Plasma Enhanced Wet Chemical Surface Activation of TiO$_2$ for the Synthesis of High Performance Photocatalytic Au/TiO$_2$ Nanocomposites

Nguyen Thi Thu Thuy 1,2, Do Hoang Tung 3,*, Le Hong Manh 3, Joon Heon Kim 4, Sergey Ivanovich Kudryashov 5, Pham Hong Minh 3 and Nguyen The Hien 1

1 Faculty of Engineering Physics and Nanotechnology, VNU University of Engineering and Technology, 144 Xuan Thuy Road, Cau Giay District, Hanoi 10000, Vietnam; thuthuyt34@gmail.com (N.T.T.T.); ngoduonghoaianh@gmail.com (N.T.H.)
2 Department of Fundamental of Fire Fighting and Prevention, University of Fire Prevention and Fighting, 243 Khuat Duy Tien, Thanh Xuan, Hanoi 10000, Vietnam
3 Institute of Physics, Vietnam Academy of Science and Technology, Vietnam, 18 Hoang Quoc Viet Street, Cau Giay District, Hanoi 10000, Vietnam; lehongmanh@gmail.com (L.H.M.); lhthu.cgd@mail.com (P.H.M.)
4 Biomedical and Nanophotonics Laboratory, Advanced Photonics Research Institute, GIST, Gwangju 61005, Korea; joonhkim@gist.ac.kr
5 Lebedev Physical Institute, Leninskiy Prospect 53, 119991 Moscow, Russia; sikiudr@sci.lebedev.ru
* Correspondence: dhtung@iop.vast.ac.vn
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Abstract: To enhance the effectiveness of TiO$_2$ as a photocatalyst, it was believed that the drawbacks of the large bandgap and the rapid electron-hole recombination can be overcome by coupling TiO$_2$ with plasmonic metal nanoparticles. The incorporation of the nanoparticles onto the TiO$_2$ surface requires a suitable procedure to achieve the proper particle adhesion. In this work, we propose a simple, clean, and effective surface activation of TiO$_2$ using plasma enhanced wet chemical surface treatment. Under only 5 minutes of plasma treatment in a 3% NH$_3$/3% H$_2$O$_2$ solution, gold nanoparticles were found better adhered onto the TiO$_2$ surface. Hence, the methylene blue degradation rate of the Au/TiO$_2$ under sunlight treated was improved by a factor of 3.25 times in comparison to non-treated Au/TiO$_2$ and by 13 times in comparison to the bare rutile TiO$_2$.

Keywords: Plasma-liquid interaction; sunlight degradation; Au/TiO$_2$ nanocomposite; surface treatment; noble metal based photocatalyst

1. Introduction

Titanium dioxide (TiO$_2$) is regarded as one of the most fascinating materials for environmental applications [1,2]. It has been intensively investigated as a photocatalyst due to its high photocatalytic activity. Despite numerous advantages, such as low fabrication cost, environmental friendliness, and high chemical stability, TiO$_2$ still cannot be widely applied due to its inherent drawbacks. TiO$_2$ has a rapid electron-hole recombination [3] and a high bandgap energy [4]. These drawbacks can be overcome by coupling the semiconductor with plasmonic metal nanoparticles [5]. The plasmonic metal nanoparticles are expected to not only improve the visible light absorption, but also to minimize the electron-hole recombination reaction in TiO$_2$. It has been demonstrated that surfacial plasmonic resonance improved the light absorption, increased the charge separation, and enhanced the suppression of electrons and holes, and thus significantly improved hydrogen generation [6].

There are many methods to support the adhesion of Au nanoparticles on the titania surface, such as photodeposition [7], deposition–precipitation [8], as well as the sol–gel method [9,10]. However, the improvement of the photocatalyst activity (PCA) in Au loaded titania is just several times higher...
than that of the original one. This may be due to the weak connection between the Au nanoparticles and the TiO$_2$ surface. It is noted that PCA shows significantly more improvement in the one spot synthesis method than in the multistep one [9].

