On the Role of Plasmonic Nanoparticles on the Photocatalytic of TiO₂ Nanoparticles for Visible-Light Photoreduction of Bicarbonate

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Abstract. The potential application of anatase titanium dioxide (TiO₂) nanoparticles for solar fuel generation has been recently attracting many attentions due to its excellent chemical stability. Nevertheless, the fast charge recombination during photoexcitation process may often reduce the photocatalytic activity. This work presents the role of plasmonic Au nanoparticles on enhancing the photocatalytic activity of TiO₂ nanoparticles for a visible-light-driven conversion of bicarbonate to formate. Here, two types of nano-sized Au and TiO₂ heterostructures, i.e., Au-TiO₂ Janus nanostructures and core-shell Au@TiO₂ nanostructures were successfully prepared and characterized using UV-Vis and HR-TEM. Results demonstrated that Au-TiO₂ Janus nanostructures had a superior photocatalytic activity compared to TiO₂ nanoparticles and core-shell Au@TiO₂ nanostructures. This photocatalytic enhancement is believed due to the presence of surface plasmon resonance (SPR) phenomenon in Au nanoparticles that provides a Fermi energy level, which could prevent the charge recombination process during photoexcitation.

1. Introduction
It is no secret that the negative environmental impact from the utilization of fossil-based fuels has led tremendous efforts on the quest for cleaner and more sustainable renewable energy resources. During the past several years, solar fuel generations such as photoreduction of CO₂ have attracted many attentions due to their economic viability, the simplicity of the production and relatively high solar to fuel conversion efficiency [1]. Besides, it has also been widely suggested that solar-driven photoreduction of CO₂ to added value chemical fuels such as CO, formic acid, methanol, and methane could be used as an effort for CO₂ utilization to significantly reduce its environmental effect as one of the greenhouse gases [2]. Nevertheless, the development of an effective and efficient system for the large-scale production of solar fuels based on such technology still remains challenging primarily due to the thermodynamic stability of CO₂. Over the last decades, tremendous efforts have been carried out to design a new type of highly active photocatalyst with excellent selectivity that could efficiently be used to facilitate solar-driven photoreduction of CO₂ into various beneficial fuel derivative compounds.

Currently, photoactive nano-sized semiconducting materials such as anatase TiO₂ have been widely used as one of the most common photocatalysts for photoreduction of CO₂ due to its excellent chemical
stability, good CO₂ photoreduction efficiency and selectivity against hydrogen evolution, environmental
to synthesis in the desired particle size and morphology [3,4]. However, recent
studies reported that the utilization of such material posts several drawbacks, especially for the
application of colloidal nano-sized TiO₂ particles in solar-driven photoreaction [5,6]. Reports have
suggest that the majority of the reduction in photocatalytic activity are due to the mismatch between
the excitation energy of TiO₂ that lies in the UV range (E₉ = 3.2 eV) and the solar energy where the
majority of the available absorption energy lies in the visible spectrum. In addition, fast charge carriers
(electrons and holes) recombination process could also further decrease the photocatalytic activity of
TiO₂ [7]. Therefore, many scientific efforts have been recently focused on developing new type of
catalyst materials that could absorb large amount of solar energy as well as prevent or reduce the fast
charge carrier recombination process.

Recent development in nanotechnology has allowed researchers to design various types of materials
and unlocked different unique new material physicochemical properties, which could be potentially
beneficial in many applications including photoreduction of CO₂. Besides, it is also reported that a
synergetic effect in physical and chemical properties could also be obtained by the heterostructuring
approach where two types of materials are combined to form a new heterostructured material. Therefore,
this work is aimed to study the effect of heterostructuring approach between anatase TiO₂ nanoparticles
and plasmonic Au nanoparticles towards its photocatalytic activity in the photo-induced reduction of
bicarbonate under visible light irradiation. It is believed that the integration of Au nanoparticles could
potentially enhance the photocatalytic activity by preventing the fast charge recombination due to the
presence of localized surface plasmon resonance (SPR) phenomenon. In this work, the effect of this
heterostructuring approach was studied by synthesizing two heterostructured materials, i.e., Janus Au-
TiO₂ nanostructures and core-shell Au-TiO₂ nanostructures. These as-prepared heterostructured
materials were characterized using HR-TEM and UV-Vis spectroscopy. Furthermore, their catalytic
activities in photoreduction of bicarbonate under visible light irradiation were also investigated in the
presence of glycerol as sacrificing donor (SD).

2. Materials and Experimental Methods

2.1. Materials

In this study, titanium(IV) isopropoxide (TTIP) (purity: 97%), NH₄OH solution (28-30% NH₃ in H₂O)
and absolute ethanol were purchased from Sigma-Aldrich and used for the preparation of anatase TiO₂
nanoparticles. To synthesize plasmonic Au nanoparticles, gold(III) chloride hydrate (HAuCl₄·xH₂O)
(purity: 99.95%), hydroxylamine hydrochloride and sodium citrate were also purchased from Sigma-
Aldrich. Hydrochloric acid was also used for the synthesis of Au-TiO₂ Janus nanostructure. All the
chemicals were directly used without additional purification.

