Broadening the photoresponsive activity of anatase titanium dioxide particles via decoration with partial gold shells

Orawan Khantamat a,b,1, Chien-Hung Li a,1, Si-Ping Liu c, Tingting Liu a, Han Ju Lee a, Oussama Zenasni a, Tai-Chou Lee c, Chengzhi Cai a,* T. Randall Lee a,*

a Department of Chemistry and the Texas Center for Superconductivity, University of Houston, Houston, TX 77204-5003, USA
b Department of Biochemistry, Faculty of Medicine, Chiang Mai University, Chiang Mai 50200, Thailand
c Department of Chemical and Materials Engineering, National Central University, Jhongli City 32001, Taiwan

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ABSTRACT
Titanium dioxide (TiO2) has gained increasing interest in materials research due to its outstanding properties and promising applications in a wide range of fields. From this perspective, we report the synthesis of custom-designed anatase TiO2 submicrometer particles coated with partial Au shells (ATiO2-AuShl). The synthetic strategy used herein yields uniformly shaped monodisperse particles. Amorphous TiO2 core particles were synthesized using template-free oxidation and hydrolysis of titanium nitride (TiN); subsequent hydrothermal treatment generated anatase TiO2 (ATiO2) particles. Coating ATiO2 particles with partial Au shells was accomplished using a simple seeded-growth method. Evaluation of the optical properties of these ATiO2-AuShl particles showed that these submicrometer composites exhibited an intense absorption peak for TiO2 in the UV region (~247 nm) and a broad extinction band in the visible range (~650 nm) arising from the incomplete Au shell. These ATiO2-AuShl composite particles provide a unique and effective means for broadening the optical response of TiO2-based nano- and micron-scale materials. The simplicity of our synthetic method should broaden the application of ATiO2-AuShl particles in various visible light-driven technologies.

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1. Introduction

TiO$_2$ is a promising material for many emerging applications. Since Fujishima and Honda discovered the photocatalytic splitting of water on a TiO$_2$ electrode in 1972 [1], the fundamental processes of TiO$_2$ photoelectrochemistry have been studied intensively. To date, TiO$_2$ has been exploited for photocatalytic water splitting, purification of pollutants, photocatalytic self-cleaning, and photocatalytic antibacterial applications as well as photovoltaics, phototronics, electrochromics, and various types of sensors [2–8]. Furthermore, TiO$_2$–based materials are now widely used due to their nontoxicity, chemical and biological stability, and low cost [9].

TiO$_2$ exists in three main polymorphs: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). Rutile is the most stable form, whereas anatase and brookite are metastable and readily transformed to rutile when heated [10]. The phase normally found in the sol-gel syntheses of TiO$_2$ is anatase, which possesses a band gap of 3.2 eV, corresponding to an absorption wavelength of 385 nm. Rutile TiO$_2$ has a smaller band gap of 3.0 eV, with excitation wavelengths that extend into the visible (410 nm). As for brookite, theoretical and experimental studies have reported band gap values both smaller and larger than that of anatase. The band gap of brookite was first estimated by extended Hückel molecular orbital calculations as 3.14 eV [11], which falls between those of anatase and rutile. Nevertheless, anatase exhibits higher photocatalytic activity when compared to rutile or brookite [12,13], which might be attributed to its higher surface adsorptive capacity and higher rate of hole trapping. For example, Degussa P25, the most popular commercial TiO$_2$ material, with a 70% anatase and 30% rutile composition, possesses excellent photocatalytic activity [14,15] due to its mixed-phase composition and high anatase crystallinity. These properties favor photo-induced charge separation and a large specific surface area.

Most TiO$_2$ nano- and micron-scale structures have a high surface-to-volume ratio, providing a large surface area on which photo-induced reactions can occur. This feature enhances the rate of light absorption, increases photo-induced carrier density on the surface, increases the photo-reduction rate, and leads to higher surface photoactivity. In addition, the high surface-to-volume ratio of the particles enhances the surface absorption of hydroxide (OH$^-$) ions and H$_2$O molecules, which also increases the photocatalytic reaction rate. The properties of TiO$_2$ particles are also influenced by the size, morphology, phase structure, surface chemical state, and synthesis process. For example, among the various TiO$_2$ particle morphologies investigated in recent years (e.g., tubes [16,17], rods [18,19], spheres [20,21], wires [22,23], and sheets [24,25]), spherical TiO$_2$ particles have been found to exhibit superior performance in environmental and energy applications due to their large specific surface area [26,27].