In order to improve the adhesion of gold nanoparticles on its surface, TiO$_2$ normally follows a lengthy complicated procedure of surface activation to attach the oxygenic or nitrogenous functional groups or even both on its surface and subsequently undergoes a surface functionalization by adding the appropriate ligands (e.g. MPTMS–3-mercapto-propyl-tri-methoxy-silane). For example, Rehacek et al. [11] used a solution of NH$_4$OH:H$_2$O:H$_2$O (5:1:1 in volume) to treat TiO$_2$ for 20 hours at room temperature or under the UV radiation for 1 hour and then illuminated with deep ultraviolet (DUV) for 10 minutes to improve its wettability. Higgins et al. [12], however, incubated TiO$_2$ at 80 °C in a NaOH solution for 1 hour to add the OH groups and then in a urea solution for 4 hours to add the nitrogenous groups.

Plasma technology has been efficiently used in the fabrication of nanomaterials [13] especially the plasma–liquid interaction method [14]. For gold nanoparticle synthesis, Au$^+$ can be reduced either by solvated electrons or by reactive species generated in the solution [15]. The two most dominant reactions are:

$$[\text{AuCl}_4]^+ + 3e_{aq}^- \rightarrow \text{Au}^0 + 4\text{Cl}^-$$

and

$$n\text{H}_2\text{O}_2 + n\text{OH} + \text{Au}^{2+} \rightarrow [\text{AuCl}_4]^+ + n\text{HO}_2^- + n\text{H}_2\text{O}$$

where $e_{aq}^-$ stands for solvated electron.

Recently, the electrochemical reduction of HAuCl$_4$ acid in dense hydrosols of high-index diamond sub-micrometer sized particles was tested as a promising “green” fabrication route for “metallic nanoparticle–dielectric” clusters in their colloidal solutions. The plasma–liquid interaction approach requires only water-based solutions with the metal precursor and is completely free of any additional reducing and/or capping agents [16]. It showed successful decoration of gold nanoparticles (AuNPs) onto the diamond surface. In the presence of the diamond particles, substantial “red” spectral shifts of the plasmonic resonance were observed for the AuNPs, being more pronounced for the decorated diamond particles ($\approx$536 nm), than for those adsorbed AuNPs on their surfaces from the mechanical mixture of their colloids ($\approx$530 nm). These shifts of the plasmonic resonance peak could be unambiguously related to the high-index dielectric environment of the AuNPs, provided by their attachment to the diamonds [17].

Many studies on nonequilibrium gas phase plasmas–fluid interactions have been performed. In particular, the reactive transient species in the interfacial plasma–fluid region play a critical role in plasma-induced liquid reactivity [18,19]. Moreover, the reactants are activated by the plasma or the heat produced by the plasma and, in some cases, the liquid can also act as a moderator suppressing or delivering plasma processes with excess energy.

In this work we propose a novel, simple, clean, and effective surface activation of TiO$_2$ using the plasma enhanced wet chemical surface treatment. Plasma–liquid interaction speeds up the surface treatment of TiO$_2$ with NH$_3$/H$_2$O$_2$ solution for the better attachment of the Au nanoparticles. This treatment helps minimize the need of NH$_3$ and H$_2$O$_2$ as well as the treatment time, but still improves the PCA of the Au/TiO$_2$ nanocomposites.

2. Materials and Methods

Commercial submicron (averaged size ca. 800 nm) rutile TiO$_2$ particles (R800) from US Research Nanomaterials, Inc. Houston, TX 77084, United States, were used in our studies. Au(III) chloride trihydrate (99.9%; HAuCl$_3$H$_2$O) was purchased from Sigma–Aldrich, while 30% hydrogen peroxide solution and 25%–28% ammonia solution were purchased from Xilong Scientific Co., Ltd, Chaoshan Road, Shantou, Guangdong 510663, China.

