Synergistic Effect of Dual Particle-Size AuNPs on TiO\textsubscript{2} for Efficient Photocatalytic Hydrogen Evolution

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Abstract: Design of efficient catalysts for photocatalytic water-splitting hydrogen evolution is of fundamental importance for the production of sustainable clean energy. In this study, a dual particle-size AuNPs/TiO\textsubscript{2} composite containing both small (16.9 ± 5.5 nm) and large (45.0 ± 9.8 nm) AuNPs was synthesized by annealing two different sized AuNPs onto TiO\textsubscript{2} nanosheets. Dual particle-size AuNPs/TiO\textsubscript{2} composites of 2.1 wt% catalyze photocatalytic H\textsubscript{2} evolution 281 times faster than pure TiO\textsubscript{2}. Control experiments indicate the observed rate increase for the 2.1 wt% dual particle-size AuNPs/TiO\textsubscript{2} composites is larger than 2.1 wt% small AuNPs/TiO\textsubscript{2} composites, or 2.1 wt% large AuNPs/TiO\textsubscript{2} composites in isolation. The observed photocatalytic enhancement can be attributed to the synergistic effect of dual particle-size AuNPs on TiO\textsubscript{2}. Specifically, small-sized AuNPs can act as an electron sink to generate more electron-hole pairs, while the surface plasmon resonance (SPR) effect of large-sized AuNPs concurrently injects hot electrons into the TiO\textsubscript{2} conduction band to enhance charge transfer. In addition, a gold-dicyanodiamine composite (GDC)-directed synthesis of 2.1 wt% dual particle-size AuNPs/TiO\textsubscript{2} composites was also completed. Notably, a photocatalytic efficiency enhancement was observed that was comparable to the previously prepared 2.1 wt% dual particle-size AuNPs/TiO\textsubscript{2} composites. Taken together, the synergistic effects of dual particle-size AuNPs on TiO\textsubscript{2} can be potentially used as a foundation to develop semiconductor photocatalyst heterojunction with enhanced photocatalytic activity.

Keywords: AuNPs/TiO\textsubscript{2}; synergistic effect; dual-size particle; photocatalytic; hydrogen production

1. Introduction

The development of clean and renewable fuels continues to attract significant attention due to the environmental concern caused by global consumption of fossil fuels. Electrochemical photolysis of water to generate hydrogen (H\textsubscript{2}) using a TiO\textsubscript{2} electrode was first reported in 1972 \cite{1}. Since that time, photocatalytic H\textsubscript{2} production has become one of the most promising routes to secure H\textsubscript{2} as an alternative energy source \cite{2}. Use of TiO\textsubscript{2} as a photocatalyst was often driven by its low cost and strong oxidizing capacity; however, the high recombination rate of photoinduced electron-hole pairs significantly limited the photocatalytic activity of TiO\textsubscript{2}. Approaches for improving the photocatalytic performance of TiO\textsubscript{2} have included: (a) heteroatom doping \cite{3}; (b) textural design \cite{4}; and (c) heterojunction formation with metals or other semiconductors \cite{5,6}. Among these
approaches, semiconductor heterojunction design, especially co-catalyst coupling, has been extensively investigated [7]. Suitable co-catalysts promote effective transfer of photogenerated electrons by serving as electron reservoirs. Additionally, co-catalysts provide extra active sites for the photocatalytic redox reactions, which results in suppressed electron-hole recombination [8,9].

Gold (Au) has been extensively studied as a co-catalyst of TiO$_2$ to enhance photocatalytic performance [10–12]. The inclusion of Au allows electrons to be readily trapped and transferred, because its Fermi level is lower than the conduction band of TiO$_2$ [13]. Additionally, the surface plasmon resonance (SPR) effect of Au nanoparticles (AuNPs) can broaden the absorption of the photocatalyst [14]. Broader light absorption increases the amount of available “hot electrons” [15], which can bolster photocatalysis performance. Indeed, recent studies have demonstrated that addition of AuNPs as co-catalysts can significantly enhance photocatalytic H$_2$ production [16,17]. However, previous studies that utilized conventional deposition–precipitation synthetic methods often focused on investigating single-sized AuNPs as co-catalysts [18–20]. Given that SPR effect is strongly dependent on Au particle size [21–23], the evaluation of how multi-sized AuNPs co-catalysts on TiO$_2$ influence its photocatalytic H$_2$ production efficiency is highly desired.

