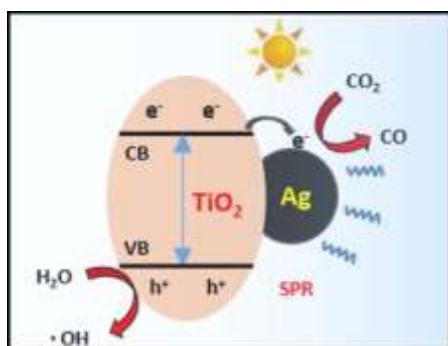


Fig. 1. A novel hierarchically porous and defective TiO_2 modified by Ag
Herein, the hierarchically porous and defective TiO_2 nanoparticles have been successfully prepared via a hydrothermal process assisted with organic surfactant, and Ag quantum dots have been uniformly deposited on the prepared TiO_2 by in-situ photo deposition process. The obtained sample Ag/TiO_2 not only owns higher BET surface area and wide pore size distribution, but also shows the intrinsic defects, such as low valence Ti and oxygen vacancies. More importantly, the deposition of Ag quantum dots not only greatly improves the visible light adsorption performance, but also accelerates the separation efficiency of photogenerated charges. As hoped, the resulting sample Ag/TiO_2 can convert CO_2 into CO efficiently under light irradiation, which can be ascribed to the synergetic effect between highly dispersed Ag quantum dots and the hierarchically porous and defective TiO_2 (Ganesh, 2012).

Need for TiO_2 modification and role of AgNPs/quantum dots

TiO_2 nanotubes attract much attention due to their high photocatalytic activity, relatively low cost, large surface area, strong adsorption capacity, and easily controllable diameter and can be prepared in a number of ways, e.g., by template-assisted, hydrothermal, and electrochemical anodization techniques. In particular, electrochemical anodization refers to the preparation of highly ordered TiO_2 nanotube arrays (TNNTA) with a vertical nanotube orientation by Ti film anodization. TNNTA

have an ordered array structure with an adjustable pore size for secure attachment to the Ti film and feature an enhanced light absorption ability due to the inhibitory effect of multiple reflections from nanotube walls on the escape of photons from the nanotubes. Compared with other one-dimensional TiO_2 nanomaterials, TNTA exhibit higher corrosion resistance, mechanical stability, and recyclability but suffer from a limited light absorption range and an ineffective separation of photogenerated electron-hole pairs. These challenges have been addressed in many ways, e.g., by sensitization with quantum dots, noble metal deposition, doping with metals or non-metals and coupling with other semiconductors (Habisreutinger et al., 2013).

The recently discovered carbon dots (CDs) display excellent biocompatibility, low toxicity, and good photoelectrical performance, e.g., good electron transport and energy storage capability as well as extensive light absorption and photoluminescence (PL). Consequently, the combination of TiO_2 with CDs promotes both electron-hole pair separation and light absorption. Ag nanoparticles (Ag NPs) are cheaper than other noble metal NPs and exhibit a surface plasmon resonance (SPR) effect that can be used to extend the light absorption of photocatalysts to longer wavelengths. In our previous study, a CD/Ag NP/P25 TiO_2 nanocomposite was shown to exhibit an enhanced light absorption capacity and charge transfer ability due to the photoelectrical properties and the SPR effect of Ag NPs (Hoffmann et al., 1995).

However, powdery photocatalysts are hard to separate from the reaction system and may therefore cause secondary pollution. Currently, no economically viable technology of spent photocatalyst separation from suspensions is available. Moreover, the abnormal light-induced charge transfer in powdery photocatalysts limits the efficiency of light energy conversion. The immobilization of the particulate photocatalyst on conducting substrate also enhances the catalytic activity by the long-range charge separation (Iravani, 2011).

