Synthesis and characterization of Au-TiO, Janus nanostructures

M F Mulyantono, J Gunlazuardi and M Khalil

Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author’s email: mkhalil@sci.ui.ac.id

Abstract. This work reports a comprehensive study on the synthesis and characterization of Au-TiO Janus nanostructures from pre-synthesized Au nanoparticles and anatase TiO₂ nanoparticles. Here, well-distributed Au nanoparticles with mean particle diameter of ~35 nm were successfully prepared using seed-mediated method, which exhibited a unique surface plasmon resonance (SPR) properties at 525.5 nm. Meanwhile, anatase TiO₂ nanoparticles with perfectly spherical morphology were synthesized via sol-gel method, which could easily be integrated by the as-prepared Au nanoparticles. Based on the result, it is found that the resultant nanostructured exhibited a Janus heterostructure feature, where Au nanoparticles were efficiently found to be attached on the surface TiO₂ nanoparticles. Furthermore, spectroscopic analyses also revealed that the integration of Au nanoparticles could widen the absorption spectrum of TiO₂ to visible range due to the presence of SPR phenomenon.

Keywords: TiO₂, nanoparticles, Au nanoparticles, Janus nanostructures, plasmonic, HR-TEM

1. Introduction

During the last several decades, research on the development of new nanostructures has become a hot topic in the fields of materials, physics, and chemistry. Furthermore, many interests have also been widely extended from one dimension to two or three-dimensional spaces, as well as the integration of multiple nanocomposites structures with controllable morphologies to achieve various new properties [1–3]. Owing to the rapid advances in synthetic nanochemistry, which enables one to fabricate numerous nanostructured materials with well-defined sizes, shapes, crystal facets, and compositions have carved the pathway for developing a new type of materials with excellent physicochemical properties [4]. Among many kinds of heterostructured nanomaterials, Janus nanostructure has been recently attracted much attention due to their exceptional abilities to generate synergetic and tunable physical and chemical properties which would not be accessible in their individual counterparts [5].

According to literature, colloidal semiconductor nanoparticles such as anatase TiO₂ nanoparticles have been widely considered as one of the most active catalytic materials for various photocatalytic reactions due to their high photo-activity, stability, low cost and corrosion resistance [6]. However, the application of colloidal TiO₂ nanoparticles as a photocatalyst for solar-driven photocatalytic reactions where the excitation energy is mostly originated from visible light can often be limited by two major issues, i.e. (1) large band gap, and (2) rapid electron-hole recombination [7]. Recently, many efforts have been carried out to circumvent these two significant issues. One of the conventional means to solve these limitations is via the utilization of heterostructured nanomaterials as the catalyst for instance by integrating TiO₂ nanocatalyst with photosensitive materials such as dyes or quantum dots nanoparticles to enhance the photocatalytic activity of TiO₂ in a broader light spectrum, or with plasmonic particles to reduce electron-hole recombination process [8–9].

Recently, tremendous efforts have been focused on the development of highly photoactive Janus Au-TiO nanostructures due to its remarkable enhanced photocatalytic performances and power
conversion efficiencies [8]. It is believed that the integration of plasmonic particles such as Au nanoparticles to TiO would introduce two new prominent features. i.e., (a) surface plasmon resonance (SPR) which enables the strong absorption at the visible area, and (b) Schottky junction which could enhance the charge separation efficiency. Furthermore, it is also reported that, upon excitation, this integration would also shift the Fermi level of TiO nanoparticles to a more negative potential, which enables one to reduce the frequent possibility of electron-hole recombination process. Nevertheless, these features are also reported to be significantly affected by various factors, such as morphology and crystal phase of the semiconductor itself, morphology of the plasmonic particles, and more importantly how stable the integration between each component in the Janus heterostructure is. In this study, an investigation of the synthesis and characterization of Au-TiO Janus nanostructure was presented. Here, plasmonic Au nanoparticles were prepared via seed-mediated approach and integrated at acidic condition onto the surface of anatase TiO nanoparticles. In this present study, anatase TiO was synthesized by a sol-gel method where titanium(IV) isopropoxide (TTIP) was used as the titanium precursor and hydrolyzed at basic condition. Furthermore, the as-prepared Au-TiO Janus nanostructure was characterized using X-Ray Diffraction (XRD), UV-Vis Spectrophotometer, Diffuse Reflectance Spectroscopy (DRS) and High-Resolution Transmission Electron Microscope (HR-TEM).

2. Materials and methods

2.1. Materials
Gold(III) chloride hydrate (HAuCl₃·xH₂O) (purity: 99.95 %), hydroxylamine hydrochloride and sodium citrate were used for the synthesis of Au nanoparticles and purchased from Sigma-Aldrich. Titanium(IV) isopropoxide (TTIP) (purity: 97 %) was obtained from Sigma-Aldrich and used as titanium precursor. NH₄OH solution (28-30 % NH₄ in H₂O) and absolute ethanol were also purchased from Sigma-Aldrich and used in the sol-gel reaction. Finally, hydrochloric acid was also used for the synthesis of Au-TiO, Janus nanostructure.