2.2. Fabrication of TiO₂ nanoparticles

For the present work, TiO₂ nanoparticles were synthesized in accordance with a method reported in the
previous work [8]. However, TTIP was used as titanium source instead of tetrabutyl titanate (TBOT).
Typically, 0.75 mL of TTIP was mixed vigorously at 45°C for 6 hours with a mixture of 100 mL of
absolute ethanol and 0.3 mL of NH₄OH solution. The mixture was then centrifuged at 6000 rpm, and
the white precipitate was collected and washed three times with ethanol. The obtained white powder
was then dried overnight in a vacuum oven before being calcinated at 450°C for 2 hours for and used
further investigation.

2.3. Fabrication of Au nanoparticles

In this work, plasmonic Au nanoparticles were synthesized using a seed-mediated approach according
to a method reported elsewhere [9]. Initially, synthesis of small Au nano-seed was carried out by adding
12.5 mL of 40 mM Na-citrate to 125 mL of 0.254 mM HAuCl₄·xH₂O aqueous solution under vigorous
mixing. The final colloidal seed solution was obtained by boiling the mixture for 15 minutes until the
color of the solution becomes deep red. Afterward, the seed solution was then used for the synthesis of bigger Au nanoparticles. Typically, 20 mL of seed solution was firstly diluted in 180 mL of deionized water. The colloidal solution was further mixed with 7 mL of 2M hydroxylamine hydrochloride and 3 mL of 10 mM of HAuCl₄.xH₂O to obtain the final Au nanoparticles colloidal solution.

2.4. Heterostructuring of Au and TiO₂ nanoparticles
To study the effect of heterostructuring between TiO₂ and Au nanoparticles towards the photocatalytic activity of the catalyst, two types of heterostructured materials, i.e., Janus Au-TiO₂ nanostructures and core-shell Au@TiO₂ nanostructured were prepared. In this work, Janus Au-TiO₂ nanostructures were made by simply mixing some amount of the previously as-prepared TiO₂ and Au nanoparticles in acidic condition (pH 3) according to a method reported by Zhang and co-workers (2016) [10]. Meanwhile, core-shell Au@TiO₂ nanostructures were made by growing TiO₂ nanocrystal on top of the as-prepared Au nanoparticles as reported in previous work reported by Li and co-workers (2012) [8]. In this method, the as-prepared Au nanoparticles were vigorously mixed with a solution containing 100 mL ethanol absolute and 0.3 mL of NH₄OH. Afterward, the mixture was then slowly mixed with 0.75 mL of TTIP while continuously stirred for 24 hours at 45°C. Finally, the obtained precipitate was then collected via centrifugation followed by washing with deionized water and ethanol, respectively.

2.5. Characterization
In this work, the formation of the desired nanoparticles and heterostructured nanomaterials was confirmed by using two characterization techniques, i.e. high-resolution transmission electron microscope (HR-TEM) and UV-Vis spectroscopy. Here, TECNAI G2 Spirit Twin High-Resolution Transmission Electron Microscope (HR-TEM) was used to study both the micrographic image and crystal pattern of the as-prepared nanoparticles and nano-sized heterostructures. Meanwhile, optical and spectroscopic properties of the particles were characterized using Shimadzu UV-2450.

2.6. Photocatalytic experiment
To further investigate the performance of the as-prepared nanoparticles and nanostructures as the catalyst, a series of photocatalytic experiments was carried out in a home-made photo-reactor equipped with a visible light bulb. Typically, 0.05 mg of catalyst was added to a solution containing 40 mL of 0.3 M NaHCO₃ and 10 mL of 2M glycerol as sacrificing donor (SD). The mixture was then irradiated under visible light while continuously stirred for a total of 24 hours of reaction time. Aliquot samples were taken every 4, 8, 12 and 24 hours and further analyzed for the quantification of formic acid. The quantification of formic acid as the reaction product was carried out using high-performance liquid chromatography (HPLC), PG instruments LC 200 where 0.1% HClO₄ and methanol (95:1) was used as the mobile phase and C-18 column as the stationary phase. The detection of formic acid was carried out using a UV detector at the wavelength (λ) of 220 nm.