Here, we employed two particle-size populations of AuNPs to decorate TiO$_2$ for remarkably enhanced photocatalytic H$_2$ evolution. Two kinds of AuNPs with different size populations were first synthesized, which were then utilized to modify pre-prepared TiO$_2$ nanosheets via a direct annealing process. After annealing, two scaled AuNPs with the size distributions of 16.9 $\pm$ 5.5 nm (“small”) and 45.0 $\pm$ 9.8 nm (“large”) were successfully anchored onto TiO$_2$. The resulting AuNPs/TiO$_2$ photocatalyst (2.1 total wt% AuNPs, 2 wt% large AuNPs + 0.1 wt% small AuNPs) produced a H$_2$ evolution efficiency 281 times greater that of TiO$_2$ alone. Control experiments indicate that the photocatalytic efficiency of AuNPs/TiO$_2$ composites decorated with both small and large AuNPs significantly outperforms AuNPs/TiO$_2$ composites containing small or large AuNPs at a total concentration of 2.1 wt% AuNPs on TiO$_2$. Inspired by this result, we wondered if analogous H$_2$ evolution could be achieved when preparing dual particle-size AuNPs/TiO$_2$ photocatalysts using a different synthetic method. We explored an alternative synthetic method for preparing 2.1 wt% AuNPs/TiO$_2$ (two similar AuNP particle size distributions) by annealing of gold-dicyanodiamine composites (GDCs) onto TiO$_2$. An enhanced photocatalytic efficiency comparable to the above synthesized 2.1 wt% AuNPs/TiO$_2$ photocatalyst was observed. Taken together, our results reveal a synergistic effect of the two AuNP particle size distributions when the resulting 2.1 wt% AuNPs/TiO$_2$ photocatalysts are used for H$_2$ generation. This work may serve as a framework for future semiconductor photocatalyst heterojunction designs for enhanced photocatalytic applications.

2. Experimental Section

2.1. Materials

Chloroauric acid hydrate (HAuCl$_4$·4H$_2$O, $\geq$47.8% Au basis), dicyanodiamine (C$_2$H$_4$N$_4$, $\geq$98%), sodium borohydride (NaBH$_4$, $\geq$98%), and triethanolamine (C$_6$H$_15$NO$_3$, $\geq$99.8%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) Titanium tetrachloride (TiCl$_4$, $\geq$99.0%) and ethylene glycol (C$_2$H$_6$O$_2$, $\geq$98.0%) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China) Glycine (C$_2$H$_5$NO$_2$, $\geq$99.0%) and sodium sulfate (Na$_2$SO$_4$, $\geq$99.0%) were purchased from Shanghai Titan Scientific Co., Ltd. (Shanghai, China) All reagents were used without further purification. High-purity water with the resistivity of $\geq$18.2 M$\Omega$cm was used in all experiments.

2.2. Preparation of TiO$_2$ Nanosheets

Titanium tetrachloride (0.125 mmol) was added to a stirring solution of ethylene glycol (EG, 77.5 mL). The solution was stirred until it became clear and no additional HCl gas was generated. Deionized (DI) water (2.5 mL) was added, and the resulting solution was transferred to a 100 mL
Teflon-lined autoclave. The reaction mixture was maintained at 150 °C for 4 h. The resulting solid was rinsed with a mixture of DI water and ethanol (volume ratio: 1/2) and subsequently freeze-dried.

2.3. Fabrication of Large (45.0 ± 9.8 nm) AuNPs/TiO₂ Photocatalysts

An aqueous solution (100 mL) containing HAuCl₄ (12.5 µmol) and glycine (1.25 mmol) was heated at 100 °C for 10 min in a microwave reactor (700 W). The as-prepared AuNPs solution (2.46 mg Au/100 mL H₂O) was then mixed with TiO₂ (100 mg) at different Au:TiO₂ ratios, freeze-dried, and annealed at 550 °C in a tube furnace for 6 h in air with a ramp of 5 °C min⁻¹. The wt% values of large sized AuNPs relative to TiO₂ were 0.1, 0.5, 1.0, 2.0, 2.1, and 3.5 wt%, respectively.