The micro-plasma system consisted of a DC high voltage source, a plasma nozzle, a gold electrode and a 50 mL glass beaker from Bomex with 20 mL treatment solution (see Figure 1). The
plasma nozzle had a Teflon housing with one end being a hollow cylinder of 15 mm in outer diameter and 10 mm in inner diameter, covering the plasma electrode, and the other end being connected to a 6 mm quick gas connector. In our experiments, the plasma electrode was a sharpened 1.6 mm diameter tungsten rod connected to the high voltage via a 100 kΩ resistor. The other polarity was grounded and connected to the gold electrode, which was submerged into the solution. The processing current was maintained constantly at 5 mA.

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Figure 1. Micro-discharge workstation for (a) the electrochemical gold reduction, (b) the TiO₂ treatment and (c) image of running plasma for gold nanoparticle synthesis from HAuCl₄ 0.06 mM precursor solution.

In order to synthesize gold nanoparticles (AuNPs) from HAuCl₄ solution, we use the above mentioned plasma system with the negative polarity of the plasma electrode (Figure 1a). Several precursor concentrations were used to study the gold nanoparticle productivity of the system.

Figure 2. Schematic synthesis and diagnostic procedures of Au/TiO₂ composites.

The schematic synthesis and diagnostic procedures of Au/TiO₂ composites are presented in Figure 2. In order to prepare the treated TiO₂ samples, 20 mL TiO₂: 0.1 g·L⁻¹, 3% NH₃, and 3% H₂O₂
were first subjected to a positive plasma (Figure 1b) for 5 minutes to modify the TiO₂ surface. After that, 0.12 mL HAuCl₄ 10 mM was added together with 0.25 mL DI water to get 20 mL solution of treated TiO₂ 0.1 g·L⁻¹ and HAuCl₄ 0.06 mM (about 0.37 mL water was vaporized under the plasma treatment). Non-treated TiO₂ samples were prepared by simply adding NH₃, H₂O₂, and H₂AuCl₄ solutions to get 20 mL TiO₂ 0.1 g·L⁻¹, 3% NH₃, 3% H₂O₂, and 0.06 mM H₂AuCl₄.

Both treated and non-treated TiO₂ were then irradiated with the negative plasma (configuration in Figure 1a) for 15 minutes to completely reduce Au(III) to form the desired Au/TiO₂ nanocomposites. The resulting solutions were subsequently vacuum dried to eliminate all remaining H₂O₂ and NH₃. Suppose all Au precursor has been reduced to AuNPs, one can easily calculate that the gold particles loaded on the TiO₂ in these Au/TiO₂ nanocomposite samples is of about 11.8% in weight. 10 mL DI water was added to the samples to get 10 mL 0.2236 g·L⁻¹ Au/TiO₂, treated and non-treated samples.

To investigate and compare the sunlight photocatalyst activity of and among the bare TiO₂, the non-treated and treated Au/TiO₂, using above sample preparation procedure we fabricated in darkness 2 mL solution of treated Au/TiO₂ 0.1118 g·L⁻¹ and Methylene blue (MB) 20 mg·L⁻¹; 2 mL solution of non-treated Au/TiO₂ 0.1118 g·L⁻¹ and MB 20 mg·L⁻¹; and 2 mL solution of 0.1 g·L⁻¹ bare TiO₂, MB 20 mg·L⁻¹.

The decomposition of MB under the solar simulator irradiation (AM 1.5) with a power of 100 mW cm⁻² (Oriel Sola) was analyzed by following the evolution of its characteristic absorbance peak at 664 nm. The time dependent concentrations of MB obtained through the experiments were fitted to pseudo-first order kinetics as follows:

\[ \ln \left( \frac{C_t}{C_0} \right) = -k \cdot t \]

where \( C_0 \) (g·L⁻¹) and \( C_t \) (g·L⁻¹) are the concentrations of MB before irradiation and at a given time \( t \) (in minute-min), respectively; \( k \) is the pseudo-first order rate constant (min⁻¹).

The UV-vis absorbance of the aqueous samples in a 1 cm wide quartz cuvette was measured with an UV-near IR spectrometer of the type V-570 (Jasco). The particle morphologies were examined in a transmission electron microscope (TEM) JEM 1010.