3. Results and Discussion
3.1. Au and TiO₂ heterostructures
Micrographic analyses from HR-TEM were carried out to study the formation of both Au and TiO₂ nanoparticles and nanostructures fabricated in this work. Based on the result, it can be observed that both sol-gel method and seed-mediation technique could be used to synthesized Au and TiO₂ nanoparticles with good dispersity and uniformity in particle size and morphology (Figure 1a-b). Results from TEM analyses also suggest that the average particle dimeter for both as-prepared Au and TiO₂ nanoparticles were in the range of 20-35 nm and 200-300 nm, respectively. Furthermore, results from heterostructuring of Au and TiO₂ materials were also confirmed by the result from HR-TEM analysis. For the first type of integration mode between Au and TiO₂ nanoparticles, it can be seen that few small Au nanoparticles were successfully integrated on the surface of bigger TiO₂ nanoparticles creating a so-called Janus Au-
TiO$_2$ nanostructures (Figure 1c). Additionally, TEM result also confirms the formation of the second integration mode where core-shell Au@TiO$_2$ nanostructures were obtained. As shown in Figure 1d, core Au nanoparticles could be distinguished from the shell TiO$_2$ by easily comparing the contrast in the TEM images. Typically, Au nanoparticles would appear darker than TiO$_2$ nanoparticles since it has more electron density.

Additional information regarding the formation of the desired nanoparticles and nanostructures could also be obtained from UV-Vis spectroscopy analysis. Figure 2 shows the UV-Vis spectra of the as-prepared nanoparticles and nanostructures. Based on the result, the formation of TiO$_2$ nanoparticles could be proven by their strong absorption at UV range (200-400 nm). Meanwhile, strong visible light absorption at $\lambda_{\text{max}} = 525$ nm could be considered due to the surface plasmon resonance (SPR) phenomenon of Au nanoparticles. Furthermore, UV-Vis spectra also revealed that both Janus Au-TiO$_2$ nanostructures and core-shell Au@TiO$_2$ nanostructures could absorb at both UV and visible light area, indicating the integration of both nanoparticles were successfully made. Nevertheless, it is also worth to mention that the visible light absorption of core-shell Au@TiO$_2$ nanostructures was significantly reduced due to the presence of shell TiO$_2$ nanoparticles.

3.2. Photocatalytic reduction of bicarbonate

As it has been mentioned earlier, the role of plasmonic Au nanoparticles to the photocatalytic activity of TiO$_2$ nanoparticles was studied by carrying out the photocatalytic experiments for conversion of bicarbonate to formic acid. Figure 3 presents the production of formic acid in photocatalytic reduction of bicarbonate to formic acid in the presence of various photocatalytic materials under visible light irradiation. According to the result, it can be observed that TiO$_2$ nanoparticles were not able to facilitate the conversion of bicarbonate to formic acid under the irradiation of visible light primarily due to the insufficient absorption energy compare to the optical bandgap of TiO$_2$ nanoparticles (3.2 eV). Interestingly, a similar result was also obtained when core-shell Au@TiO$_2$ nanostructures were used as the catalyst. It is believed that this phenomenon is mainly due to the inability of photon particles from
visible light to efficiently penetrate the TiO$_2$ shell and interact with the core plasmonic Au nanoparticles for SPR process. As a result, integration of Au nanoparticles was not able to facilitate the enhancement of photocatalytic activity of TiO$_2$ nanoparticles (Figure 3).

Nevertheless, significant enhancement in photocatalytic activity was obtained when the integration between two nanoparticles was made by fabricating Janus Au-TiO$_2$ nanostructures. Based on the result from the photocatalytic experiment in Figure 3, it is obvious that a substantial amount of formic acid could be produced when Janus Au-TiO$_2$ nanostructures were used as the catalyst even though the photocatalytic reaction was performed under visible light irradiation. It is believed that this photocatalytic enhancement is primarily to the presence of SPR phenomenon in Au nanoparticles that provides a Fermi energy level, which could prevent the charge recombination process during photoexcitation. Furthermore, it is also believed that plasmonic process may be associated with the generation of high-energy (hot) electrons, which can be injected to the conduction band of TiO$_2$ nanoparticles and used for reduction of bicarbonate. Figure 4 shows the proposed schematic mechanism of the photocatalytic enhancement in Janus Au-TiO$_2$ nanostructured materials.

4. Conclusions
The role of plasmonic Au nanoparticles to the photocatalytic activity enhancement of TiO$_2$ nanoparticles was carried out in this study. Here, Au nanoparticles were successfully integrated with TiO$_2$ nanoparticles by fabricating two types of heterostructured materials, i.e., Janus Au-TiO$_2$ and core-shell Au@TiO$_2$ nanostructures and used as the catalyst in the photocatalytic conversion of bicarbonate to formic acid under visible light irradiation. Based on the result, it is demonstrated that Janus Au-TiO$_2$ nanostructures were able to facilitate the photoconversion of bicarbonate (0.32 mmol of formic acid/g cat. at 24 hrs. light irradiation). Meanwhile, no formic acid was obtained when both TiO$_2$ nanoparticles and core-shell Au@TiO$_2$ nanostructures were utilized. It is believed that this photocatalytic enhancement is caused by not only the injection of hot electron from Au nanoparticles to conduction
band of TiO₂ but also the prevention of fast charges recombination as the result of the presence of surface plasmonic resonance (SPR) phenomenon.

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