Monodisperse TiO$_2$ particles can be synthesized using a variety of methods, including sol-gel, hydrothermal, solvothermal, chemical vapor deposition, or template-based methods [28–31]. The traditional sol-gel route proceeds via hydrolysis of a titanium alkoxide precursor [9,28,32]. This process is typically fast but moisture-sensitive, making it difficult to control the size of the generated TiO$_2$ particles. Although the strategy of constructing amorphous TiO$_2$ particles and subsequent hydrothermal treatment provides a simple route for generating particles with targeted sizes, achieving monodispersity with this conventional method remains a challenge [26,33]. Other routes for preparing TiO$_2$ particles using templates, such as polystyrene (PS) [31] or SiO$_2$ [34] spheres, have been well documented, but are cost-prohibitive due to the high price of Ti-precursors. Moreover, the complicated synthetic conditions and use of an additional structural directing agent or surfactant often limit the use of this strategy in practical applications.

Although TiO$_2$ materials exhibit excellent properties as photo-activated catalytic materials, one major limitation involving the use of TiO$_2$ is the need for activation with UV light, since the absorption peak is narrow and lies largely in the near-UV region. To address this issue, researchers have attempted to increase the efficiency of TiO$_2$ by shifting its absorption window to the visible region through the incorporation of non-metal and transition metal dopants such as nitrogen, carbon, chromium, and iron [35–38]. These dopants decrease the band gap of TiO$_2$, which shifts the absorption toward the visible region of the spectrum, which can increase the efficiency of the photoactivity of the modified TiO$_2$. However, transition metal dopants can also act as electron-hole recombination sites for the photo-induced charge carriers and thus decrease the photocatalytic activity [39].

Alternatively, researchers have loaded TiO$_2$ with metal nanoparticles such as gold, silver, platinum, and palladium because such nanoparticles can act as electron sinks to enhance charge transfer and thus decrease the possibility of charge-hole recombination [40–43]. Furthermore, researchers recently have discovered the generation of photoexcited electrons (hot electrons) from plasmonic nanomaterials such as gold and silver [44–46]. Energy transfer to hot electrons arises from the light-driven surface plasmon resonance excitation of the nanomaterials. Importantly, the injection of hot electrons to TiO$_2$ has been shown to inhibit electron-hole recombination to enhance the efficiency of photocatalytic activities [44–46].

In the studies reported herein, we optimized a simple alkoxide-free sol-gel synthetic method requiring no templates or structure-directing agents to prepare submicrometer TiO$_2$ particles with selected dimensions and properties. Using our synthetic route, the size of these amorphous TiO$_2$ particles can be easily tuned by adjusting the Ti species or reaction temperature. These amorphous TiO$_2$ particles readily undergo phase transformation via hydrothermal treatment. Inspired by the plasmonic properties of gold nanomaterials, the hydrothermally-treated TiO$_2$ particles (ATiO$_2$) were decorated with an incomplete Au shell on the ATiO$_2$ surface (ATiO$_2$-Au shells, ATiO$_2$-AuShi particles). To the best of our knowledge, this is the first report on the use of simple seeded-growth method for coating ATiO$_2$ particles with partial Au shells. Like TiO$_2$, gold is known to be non-toxic and environmentally friendly [47,48]. With Au shell decoration, these TiO$_2$-AuShi particles have the capacity to augment the optical properties of TiO$_2$ particles by broadening the range of absorbed UV–Vis (solar/white) light, thereby increasing their efficiency in photo-driven applications under a variety of conditions, such as the photocatalytic degradation of organic pollutants and the photocatalytic production of hydrogen. The overall strategy used to prepare our ATiO$_2$-AuShi particles is illustrated in Scheme 1.

2. Experimental

2.1. Materials

The following analytical-grade chemicals were purchased from the indicated suppliers and used without purification: titanium nitride, TiN (99%, Aldrich); hydrogen peroxide, H$_2$O$_2$ (30%, Macron Fine Chemicals); ammonium hydroxide, NH$_4$OH (28–30%, BDH® VWR Analytical); (3-aminopropyl)trimethoxysilane, APTMS (97%, Aldrich); tetrakis(hydroxymethyl)phosphonium chloride, THPC (80%, Aldrich); hydrogen tetrachloraurate(III) hydrate, HAuCl$_4$·xH$_2$O (49% Au, Strem Chemicals); potassium carbonate, K$_2$CO$_3$ (≥99.0%, J.T. Baker); formaldehyde (35–40%, Macron Fine Chemicals); methylene blue, MB (ACROS Organics®); potassium sulfite, K$_2$SO$_3$ (Sigma Aldrich); sodium sulfide hydrate, Na$_2$S·xH$_2$O (Sigma Aldrich). Water was purified to a resistivity of 18 MΩ·cm
2.2. Synthesis of anatase TiO₂ particles

2.2.1. Preparation of Ti-peroxo solution

The synthetic procedure began with the preparation of the Ti-peroxo complex solution by dissolving commercial TiN in water in the presence of hydrogen peroxide (H₂O₂) and aqueous ammonia (NH₄OH). Specifically, the TiN (0.10 g) was dispersed in 100 mL of Millipore water followed by the addition of 10 mL of 30% hydrogen peroxide (H₂O₂) and 10 mL of 25% aqueous ammonia solution. After 2 h of vigorous stirring, the transparent yellow solutions of Ti-peroxo complex were obtained.