2.2. Synthesis of Au nanoparticles
In this study, Au nanoparticles were synthesized via seed-mediated technique according to a method reported by Hais and co-workers [10]. Accordingly, Au seeds were firstly synthesized by rapidly adding 12.5 mL of 40 mM sodium citrate solution into 125 mL of 0.254 mM HAuCl₃·xH₂O under vigorous stirring until the color of the solution becomes deep red. To obtain Au nanoparticle seeds, the mixture was then boiled for 15 minutes and then cooled to room temperature. To prepare Au nanoparticles with bigger particle size, 20 mL of Au seeds solution was diluted with 180 mL of water. The solution was then mixed with 7 mL of 2 M hydroxylamine hydrochloride (NH₄OH·HCl) followed by the dropwise addition of 6 mL of 25.4 mM of HAuCl₃·xH₂O under vigorous stirring at room temperature. The resulting Au nanoparticles solution was then stored at 4 °C in darkness and used for further investigations.

2.3. Synthesis of anatase TiO nanoparticles
In this work, a sol-gel method reported by Li and co-workers was used to synthesize anatase TiO nanoparticles [11]. However, TTIP was used as titanium source instead of tetrabutyl titanate (TBOT). Typically, 0.75 mL of TTIP was added into a mixture of 100 mL of absolute ethanol and 0.3 mL NH₄OH which was then vigorously stirred at 4 °C for 24 hours. The result solution was then centrifuged at 6000 rpm, and the obtained white precipitates were collected, washed with deionized water and ethanol, respectively. The precipitate was dried at 60 °C overnight and then calcined at 450 °C for 2 hours and used for further investigations.

2.4. Preparation of Au-TiO Janus nanostructure
Au-TiO Janus nanostructure was fabricated by integrating Au nanoparticles onto the surface of anatase TiO nanoparticles at acidic condition. Here, 0.05 g of the as-synthesized nanoparticle TiO powder was added into 25 mL of the colloidal as-synthesized Au nanoparticles solution. The mixture was then vigorously stirred at room temperature while the pH of the solution was adjusted to pH 3 by slowly adding 0.01M of HCl solution. The mixture was then stirred for 30 minutes at room temperature, and the precipitate was recovered by centrifugation, followed by washing with deionized water and ethanol, respectively. The powder was then dried in a vacuum oven at 60 °C overnight and used for further investigations.
2.5. Characterization

To study the physical and chemical properties of the as-prepared nanoparticles, several characterization techniques were carried out in this work. To investigate the crystal structure of the as-synthesized nanoparticles, X-Ray Diffraction (XRD) analysis was carried out using PANanalytical X’Pert Pro MPD (PANanalytical B.V., Almelo, Netherlands) equipped with fast detector X’Celerator and CuKα radiation as the source. Meanwhile, micrographic images of the nanoparticles were collected using TECNAI G2 Spirit Twin High-Resolution Transmission Electron Microscope (HR-TEM). To further determine the spectroscopic properties of the as-prepared nanoparticles, both spectroscopic UV-Vis and DRS analyses were carried out using Shimadzu UV-2450.

3. Results and discussion

3.1. Synthesis of Au nanoparticles

In general, tremendous efforts have been conducted to develop a facile method for the synthesis of Au nanoparticles with full control of size and morphology. In this work, Au nanoparticles were prepared using a seed-mediated method where a smaller Au nanoparticles seeds were firstly made using sodium citrate as strong reducing and capping agent. These Au seeds were then used to fabricate bigger Au nanoparticles using a milder reducing agent, i.e., hydroxylamine hydrochloride. Figure 1 presents the TEM images of Au seed particles and the final Au nanoparticles. Based on the result, it is shown that monodisperse polyhedral Au seed particles with average particle diameter ~13 nm were successfully synthesized (figure 1a). Furthermore, bigger polyhedral Au nanoparticles with an average particle diameter of around ~35 nm could easily be fabricated from these seed particles (figure 1b).

In general, the mechanism of Au nanoparticle growth in a seed-mediated method could be described using LaMer’s nucleation theory [12]. Typically, the nanoparticles growth could be divided into three consecutive stages, i.e. (i) atom production from reduction reaction of the metal precursor, (ii) nucleation of seed particles, and (iii) nanocrystal growth due to the addition of atoms into the particle seeds. During the first and second stages, fast reduction of metal precursor using strong reducing such as sodium citrate is typically preferred to induce more self-nucleation atom events, which ultimately lead to the formation of many small nanoparticle seeds. Meanwhile, mild or weak reducing agent often renders a fewer self-nucleation process which often leads to the creation of less and bigger particles. It is believed that this phenomenon occurs due to the rapid build-up of the atom saturation. Finally, the particles size would gradually increase due to the continuous addition of metal atoms until the activation energy for fluctuation of the crystal structure becomes very high. At this point, mild or weak reduction agent such as hydroxylamine is typically preferred to avoid the fast addition of metal atoms into the particle clusters creating large particles with wide size distribution [13].