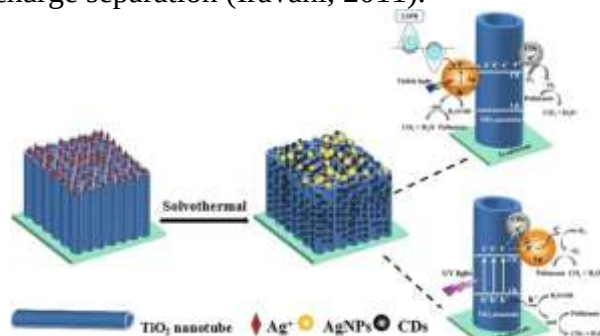


Fig. 2. A silver nanoparticle (Ag NP)/carbon dot (CD)/ TiO_2 nanotube array (TNTA) composite with enhanced photocatalytic activity

Herein, we report the one-step solvothermal fabrication of Ag/CD/TNTA nanocomposites with variable Ag loadings from TNTA (prepared by electrochemical anodization), ethylene glycol (EG), and AgNO_3 as raw materials, comparing the photocatalytic performances (photodegradation of methylene blue (MB) and recyclability of different catalysts and analyzing the photocatalytic degradation mechanism (Kamat, 2008).

Synthesis Strategies

The synthesis of TiO₂ nanoparticles, silver nanoparticles (AgNPs), and quantum dots for visible-light photocatalysis has been widely explored using chemical, physical, and biological approaches to achieve controlled size, morphology, and enhanced optical properties. Conventional methods such as sol-gel, hydrothermal, solvothermal, chemical reduction, and co-precipitation are commonly employed due to their reproducibility and scalability, enabling precise tuning of crystallinity and band-gap characteristics. Physical techniques, including sputtering, laser ablation, and thermal evaporation, offer high-purity nanomaterials but are often limited by high energy consumption and cost. In recent years, green synthesis strategies utilizing plant extracts, microorganisms, and biopolymers have gained significant attention as environmentally benign alternatives, providing natural reducing and capping agents that improve biocompatibility and sustainability (Iravani, 2011). Furthermore, advanced strategies such as metal and non-metal doping, formation of TiO₂-Ag heterojunctions, and integration of quantum dots have been shown to effectively extend light absorption into the visible region while suppressing charge recombination, thereby significantly enhancing photocatalytic performance under solar irradiation (Kamat, 2012).

TiO₂ nanoparticles and quantum dots

In recent years, the semiconductor photocatalysts have attracted considerable attention to solve current environmental and energy issues. In particular, titanium dioxide (TiO₂) has been commonly recognized as one of the most promising photocatalysts because of its excellent photocatalytic activity, relatively low cost, long-term stability and low toxicity. Nonetheless, the low visible light responsivity of TiO₂ owing to its large band gap (3.2 eV) and the fast recombination of photogenerated electron-hole pairs restrict its applications in photocatalysis. A great deal of approaches have been developed to modify TiO₂ so as to improve its photo-response capability, such as modification on TiO₂ crystal or morphology, sensitization with quantum dot or organic dye, noble metal deposition, doping with metal or nonmetal elements coupling with the other semiconductors (Kamat, 2012).

Among the above approaches, sensitization with quantum dot refers to the combination of TiO₂ and quantum dots. It can adjust the band width of TiO₂ and broaden the photo-response range. However, the traditional quantum dots often contain toxic heavy metal ions constituents, which is a serious threat to the environment and human health. Carbon dots (CDs), as a new class of carbon nanomaterial, are composed of sp²/sp³ hybridized carbon atoms. And the surface of CDs usually has abundant functional groups. Compared with the traditional quantum dots, CDs are superior in good biocompatibility, low toxicity, high aqueous solubility, easily functionalized modifications and chemical inertness. In addition, CDs exhibit excellent photoelectrical properties including favorable electron transport and reservoir capability, photoluminescence (PL) and wide light absorption. Some CDs with up-conversion PL property can absorb long-wave light and then emit short-wave light, which would further help to enhance the light utilization. It has been found that semiconductors combined with CDs can enhance the light absorption and promote the separation of photogenerated electron-hole pairs. To date, many researches on CDs/TiO₂ composites have been explored. And TiO₂ with various microstructures

were used to combine with CDs, including nanoparticles, nanofibers, nanotubes, nanorods, nanosheets and nanobelts (Lei et al., 2013).