2.2.2. Synthesis of amorphous submicrometer TiO₂ particles

Amorphous submicrometer TiO₂ particles were synthesized via hydrolysis of the Ti-peroxo complex solution. A 1.25% aqueous solution of THPC (triethylenglycol bis(hydroxyethyl)phosphonic acid) was added, and the solution was aged at 4 °C in the dark for 16 h. Then, 1 mL of 1 M NaOH was added to 90 mL of Millipore water, followed by the addition of 2 mL of a 1.25% aqueous THPC solution. The mixture was stirred for 5 min, and then 4 mL of 1 wt% HAuCl₄ in water was added quickly to the stirred solution. The solution (~100 mL) containing the colloidal particles was stored at 4 °C for 2 days and then concentrated to 10 mL using a rotary evaporator.

A portion of the concentrated gold colloidal solution (5 mL) was then mixed with a 2-mL aliquot of ATiO₂-APTMS solution (5 mg/mL). After vigorous stirring for 1 h, the solution was allowed to equilibrate for 2–5 days to allow the gold colloidal particles to attach to the TiO₂ surface. The resulting ATiO₂-Au seeds particles were then washed by centrifugation and redispersed in Millipore water.

2.3. Synthesis of submicrometer ATiO₂ particles coated with partial Au shells (ATiO₂-AuShl)

To synthesize submicrometer ATiO₂ particles coated with partial Au shells, we first deposited colloidal gold on the ATiO₂-Au seeds particles using a self-assembly method [49]. A solution of colloidal gold particles (1–3 nm diameter) was prepared by the reduction of a 1 wt% aqueous solution of HAuCl₄ with THPC. Under rapid stirring, 1 mL of 1 M NaOH was added to 90 mL of Millipore water, followed by the addition of 2 mL of a 1.25% aqueous THPC solution. The mixture was stirred for 5 min, and then 4 mL of 1 wt% HAuCl₄ in water was added quickly to the stirred solution. The solution (~100 mL) containing the colloidal particles was stored at 4 °C for 2 days and then concentrated to 10 mL using a rotary evaporator.

A portion of the concentrated gold colloidal solution (5 mL) was then mixed with a 2 mL aliquot of ATiO₂-Au seeds solution (5 mg/mL). After vigorous stirring for 1 h, the solution was allowed to equilibrate for 2–5 days to allow the gold colloidal particles to attach to the TiO₂ surface. The resulting ATiO₂-Au seeds particles were then washed by centrifugation and redispersed in Millipore water.

2.3.2. Submicrometer ATiO₂ particles coated with gold-seeds (ATiO₂-Au seeds)

To provide a preliminary assessment of the photocatalytic activity of ATiO₂-AuShl particles, we monitored the degradation of methylene blue (MB) by ATiO₂-AuShl particles.

2.4. Photocatalytic degradation of methylene blue (MB) by ATiO₂-AuShl particles

To provide a preliminary assessment of the photocatalytic activity of ATiO₂-AuShl particles, we monitored the degradation of methylene blue upon exposure to visible light. Briefly, 12 mL of a solution of TiO₂ particles was prepared by mixing the particles with a 0.005 mg/mL aqueous solution of MB. The particle concentration was adjusted to 5 × 10¹⁰ particles/mL (~0.3 mg/mL), and the resulting mixture was sonicated for 10 min in the dark.
Subsequently, a 4-mL aliquot of the mixture was centrifuged, and the supernatant was used as a reference for UV–Vis spectroscopic analysis. The remaining mixture was then divided into two separate portions for incubation in the dark and under 60 W incandescent white light (or fluorescent light) for 4 h. The samples were then centrifuged, and the supernatant was collected for analysis by UV–Vis spectroscopy.

2.5. Photocatalytic hydrogen production by ATiO$_2$-AuShl particles

The preliminary assessment of the photocatalytic reaction for hydrogen production was conducted in a 225-mL custom-built cylindrical glass cell with a quartz side window and an illumination area of 23 cm$^2$. The sacrificial agent needed to drive the reaction was prepared by adding potassium sulfite (55 mmol) and sodium sulfide (77 mmol) to DI water (220 mL). An aliquot of 1 mL of ATiO$_2$-AuShl particles in aqueous solution (1 × 10$^{10}$ particles/mL) was then added to the sacrificial solution, and the photocatalytic reactor was irradiated with a 300 W Xe lamp. The intensity was set at 100 mW/cm$^2$ and monitored by an optical meter (Newport 1918-R). The temperature was maintained at 25 °C during the reaction, and H$_2$ gas was collected for at least 5 h using a water displacement method. The evolved gas was analyzed using a China Chromatography GC 3000 gas chromatograph.