2.4. Fabrication of Small (16.9 ± 5.5 nm) AuNPs/TiO₂ Photocatalysts

A freshly prepared aqueous NaBH₄ solution (10 mL, 0.5 M) was rapidly added into an aqueous HAuCl₄ (0.5 mmol, 190 mL) solution under vigorous stirring. The resulting solution was stirred at room temperature (ca. 22 °C) for 2.5 h. The as-obtained AuNPs solution was combined with TiO₂ (100 mg), vortexed to ensure thorough mixing, and freeze-dried. Annealing was completed at 550 °C in a tube furnace for 6 h in air with a ramp of 5 °C min⁻¹. The wt% values of small AuNPs relative to TiO₂ were 0.02, 0.05, 0.1, 1.0, 2.0, and 2.1 wt% respectively.

2.5. Preparation of Dual Particle-Size AuNPs/TiO₂ Photocatalysts

TiO₂ (100 mg) was added to a 10 mL aqueous solution containing both 2.0 wt% large AuNPs and 0.1 wt% small AuNPs. The resulting solution was sonicated until thoroughly mixed, freeze-dried, and annealed in a tube furnace at 550 °C for 6 h in air with a ramp of 5 °C min⁻¹.

2.6. Preparation of GDC-Directed Dual Particle-Size AuNPs/TiO₂ Photocatalysts

An aqueous solution containing HAuCl₄ (0.02 M) and dicyanodiamine (0.006 M) was heated at 60 °C for 30 min to synthesize gold-dicyanodiamine composites (GDCs). The resulting solid was rinsed multiple times with DI water. The 2.1 wt% dual particle-size AuNPs/TiO₂ was also achieved by mixing appropriate amounts of GDCs and TiO₂ nanosheets, and annealing them in a tube furnace at 550 °C in air for 6 h with a ramp of 5 °C min⁻¹.

2.7. Characterization Methods

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a field emission transmission electron microscope (Tecnai G2 F30 S-TWIN, FEI, Hillsboro, OR, USA) at an acceleration voltage of 300 kV. X-ray diffraction (XRD) measurements were completed on an X-ray diffractometer (D8 Advance, BRUKER-AXS, Billerica, MA, USA) with Cu Kα radiation. UV-vis diffuse reflectance spectra (DRS) were obtained with a UV-Vis-NIR spectrophotometer (Cary-5000, Varian, Palo Alto, CA, USA). Photoluminescence (PL) spectra were measured on a spectrophuorometer (F-4500, Hitachi, Tokyo, Japan, Xe lamp as light source). Time-resolved fluorescence spectra were obtained with time-resolved spectroscopy (FLSP20, Edinburgh Instruments, Edinburgh, UK). Surface electronic states and compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB250 Xi, Thermo Scientific, Somerset, NJ, USA). Brunauer-Emmett-Teller (BET) specific surface area (SBET) was determined by nitrogen adsorption-desorption isotherm measurements (ASAP 2020 HD88, Micromeritics, Norcross, GA, USA).

2.8. Photocatalytic Activity Evaluation

Photocatalytic activity was evaluated by H₂ generation from water splitting. The photocatalytic H₂ evolution reactions were carried out in a Pyrex reactor under vacuum. The temperature of the reactant solution was kept at 6 °C by flowing cooling water. Each as-prepared photocatalyst (10 mg)
was dispersed in a mixture of 80 mL DI water and 20 mL triethanolamine solution. Subsequently, the resulting suspensions were illuminated by a 300 W xenon lamp (CEL-HXF 300, CEAULIGHT, Beijing, China, 350–780 nm). Gas chromatography with a thermal conductivity detector (TCD) was employed for H₂ production analysis using N₂ as carrier gas.

2.9. Electrochemical Characterization

Transient photocurrent and electrochemical impedance spectroscopy (EIS) were conducted in Na₂SO₄ (0.1 M) using an electrochemical instrument (Gamry Interface 1010, Warminster, PA, USA) with a traditional three-electrode system under light irradiation (300 W Xe-lamp). The applied photocurrent bias was 0.9 V. The working electrode was prepared by dispersing each photocatalyst (5 mg) in 1 mL of ethanol (containing 25 μL of nafion solution) and dropped on FTO glass. Ag/AgCl and Pt electrodes were used as the reference electrode and counter electrode, respectively.