Furthermore, UV-Vis absorption was measured to investigate the spectroscopic properties of the as-synthesized Au nanoparticles. Figure 2 shows the UV-Vis spectrum of the as-synthesized Au nanoparticles. Based on the result, it could be seen that the as-synthesized Au nanoparticles absorbed strongly at 525.5 nm due to the surface plasmon resonance (SPR) phenomenon ($\lambda_{\text{SPR}}$). It is believed that
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Figure 2. UV-Vis spectrum of the as-synthesized final Au nanoparticles synthesized using seed-mediated method.

the position of this peak is strongly affected by the size and shape of the nanoparticles. Reports have shown that the position of \( \lambda_{\text{SPR}} \) is typically shifted to higher wavelength as the particle size increases. Recently, Haiss and co-workers have accurately estimated the diameter of Au nanoparticles using the following equation [10]:

\[
d = \frac{\ln(\frac{\lambda_{\text{SPR}}}{\lambda_0})}{L_2}
\]

where, \( d \) is the particle diameter (nm), \( \lambda_{\text{SPR}} \) represents the experimental peak position for SPR. Meanwhile, \( \lambda_0 \), \( L_1 \), and \( L_2 \) are the fit parameters determined from the theoretical values. The values for \( \lambda_0 \), \( L_1 \), and \( L_2 \) are 512, 6.53 and 0.0216, respectively [10]. Based on the calculation using equation (1), it can, therefore, be estimated that the calculated particle diameter of the as-synthesized was 33 nm, which is very close to the experimental average particle diameter obtained from TEM analysis (~35 nm) (figure 1b).

3.2. Synthesis of anatase TiO\(_2\) nanoparticles

Anatase TiO\(_2\) nanoparticles were synthesized via a sol-gel method where TTIP was used as the titanium precursor in basic condition. In this work, XRD analysis was carried out to investigate the crystalline structure of the as-synthesized TiO\(_2\) nanoparticles. Figure 3a shows the XRD diffractogram of the reaction products before and after calcination. Based on the result, it can be observed that an amorphous phase was initially obtained after the sol-gel reaction. Nevertheless, the crystalline structure transformed into anatase after calcination at 450°C for 2 hours. Results demonstrated that all the Bragg peaks suggest that the primary crystal phase of the reaction product after calcination could be unambiguously indexed as anatase phase and no other peaks were obtained for both rutile or brookite phases (JCPDS, No. 21-1272). Furthermore, the broadening of major peak for (101) anatase phase could also be used as an indication for the formation of nano-scale TiO\(_2\) particles grains.

Besides, TEM analysis was also carried out to obtain micrographic information about the morphology, particle size and particle size distribution of the as-synthesized anatase TiO\(_2\) nanoparticles. According to the result (figure 3b), the sol-gel reaction of TTIP at basic condition followed by calcination was able to produce a highly monodisperse spherical anatase TiO\(_2\) nanoparticles with an average particle size diameter of around ~520 nm. According to literature, the crystal growth mechanism of these nanoparticles was initiated by the formation of small TiO\(_2\) seed particles which cluster together to form a spherical TiO\(_2\) nanocluster via LaMer’s growth and Ostwald ripening process [11].
3.3. Synthesis of Au-TiO Janus nanostructure
In this work, the formation of Au-TiO Janus nanostructures was firstly investigated by determining the UV-Vis reflectance of the reaction products obtained from the integration of Au and TiO$_2$ nanoparticles reaction. Based on the result (figure 4a), it could be observed that Au nanoparticles could easily be integrated onto the surface of the as-prepared TiO$_2$ nanoparticles at low pH. This is proven by the strong absorption of both UV (200-350 nm) and visible light (525.5 nm). Strong absorption at UV region is believed due to the presence of the energy band gap between TiO$_2$ valance and conduction band (3.2 eV). Meanwhile, the strong absorption of energy at visible region can be ascribed due to the presence of SPR phenomenon of Au nanoparticles. The successful integration of Au nanoparticles onto the surface of TiO$_2$ was also supported by the result obtained from TEM analysis. The result from micrographic image analysis of the reaction product shows that few Au nanoparticles ($\phi \approx 35$ nm) were attached on the surface of TiO$_2$ nanoparticles ($\phi \approx 520$ nm) suggesting the successful formation of Janus nanostructure (figure 4b). Besides, TEM image also shows that during the integration of Au nanoparticles on the surface of TiO$_2$ at low pH, the morphological properties and size of both nanoparticles were pertained and remain unchanged.
4. Conclusions
The successful formation of Au-TiO$_2$ Janus nanostructure was reported in this work. Here, the as-prepared Au nanoparticles (φ = ~ 35 nm) synthesized via seed-mediated method could easily be attached to the surface of anatase TiO$_2$ nanoparticles (φ = ~ 520 nm) prepared by sol-gel method at low pH. The result from UV-Vis DRS analysis demonstrated that the as-synthesized Au-TiO$_2$ Janus nanostructures were strongly absorbing at both UV and visible region, i.e., 200–350 and 525.5 nm, respectively. The strong absorption at UV region is believed due to the presence of TiO$_2$ band gap, whereas SPR phenomenon of Au nanoparticles renders a strong absorption visible region. Moreover, results also show that the morphology and particle size of both Au and TiO$_2$ nanoparticles remained unchanged during the integration process.

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