2.6. Characterization methods

The dimensions and morphologies of the as-prepared particles were characterized using scanning electron microscopy (SEM; LEO-1525) operating at an accelerating voltage of 15 kV, and transmission electron microscopy (TEM; JOEL-2000 FX) operating at an accelerating voltage of 200 kV. To obtain high-resolution images from the SEM analyses, all samples were deposited on a silicon wafer and allowed to dry. For the TEM analyses, the particles were deposited on 300 mesh holey carbon-coated copper grids and allowed to dry. To determine the size distribution and surface charge of the particles, dynamic light scattering (DLS) and zeta potential data were collected using a Zetasizer Nano ZS (Malvern Instruments) operating with a 514.5 nm light source at a fixed scattering angle of 90°. The concentration of the particles was measured using a NanoSight (Malvern Instruments).

The phase structure of the particles was analyzed using X-ray diffraction (XRD; D5000 X-ray diffractometer, Siemens (now Bruker), Karlsruhe, Germany). A concentrated sample of particles in ethanol was deposited on a Piranha-cleaned glass slide, and XRD was carried out using Cu Kα radiation (λ = 1.540562 Å) in the 2θ range from 10° to 100°. [Caution: Piranha solution is highly corrosive, should never be stored, and should be handled with extreme care.]

The composition of the interfaces of the synthesized particles was examined using X-ray photoelectron spectroscopy (XPS; PHI 5700 XPS) equipped with a monochromatic Al Kα X-ray source (hv = 1486.7 eV) incident at 90° relative to the axis of a hemispherical energy analyzer. For XPS analyses, a concentrated sample of particles in water was deposited on a copper-tape-covered silicon wafer and allowed to dry under ambient conditions. The number of scans used to collect the data for each element was: Au (1), C (1), N (4), O (1), Si (2), and Ti (2). The XPS data were processed by Multi-pak software, and the binding energy of all spectra were calibrated on Ti 2p$_{3/2}$ at 458.8 eV [51]. Optical extinction spectra of suspensions containing the dispersed particles were collected using a Cary 50 Scan UV–visible (UV–Vis) spectrometer over the wavelength range of 200–1000 nm. Photoluminescence (PL) spectra were obtained at a concentration of 2 × 10$^{9}$ particles/mL using a PL spectrometer (PerkinElmer LS-55) with 353 nm incident light from a Xe flash lamp used for the excitation.

3. Results and discussion

3.1. Synthesis of amorphous submicrometer TiO$_2$ particles

Studies have shown that the properties of TiO$_2$ particles are governed by their size, morphology, and crystalline phase [52–54]. The conventional sol-gel method, the most widely applied approach for preparing amorphous TiO$_2$ particles, relies on the hydrolysis of a Ti precursor with subsequent condensation to form an inorganic framework. However, the TiO$_2$ particles prepared using this method tend to agglomerate and generally lack uniformity in size and shape [9]. In fact, there are several parameters that affect this sol-gel process. The concentration of the Ti precursor/ species greatly impacts the crystallization behavior and the resulting characteristics of the synthesized particles [55]. The size, stability, and morphology of the produced sol from the Ti precursors are strongly affected by the water-to-Ti molar ratio (r = [H$_2$O]/[Ti]) [56,57]. Also, the peptization process (carried out by heating the solution or using a peptization agent) has a strong effect on the characteristics of the TiO$_2$ particles prepared via the sol-gel method [58]. In summary, obtaining TiO$_2$ particles with controlled size and narrow polydispersity is critical and can be accomplished by optimizing the synthesis conditions.

Using a modified protocol of the facile solution route developed by Wang et al. [26], we prepared monodisperse amorphous TiO$_2$ particles having targeted sizes. In this process, titanium nitride (TiN) is oxidized to Ti$^{4+}$ by dissolving the material in purified water in the presence of H$_2$O$_2$ and NaOH. These alkaline conditions transform the Ti$^{4+}$ rapidly to the transparent yellow color of a stable Ti precursor, Ti-peroxo complex [Ti(OH)$_2$O$_2$] $^+$, which is soluble in water but sparingly soluble in alcohol. Thus, the addition of ethanol to an aqueous solution of the Ti-peroxo complex turns the color of the solution from yellowish to milky. After heating, the hydrolysis and condensation reactions afford small, amorphous TiO$_2$ particles that gradually increase in size to form amorphous TiO$_2$ particles as a white precipitate. The formation of the particles can be described as follows:

$$\text{Ti}^{4+} + \text{H}_2\text{O}_2 + 5 \text{OH}^{-} \rightarrow \text{[Ti(OH)]}_2\text{O}_2\text{]}^- + 2 \text{H}_2\text{O}$$

$$2\text{[Ti(OH)]}_2\text{O}_2\text{]}^- \rightarrow 2\text{TiO}_2 + 2\text{H}_2\text{O} + \text{O}_2 + 2 \text{OH}^-$$

$$2\text{Ti}^{4+} + 2\text{H}_2\text{O} + 10 \text{OH}^- \rightarrow 2\text{TiO}_2 + 6\text{H}_2\text{O} + \text{O}_2 + 2 \text{OH}^-$$