However, the current synthesis routines usually consisted of two parts: (1) the synthesis of CDs; (2) the combination of CDs and TiO₂ using solvothermal treatment, electrochemistry deposition [39] or physical mixing method. The complex synthesis procedures are still far from satisfactory. Additionally, though the light absorption of CDs/TiO₂ nanocomposites in the visible and even the near infrared light region is enhanced, it is still weak for practical applications compared with that in ultraviolet (UV) light region, which needs further improvements all the time. The noble metal nanoparticles (e.g. Au, Ag and Pt) are often used to improve the photocatalytic activities of semiconductor photocatalysts since they can act as irreversible electron sinks to enhance the separation efficiency of photogenerated electron-hole pairs. Among these noble metal nanoparticles, Ag nanoparticles (AgNPs) possess a relatively lower price than the others. And the surface plasmon resonance (SPR) effect of AgNPs could also help semiconductor photocatalysts to extend their light absorption to long-wave regions. Furthermore, AgNPs can provide abundant chemically active sites where relevant chemical transformations would take effect with lower activation barriers than that on the semiconductors (Li et al., 2016).

Considering the excellent photocatalytic activity of TiO₂, the photoelectrical properties of CDs and the SPR effect of AgNPs, we think that the combination of components may be a good system with more efficient photocatalytic performance. CDs could be synthesized by using ethylene glycol (EG) as the carbon source through a solvothermal method. Herein, we designed a one-pot solvothermal method for the fabrication of ternary nanocomposites. Typically, EG was used as the carbon source. TiO₂ nanoparticles (Degussa P25) were added to EG followed by the addition of Ag ions under vigorous stirring. Then the mixture solution was heated at high temperature. Finally, CDs were synthesized through a solvothermal method. Meanwhile, Ag ions in the solution were reduced to AgNPs due to the reducing capacity of CDs. Therefore, it was fabricated without the assistance of additional chemicals or special reducing agent. And AgNPs and CDs were tightly attached onto the surface of TiO₂ nanoparticles through the solvothermal process (Linic, et al., 2011)

Silver nanoparticles (chemical, green, physical methods)

The controlled fabrication of visible/solar light responsive photocatalysts for wastewater or contaminated air treatments has been attracted widely interdisciplinary attention. Titanium dioxide (TiO₂) is the most promising photocatalyst for water splitting and environmental remediation because of its low cost, good photostability, low toxicity, large abundance, strong oxidizing activity, good physical and chemical stability, high redox ability, excellent electronic and optical properties, and well-positioned valence and conduction bands. However, its wide practical applications are hampered by some obstacles, including low activity in the visible range due to its relatively wide band gap and low quantum efficiency because of the rapid recombination rate of photogenerated electron-hole pairs (Liu and Chen, 2014).

Numerous research efforts have been employed to enhance the photocatalytic performance of TiO₂ via adding a secondary component, including metal, non-metal,

or other semiconductor. The photocatalytic performance of TiO₂@S,N co-doped graphene quantum dots (GQDs) composites in degrading Rhodamine B (RhB) under visible light was reported. It was revealed that the degradation rate of the composite is three and ten times greater than that of N-doped GQDs/TiO₂ and P25 (a mixture of 80% anatase and 20% rutile), respectively. In order to enhance the photocatalytic activity of TiO₂, a variety physical method was proposed by controlling the particle size and structure, i.e. without adding a second component (Osterloh, 2013).

Visible-Light Photocatalytic Mechanisms

Photocatalysis widely refers to the process of using light to activate a substrate (photocatalyst), which modifies or facilitates the kinetics of a chemical reaction but itself remains unconsumed.^{1–4} During photocatalysis, a semiconductor metal oxide such as titanium dioxide (TiO₂) or zinc oxide (ZnO) is irradiated with light (where, the energy of the excitation source is higher than the band gap energy of the material), which results in photon absorption and excitation of an electron (e[–]) from valence band to the conduction band, thereby generating a positive electron hole (h⁺) in the valence band. The electron–hole charge carriers (h⁺ VB + e[–] CB) can in turn undergo recombination and dissipate the excess energy through nonradiative mechanisms. This reduces the overall efficiency of the photoinduced process. The charge carriers, which do not undergo charge annihilation, can migrate to the surface of the catalyst and initiate secondary reactions with the surface adsorbed materials (Saud, 2015).