3. Results and Discussion

In order to investigate the activating ability of plasma on the solution, we compared the decolorization of methylene blue (MB) with three solutions; 20 mL 10% hydroperoxide, 20 mL 10% hydroperoxide treated with 5 minutes of plasma (plasma activated H₂O₂), and 20 mL deionized water treated with 5 minutes of plasma (plasma activated DI). UV-vis absorption spectroscopy was used to trace the time evolution of 665 nm absorption peak after 1 mL solution of MB 40 mg·L⁻¹ was added into these solutions (see Figure 3). The MB concentration gradually decreased in the untreated H₂O₂. In contrast, it showed a small drop of about 2% in plasma activated DI then remained unchanged. However, in plasma activated H₂O₂, the concentration showed a stepwise evolution with a large drop of about 17% then followed by a gradual decrease with larger slop in comparison to the untreated H₂O₂.
Figure 3. Time evolution of absorption peak at 665 nm of methylene blue after being added to plasma activated 10% H₂O₂, 10% H₂O₂, and plasma activated deionized water solutions.

The concentration drops in the plasma treated solutions were attributed to the transient reactive species created by plasma which react very fast with MB. This result confirms the activating ability of plasma on reactant solutions. With the presence of H₂O₂ in the liquid, plasma can create significant amount of transient reactive species, making the plasma treated solution become more reactive.

In order to find out the optimal conditions for the gold nanoparticle synthesis using our plasma–liquid interaction system [16], different precursor concentrations were used and treated with negative plasma for 15 minutes and the absorption spectra of the as-obtained solutions were checked. As can be seen in Figure 4, the UV-vis absorption spectra of the as-obtained solutions show the characteristic absorption peaks of the gold nanoparticles. The position and the intensity of the absorption peaks significantly depend on the precursor concentration. When the precursor concentration increases from 0.015 mM to 0.12 mM, the absorption peak position shifts up from ca. 528 nm to ca. 558 nm, while the peak intensity first increases sharply with precursor concentration, reaches its maximum with HAuCl₄ concentration of 0.06 mM then gradually decreases. For this investigation, therefore, we used 0.06 mM HAuCl₄ as an optimal precursor to generate AuNPs for the synthesis of Au/TiO₂ nanocomposites. At this precursor concentration, the plasma–liquid interaction creates fairly uniform spherical AuNPs with the size in the range of about 35–45 nm (see Figure 4) and the characteristic absorption peak at about 534 nm.

Figure 4. Absorption spectra (a) and images (b) of the different gold nanoparticle solutions synthesized from different precursor concentrations.
Gold nanoparticles were also generated at the 0.06 mM precursor concentration with another plasma–liquid interaction configuration as reported in [20]. The authors there have attained smaller particle sizes distributed around about 20 nm, but the characteristic absorption peak was positioned at about 534 nm like in our case. The reason for the discrepancy in the particle size may be attributed to the shape of the obtained AuNPs. As reported in [9], AuNPs were obtained in quite diverse shapes including spherical, triangular, cubic, hexagonal, and pentagonal grains and also bars, whereas in our experiments the AuNPs were mostly in the spherical shape with rather uniform size (see Figure 5). In their setup, the authors used a hollow electrode type so the plasma channel was surrounded by air. Meanwhile, in our case, the rod electrode was surrounded by the Ar medium. This difference in the plasma medium may be attributed to the difference in the Ar nanoparticle shapes.

Figure 6 presents the TEM images of the nontreated Au/TiO₂ nanocomposite. One can easily see that the AuNPs are no longer homogenous and uniform in shape, but their size is distributed in the range from about 10 nm to around 55 nm. This is in line with the broader absorption band in their UV-vis absorption spectra (Figure 7). It is likely that these AuNPs are formed in the solution before being attached to TiO₂ surface because they show similar size distribution as those generated from
the pure HAuCl₄. All generated AuNPs are seen immobilized on the TiO₂ surface with clear and sharp boundaries indicating a rather weak connection between them. This also supports a small red shift of about 15 nm compared to the situation with the pristine AuNPs. The influence of TiO₂ on the reduction mechanism of Auric ions may be twofold: catalyst effect under UV radiation from plasma which enhances the particle formation, resulting in bigger particles and growth termination by capturing the growing particles onto the titania surface.