The growth of the TiO$_2$ particles is controlled by the concentration of Ti species in solution. In our study, a high concentration of Ti precursor (0.2 wt% TiN) gave relatively large and inhomogeneous TiO$_2$ particles (Fig. S1) due to the simultaneous nucleation and growth that occurs with an abundance of monomer. In contrast, a low concentration of initial Ti species (0.075 wt% TiN) leads to heterogeneous nucleation, followed by growth, where the spontaneous growth process is dominant. These phenomena gave TiO$_2$ particles that are more homogeneous and smaller in size (Fig. S2a).

When keeping the concentration of the TiN constant at 0.075 wt%, an increase in the reaction temperature (from 80 to 90 °C) gave systematically smaller TiO$_2$ particles due to the rapid continuous nucleation of TiO$_2$, leading to a decrease in average size of the amorphous TiO$_2$ particles (Fig. S2a–c). In this synthetic methodology, the ratio of the solvent (such as ethanol or isopropanol) to Ti species is restricted to a relatively narrow range [26]. For our experiments, the ratio of Ti species to ethanol was set at 1:2. The influence of the concentration of initial Ti species and the reaction temperature on the average size of TiO$_2$ particles is summarized in Table S1, where the average particle diameter was determined from both SEM images and DLS measurements.
The ability to control different sizes and shapes of TiO$_2$ particles is pivotal to realizing their targeted applications. Therefore, TiO$_2$ particles of many different sizes and shapes have been synthesized to take advantage of their size- and shape-dependent properties [59]. For example, a fine level of size control in the range of 10–100 nm is considered necessary for synthetic nanobiology [60]. Furthermore, if the size of the particles decreases, which increases the specific surface area, then the increase in surface energy of such particles can facilitate their aggregation [61]. This phenomenon can cause agglomeration of small TiO$_2$ particles, which limits their applications. On the other hand, large TiO$_2$ particles, which are superior for photocatalysis due to the long charge-recombination times associated with the longer diffusion length of electrons in such TiO$_2$ particles [62], are also unstable in the liquid phase because they agglomerate due to their enhanced van der Waals attraction [63]. These considerations necessitate the synthesis of TiO$_2$ particles having specific sizes and optical properties. In this study, we sought to prepare amorphous TiO$_2$ particles in the range of 200–250 nm since these particles could be well dispersed in the aqueous phase. Fig. 1a shows a typical SEM image of the amorphous TiO$_2$ particles prepared in our hands using 0.1 wt% TiN at 80 °C with a 1:2 volume ratio of Ti-peroxo complex solution to ethanol. The as-synthesized amorphous TiO$_2$ particles exhibit a smooth outer surface with only few irregularities in the interfacial structure with an average size of 245 ± 46 nm and 276 ± 55 nm as measured by SEM (Fig. 1a) and DLS (Fig. 1b), respectively.

3.2. Morphology and crystallinity of submicrometer anatase TiO$_2$ particles

Several studies have highlighted the importance of crystallinity in tuning the photocatalytic properties of TiO$_2$ [52,53]. The hypothesis is that larger crystals provide the required charge separation and increase the time taken for $e^-$ $h^+$ pairs to recombine, thereby giving rise to enhanced photocatalytic properties. Additionally, studies have shown that particles having high anatase content also have a low number of hydroxyl groups, and this latter feature is responsible for the superior properties. Less hydroxyl groups correspond to fewer photocatalysis-impairing peroxides. Therefore, in our efforts to synthesize TiO$_2$ particles with enhanced properties for photocatalytic applications, we directly tuned the crystallinity of the as-synthesized amorphous TiO$_2$ particles to anatase TiO$_2$ particles (ATiO$_2$) via hydrothermal treatment.

The hydrothermal treatment of amorphous TiO$_2$ particles introduced morphological changes to the outer surfaces of the TiO$_2$ particles with a change in particle size but not shape, which was retained. Fig. 2a and b show the morphologies of the ATiO$_2$ particles measured using SEM and TEM, respectively. After the hydrothermal reaction, the resultant ATiO$_2$ particles exhibit rough surfaces, which consist of a number of small protrusions. The average diameter of the ATiO$_2$ particles also diminished upon hydrothermal treatment from 245 ± 46 nm to 193 ± 43 nm, as measured by SEM. The diffraction patterns of the ATiO$_2$ structures obtained by XRD (see Fig. 2c) can be indexed to the anatase crystalline phase of TiO$_2$ (reference ICSD 9852) [64]. In addition, the observed sharp diffraction peaks indicate a high degree of crystallinity for the anatase TiO$_2$ particles. From the full width at half maximum (FWHM) of the strongest (1 0 1) diffraction of anatase, our ATiO$_2$ particle crystallite size was calculated using the Scherrer equation [65] to be ~20 nm.