Photoelectrochemical decomposition of water using TiO₂ as an anode and platinum as a counter electrode. TiO₂-based photocatalysts also offer the advantages of high physical and chemical stability, low cost, easy availability, low toxicity, and excellent photoactivity. Titanium dioxide exists in three naturally occurring polymorphic forms such as anatase, rutile, and brookite, where rutile represents the thermodynamically stable form and anatase shows higher kinetic stability. The anatase form of TiO₂ is reported to show higher photocatalytic activity compared to rutile or brookite.^{1,3} The major drawbacks of TiO₂-based photocatalysts arise from the rapid charge recombination of the electron–hole pairs, thereby suppressing the quantum efficiency, and the wide band gap (3.0 eV for rutile and 3.2 eV for anatase) of the material, which restricts light absorption to only ultraviolet region (wavelength process, resulted in a nitrogen-doped photocatalyst that demonstrated visible light activity (Serpone and Emeline, 2002).

TiO₂–AgNPs and Quantum Dot-Based Composites

TiO₂–AgNPs and quantum dot-based composite photocatalysts have emerged as highly efficient systems for visible-light-driven applications due to synergistic interactions between their constituent materials. The incorporation of AgNPs onto TiO₂ surfaces enhances visible-light absorption through localized surface plasmon resonance and facilitates efficient charge separation by acting as electron sinks, thereby reducing recombination losses (Linic et al., 2011; Kamat, 2012). Similarly, coupling TiO₂ with semiconductor quantum dots enables band-gap modulation and extended light harvesting by introducing size-dependent electronic states that promote interfacial charge transfer under visible-light irradiation (Zhang et al., 2018). Various fabrication strategies, including in situ deposition, photoreduction, and layer-by-layer

assembly, have been employed to achieve uniform dispersion and strong interfacial contact, which are critical for optimal photocatalytic performance. These composite systems have demonstrated superior efficiency in pollutant degradation, antimicrobial activity, and solar energy conversion compared to pristine TiO₂, highlighting their potential for advanced environmental remediation and renewable energy applications (Sun et al., 2006)

Applications under Visible Light

TiO₂-AgNPs and quantum dot-based photocatalysts have demonstrated broad applicability under visible-light irradiation, particularly in environmental and energy-related fields. In wastewater treatment, these nanocomposites exhibit enhanced efficiency for the degradation of organic pollutants, dyes, pharmaceuticals, and pesticides by generating reactive oxygen species under solar and indoor light conditions (Hoffmann et al., 1995; Zhang et al., 2018). Their strong antimicrobial and antiviral activities further support applications in water disinfection, self-cleaning surfaces, and medical coatings, largely attributed to the combined photocatalytic and plasmonic effects of AgNPs (Kamat, 2012). Additionally, visible-light-responsive TiO₂-based composites have shown promise in renewable energy technologies, including photocatalytic hydrogen evolution, CO₂ reduction, and photoelectrochemical cells, where improved charge separation and extended light absorption significantly enhance conversion efficiencies (Chen & Mao, 2007). Collectively, these applications underscore the potential of TiO₂-AgNPs and quantum dot systems as versatile and sustainable photocatalysts for next-generation visible-light-driven technologies (Zhao et al., 2015).

Challenges and Future Perspectives

Despite significant progress, challenges such as charge recombination, photocorrosion of AgNPs, and long-term stability under visible light still limit large-scale applications of TiO₂-AgNPs and quantum dot-based photocatalysts. Precise control over particle size, interfacial architecture, and dopant distribution remains critical for reproducible performance (Zhu et al., 2013). The development of low-cost, scalable, and green synthesis routes is essential to ensure environmental and economic sustainability. Future research should emphasize mechanistic understanding of charge-transfer pathways using advanced in situ characterization techniques. Additionally, integrating these nanocomposites into practical reactors and real-world systems will be crucial for commercial implementation (Wang et al., 2016).

Conclusions

This review highlights the significant advancements in the synthesis and application of TiO₂ nanoparticles, silver nanoparticles, and quantum dots for visible-light-driven photocatalysis. Various chemical, physical, and green synthesis strategies have been shown to effectively tailor the structural and optical properties of these nanomaterials, while composite systems such as TiO₂-AgNPs and quantum dot-coupled TiO₂ exhibit superior photocatalytic performance due to enhanced light absorption and efficient charge separation. The demonstrated applications in environmental remediation, antimicrobial activity, and renewable energy conversion underscore their versatility

and practical relevance under visible-light conditions. Although challenges related to stability, scalability, and long-term performance persist, continued progress in material design, eco-friendly synthesis, and mechanistic understanding is expected to drive the development of efficient, sustainable, and commercially viable photocatalysts for future solar-driven technologies.

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