Unlike the non-treated Au/TiO₂, there are two types of AuNPs existing in the treated Au/TiO₂, one with a similar size distribution as in the non-treated Au/TiO₂ composites and the other with very small sizes ranging from 4 nm to 9 nm (Figure 8). Both of these types exhibit noticeably close contacts to the TiO₂ surface with seemingly undetectable boundaries. The small particles even seem to be submerged into the TiO₂ matrix (see Figure 8). The UV-vis spectra (Figure 7) of this sample show a good agreement with the TEM results. The spectra of the treated Au/TiO₂ show two absorption peaks which can be attributed to the two classes of AuNP particle size (there is no AuNP aggregation). The absorption peaks are strongly red shifted from about 523 nm to 538 nm (for smaller AuNPs) and from 534 nm to around 680 nm (for larger AuNPs). Using the refractive index difference of 1.279 (rutile TiO₂ has refractive index of 2.609) applied for the situation presented in Figure 5 in [21], one can easily estimate the red shift for particles with the original plasmonic resonance of 534 nm in water (n = 1.33) to be about 130 nm which is in good agreement with the red shift of the larger sized AuNPs in the treated Au/TiO₂. This result again confirms a strong contact between the treated TiO₂ and the AuNPs in treated Au/TiO₂ nanocomposites.

![Figure 7](image_url)

**Figure 7.** Extinction UV-vis spectra of (a) non-treated rutile TiO₂ (red curve), treated rutile TiO₂ with 3% NH₃, 3% H₂O₂ under a 5 minute plasma treatment (black curve) and (b) bare Au-nanoparticles generated from 0.06 mM HAuCl₄ (red curve), non-treated Au/TiO₂ nanocomposite (blue curve), and treated Au/TiO₂ nanocomposite (black curve).
As expected from the above analysis, the MB sunlight degradation rate of the non-treated Au/TiO$_2$ was improved in comparison to that of bare TiO$_2$ (Figure 9). Even weakly attached AuNPs already increased the degradation rate by a factor of 4 from 0.01 min$^{-1}$ with TiO$_2$ to 0.04 min$^{-1}$, with non-treated Au/TiO$_2$ supporting the electron–hole separation and absorption spectra broadening. This effect is maximized in the treated Au/TiO$_2$ as the degradation rate reaches the extremely high value of 0.13 min$^{-1}$. This value is far better than the MB sunlight degradation rate in the order of only 0.022 min$^{-1}$ obtained with the AuNPs doped TiO$_2$ prepared by the chemical method, as reported by S. Padikkaparambil et al. [22].
4. Conclusions

A high performance sunlight photocatalyst of the type Au/TiO$_2$ nanocomposite has been successfully synthesized by the incorporation of gold nanoparticles (AuNPs) onto the TiO$_2$ surface using the plasma–liquid interaction method. This method is proven to be efficient and environmentally clean in terms of minimizing processing time and the usage of treating agents. There are two types of AuNPs confined in the treated Au/TiO$_2$ samples: the small size AuNPs, with the size of about 2 nm, may grow directly on the TiO$_2$ surface, while the larger size AuNPs with the particle size distributed around about 40 nm grow in the solution before being attached onto the TiO$_2$ surface.

The plasma enhanced surface activation has brought a potentially strong improvement of the grafting of AuNPs onto the TiO$_2$ surface. The contact between the AuNPs and TiO$_2$ in the treated Au/TiO$_2$ sample is tight which results in a very strong red shift of the plasmonic resonant peak. The sunlight degradation rate of MB with treated Au/TiO$_2$ has increased 3.25 times in comparison to that of the non-treated Au/TiO$_2$ and even by the factor of 13 in comparison to that of the bare rutile TiO$_2$.

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