Given that the ATiO$_2$ particles were derived directly from the homogeneous TiO$_2$ particles shown in Fig. 1, and that they failed to undergo degradation throughout the APTMS functionalization process and the subsequent Au shell growth process described below, argue strongly against their existence as aggregates. Furthermore, measurements of the size distribution of the ATiO$_2$ particles by DLS found no aggregates present in the solution (please see the DLS size distribution by intensity plot for the ATiO$_2$ particles in Fig. S3b, which shows a single peak).

3.3. Synthesis of submicrometer TiO$_2$ particles coated with partial Au shells

Gold nanoparticles (AuNPs) enjoy strong extinction maxima in the visible region due to a localized surface plasmon resonance (LSPR) that is generated by the collective oscillation of surface electrons. The exploitation of the LSPR of AuNPs to induce visible light photocatalytic activity in TiO$_2$ remains a challenging task because the LSPR is influenced by the size of the nanostructures. In this case, altering the size of the gold surface in contact with the TiO$_2$ particles might aid in optimizing the efficiency of the photoexcited ("hot") electron transfer from Au to TiO$_2$ [66–68]. Furthermore, using larger gold nanoparticles to decorate TiO$_2$ particles gives rise to enhanced photocatalytic activity due to the concomitantly stronger plasmonic near-fields [66,67]. Here, we designed and synthesized the structures to have TiO$_2$ cores sufficiently large to serve as templates for growing discontinuous Au shells (Au patches). The TiO$_2$ particles coated with partial Au shells might provide advantages over decorating the surfaces with small gold nanoparticles, given the broadened extinction spectrum (i.e., into the near infrared) of particles having the TiO$_2$-Au shell structure (i.e., TiO$_2$-AuShl).

Fabrication of the partial Au shells on the TiO$_2$ particles was accomplished using an established seeded-growth method [49]. In this synthetic strategy, APTMS-functionalized TiO$_2$ particles were initially prepared and then decorated with colloidal Au particles, prepared as described previously [49]. These attached gold nanoseeds were then used to nucleate the growth of a partial gold shell in the presence of HAuCl$_4$ and formaldehyde as the reducing agent.

![Fig. 1. Amorphous submicrometer TiO$_2$ particles: (a) SEM image and (b) DLS size distribution by intensity.](Image 145x55 to 456x179)
3.3.1. Surface composition and charge of APTMS-Functionalized ATiO2 particles

To characterize the surface composition and charge of the APTMS-functionalized ATiO2 particles, we collected data from analysis by XPS and zeta potential measurements, respectively. The high resolution XPS data of the synthesized ATiO2-APTMS particles are shown in Fig. 3, and the corresponding survey spectrum is shown in Fig. S4. The XPS spectrum in the Ti 2p region for the ATiO2 particles showed Ti 2p₃/₂ and Ti 2p₁/₂ spin-orbit splitting photoelectrons located at binding energies (BE) of 458.8 and 464.5 eV, respectively, with an energy difference of 5.7 eV [51]. The O 1s signal for ATiO2-APTMS shows a peak at 530.1 eV and a shoulder located at a higher binding energy of 532.3 eV. The O 1s peak at 530.1 eV can be assigned to oxide species (TiO2), and the peak at 532.3 eV is consistent with the reported O 1s binding energy for Si-O-Ti species [69], which reflects the bonding of APTMS to the surface of the ATiO2 particles. The XPS spectrum in the N 1s region confirmed the presence of a nitrogen peak associated with the APTMS molecules attached to the surface of ATiO2. The peak consisted of two types of nitrogen, where the lower binding energy at 399.9 eV is consistent with R-NH₂, and the higher binding energy at 401.6 eV is consistent with the positively charged nitrogen of NH₃⁺ [70].

The average zeta potential (surface charge) of the ATiO2-APTMS particles in aqueous solution was 43.5 ± 6.1 mV. These results indicate that the surfaces of particles are positively charged, plausibly due to the amino groups of APTMS. The large value for the zeta potential (≥30 mV) is consistent with a model in which the presence of charges on the surface confers colloidal stability to the APTMS-functionalized TiO2 particles, preventing their aggregation [71,72]. TEM images of the subsequently prepared ATiO2-Au seed particles are shown in Fig. S5, which reveals the presence of the colloidal Au seeds.

3.3.2. Morphology, phase structure, surface composition, and surface charge of ATiO2-AuShl

Fig. 4a and b show SEM and TEM images, respectively, of the synthesized ATiO2-AuShl particles. The SEM images depict a partial Au shell (i.e., Au patches) on the TiO2 particles, with average diameters of 199 ± 26 nm (see also Fig. S6 in the Supporting Information). The gold coating is discontinuous with topographical roughness on the nanometer scale. The growth of the partial gold shell on the TiO2 surface can be controlled by adjusting the ratio of the Au-seeded TiO2 and K-Au solutions. At a low concentration of gold salt (0.05 mM HAuCl4) and an excessive amount of reducing agent (29 mM formaldehyde), the incomplete shell structure surrounding the TiO2 particles formed gradually. Notably, our interpretation of partial coverage is supported by XPS analysis, which is a surface-sensitive analytical technique (vide infra).

We used XRD to characterize the phase structure of the ATiO2-AuShl particles (Fig. 4c). Due to the amount of Au deposition on the surface of TiO2 particles, gold was the main diffraction pattern found in the ATiO2-AuShl particles. Based on the XRD patterns, anatase peaks from our samples were still observed, especially...
the peak at 25.3°. While the deposition of the partial Au shell gave weaker intensities for the anatase peaks (compared to Fig. 2c), the partial Au shell exerted no influence on the crystalline structure of ATiO₂.

The surface composition of these ATiO₂-AuShl particles was analyzed by XPS; Fig. 5 provides a high-resolution XPS spectrum of the Au 4f binding energy region, and Fig. S7 shows the corresponding survey spectrum. These results confirm the presence of gold on the ATiO₂ particles. Moreover, weak peaks are evident in the N 1s and Si 2p spectral regions – an observation that is consistent with the formation of an incomplete Au shell on the surfaces of the APTMS-functionalized ATiO₂ particles. The Ti-to-Au ratio calculated from the Ti 2p and Au 4f peak intensities was 0.25 for the ATiO₂-AuShl particles. From these data, we can estimate crudely that the Au shells cover more than 50% of the surface of the ATiO₂ particles (please see the Supporting Information for details).

The surface charge of the particles in aqueous solution was measured using a Zetasizer Nano ZS. The average surface charge of the APTMS-functionalized ATiO₂ particles was 43.5 ± 6.1 mV, indicating that the particles were positively charged. However, the surface of the TiO₂ particles became negatively charged after decorating with either colloidal gold (−21.2 ± 6.8) or a partial gold shell (−26.8 ± 7.1). The negative charges on the surface of the particles can be attributed to the presence of THPC-stabilized colloidal
gold [73] or formate ligands present during the growth of the shell [49,74], respectively.

3.4. Optical properties of ATiO2-AuShl particles

The optical properties of the ATiO2-AuShl particles presented in Figs. 4 and S6 were examined by UV–Vis spectroscopy. Fig. 6 shows that the unmodified ATiO2 particles exhibited a sharp absorption maximum at ~320 nm, which tapered off rapidly without extending into the visible region. As a consequence of the deposition of Au patches on the TiO2 surface, the ATiO2-AuShl particles exhibited not only a distinct peak at ~326 nm arising from TiO2 [66,67], but also a broad peak centered at ~650 nm arising from the partial Au shell [75]. These results illustrate the effect of the LSPR of the Au shells on the extinction spectra of the TiO2-AuShl structures [75]. ATiO2-AuShl particles exhibited broad extinction spectra that extended to the visible region, affording good overlap with the emission wavelengths of incandescent and fluorescent light bulbs, which we used as a visible light source in applications involving photocatalysis (vide infra).

The effect of Au clusters on the extinction spectra of TiO2-Au structures has been reported [66,67], but relatively few studies
have focused on spherical TiO$_2$ structures. Seh et al. [67] compared the LSPR of core-shell Au-TiO$_2$ structures with that of Janus particles in which TiO$_2$ was coated on only one side of the AuNPs. These researchers found a larger red-shift in the LSPR peak for core-shell structures when compared to their Janus counterparts. Claverie and co-workers [66] showed that the plasmonic extinction of Au-TiO$_2$ nanohybrids is enhanced by the presence of a whispering gallery mode (WGM) resonance by increasing the size of the TiO$_2$ and/or AuNP component(s). Furthermore, the observed enhancement in the latter nanohybrids strongly depends on the penetration of the AuNPs within the TiO$_2$ matrix. In our case, the roughness and incomplete Au shell together with its LSPR likely influences the extinction spectra of the ATiO$_2$-AuShl particles [75,76], giving rise to the broadening of the peak in the visible region. We note also that, upon growing the partial Au shell, we observed a small red shift in the absorption maximum of TiO$_2$, and the slope of the edge of the absorption related to the band gap of TiO$_2$ was flattened; the latter, however, might arise from interband transitions of Au [77].

3.5. Photocatalytic degradation of methylene blue by ATiO$_2$-AuShl particles

The photocatalytic activity of the ATiO$_2$-AuShl particles shown in Figs. 4 and S6 under visible light was characterized by measuring the degradation of MB in an aqueous suspension under incandescent and fluorescent light. Fig. 7 shows the effects of visible light in conjunction with the ATiO$_2$ particles and ATiO$_2$-AuShl particles on the absorption spectra of an aqueous solution of MB. The intensity of the absorption maxima of MB decreased markedly in response to illumination of both incandescent and fluorescent light in the presence of particularly the ATiO$_2$-AuShl particles, which can be interpreted as the degradation of MB. In contrast, there was no significant change in the extinction spectra of MB when illuminated by visible light in the presence of the simple ATiO$_2$ particles, and there was no spectral shifts or changes in intensity for MB in the presence of any of the particles under dark conditions (i.e., no illumination whatsoever). More importantly, the MB degradation in the presence of the ATiO$_2$-AuShl particles during incandescent light activation was observed to be greater than that of fluorescent light illumination due to the broad emission spectrum of incandescent light, which overlapped well with the extinction spectra of the ATiO$_2$-AuShl particles (Fig. 6).

3.6. Photocatalytic hydrogen production by ATiO$_2$-AuShl particles

Data collected from a preliminary assessment the photocatalytic reaction for hydrogen production catalyzed by the ATiO$_2$-AuShl particles are shown in Fig. 8. The experiments were performed under irradiation using a 300-watt xenon lamp, with the resulting gas collected using a water-displacement method. The amounts of hydrogen gas collected for both ATiO$_2$ and ATiO$_2$-AuShl particles are shown in Fig. 8. The hydrogen evolution rate for reactions involving ATiO$_2$ and ATiO$_2$-AuShl particles remained steady for a period of 6 h. Importantly, the results indicate that the photocatalytic activity of the ATiO$_2$-AuShl particles is much greater than that of the ATiO$_2$ particles, especially after 1 h of reaction time.

3.7. Photoluminescence emission spectra and electron-hole recombination of ATiO$_2$-AuShl particles

Photoluminescence (PL) emission spectra have been widely used to investigate the efficiency of charge-carrier trapping, migration, and transfer, as well as to understand the fate of electron-hole pairs in semiconductor particles [78]. Anatase TiO$_2$ powder shows...
a broad PL emission peak at ~500 nm [79]. In this study, we measured the PL emission spectra of ATiO$_2$ particles and ATiO$_2$-AuShl particles at room temperature using an excitation wavelength of 353 nm. Fig. 9 shows the PL emission spectra of ATiO$_2$ particles and ATiO$_2$-AuShl particles over the wavelength range of 450–600 nm. At the same concentration, the intensity of the PL spectra of the ATiO$_2$ particles was higher than that of the ATiO$_2$-AuShl particles (i.e., the PL intensities decreased due to the growth of the partial gold shells). In these systems, the PL emission arises from the radiative recombination of self-trapped excitons [80,81]. Therefore, the observed reduction in PL intensity indicates a decrease in the radiative recombination process. The results appear to be consistent with a model in which the Au shells create photoexcited electrons via plasmonic modulation [44–46] and capture photoexcited electrons from TiO$_2$ [82], giving rise to a recombination route that involves no PL. As a consequence, the probability for excited electrons to recombine radiatively with holes in TiO$_2$ is strongly suppressed. The PL emission spectra for ATiO$_2$-AuShl particles imply reduced recombination and increased photocatalytic activity, which is consistent with the enhanced photocatalytic activity observed above for the ATiO$_2$-AuShl structures in the degradation of MB and hydrogen evolution described above.

4. Conclusions

Submicrometer anatase TiO$_2$ particles coated with partial Au shells (ATiO$_2$-AuShl) were synthesized using a seeded-growth method without the need of any structure-directing templates or surfactants. The synthetic strategy used to prepare the composite particles gave structures with good uniformity and controlled dimensions of TiO$_2$ core particles, which provided a facile pathway to the targeted monodisperse ATiO$_2$-AuShl particles. Measurements of the optical properties of the ATiO$_2$-AuShl particles found intense absorptions in the UV region (~326 nm) associated with TiO$_2$ and broad extinctions in the visible range (~650 nm) associated with the deposition of Au. In studies of potential applications, the ATiO$_2$-AuShl particles were found to enhance both the photocatalytic degradation of methylene blue (a model organic pollutant) and the photocatalytic generation of hydrogen via water splitting. Importantly, the growth of the partial Au shells on the surface of the TiO$_2$ core particles led to an overall broadening of the absorption of light across a range of wavelengths, giving access to mechanisms that inhibit electron-hole recombination and consequently enhance photocatalytic activity. The simplicity of the synthetic method, absence of toxic components, and tunability of particle size afforded by the strategies and materials reported here should permit the use of ATiO$_2$-AuShl particles in various light-driven technologies in fields ranging from medicine to energy.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2017.10.053.

References