3. Results and Discussion

Large AuNPs/TiO₂ and small AuNPs/TiO₂ photocatalysts with different AuNPs weight ratios were synthesized to determine the optimum weight percent of AuNPs for photocatalysis. TEM was utilized to evaluate the microstructures of the prepared photocatalysts. The large AuNPs/TiO₂ composite (Figure 1a,b) had an average Au nanosphere size of 45.0 ± 9.8 nm (Figure S1), while the small AuNPs/TiO₂ composite (Figure 1d,e) had an average Au nanosphere size of 16.9 ± 5.5 nm (Figure S2). Both composites appeared to be well distributed onto the TiO₂ matrix. The 0.235 nm lattice spacing observed in these composites can be ascribed to the d spacing of Au (111) crystal plane, while the 0.352 nm lattice spacing belongs to the TiO₂ (101) crystal plane (Figure 1c,f) [24,25].

Photocatalytic performance of all synthesized photocatalysts was evaluated by measuring H₂ evolution rates from water splitting. Each photocatalyst was evaluated for 3 h to minimize experimental errors. The H₂ evolution rate using large AuNPs/TiO₂ composites increased up to 2 wt% AuNPs and then decreased at 3.5 wt% (Figure 2a). The highest H₂ evolution rate of 4006 μmol h⁻¹ g⁻¹ (2 wt% AuNPs) was approximately 215 times greater than that of TiO₂ (18.67 μmol h⁻¹ g⁻¹) under
the same conditions. Small AuNPs/TiO₂ composites exhibited increasing H₂ evolution up to 1 wt% AuNPs; however, no significant increase was observed above 0.1 wt% (Figure 2b). The 0.1 wt% small AuNPs/TiO₂ composites exhibited H₂ production with a generation rate of 3340 μmol h⁻¹ g⁻¹, which was approximately 179 times greater than that of pure TiO₂.

Based on the observations above, we hypothesized that a dual particle-size AuNPs/TiO₂ composite (2 wt% large AuNPs + 0.1 wt% small AuNPs) could exhibit a synergistic effect that would further increase the rate of H₂ evolution. Indeed, a hydrogen evolution rate of 5245 μmol h⁻¹ g⁻¹ was higher than the rate observed with either single particle-size AuNPs/TiO₂ composite (Figure 2c). Control experiments with 2.1 wt% small AuNPs/TiO₂ or 2.1 wt% large AuNPs/TiO₂ failed to achieve the H₂ evolution rate observed for the 2.1 wt% dual particle-size AuNPs/TiO₂ composite (Figure 2d). These results indicate the fabrication of both small and large AuNPs populations onto TiO₂ appears to lead to a synergistic effect for photocatalytic H₂ evolution.

![Figure 2](image)

**Figure 2.** (a,b) Photocatalytic H₂ generation rates for different concentrations of large AuNPs/TiO₂ and small AuNPs/TiO₂ photocatalysts under light irradiation (350–780 nm). (c) Photocatalytic H₂ generation rates of pure TiO₂, small AuNPs/TiO₂, large AuNPs/TiO₂, and dual particle-size AuNPs/TiO₂ photocatalysts under light irradiation (350–780 nm). (d) Photocatalytic H₂ generation rates of 2.1 wt% small AuNPs/TiO₂, 2.1 wt% large AuNPs/TiO₂, and 2.1 wt% dual particle-size AuNPs/TiO₂ under light irradiation (350–780 nm).

The successful fabrication of a dual particle-size 2.1 wt% AuNPs/TiO₂ composite was confirmed by TEM and HRTEM images (Figure 3). Two distinguishable AuNP size distributions, of 17.3 ± 7.5 nm and 46.3 ± 6.1 nm, were found by measuring 100 individual AuNPs (Figure S3). Significantly, these particle-size distributions were very similar to those observed with the single particle-size composites described above. The Au (111) (0.235 nm) and TiO₂ (101) (0.352 nm) crystal planes seen in Figure S3 indicated that both Au and TiO₂ were successfully incorporated in the composite structure. The crystal phase of pure TiO₂, 0.1 wt% small AuNPs/TiO₂, 2 wt% large AuNPs/TiO₂, and 2.1 wt% dual particle-size AuNPs/TiO₂ were investigated using powder XRD. All XRD patterns showed several characteristic peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3°, and 75.0°.
corresponding to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) planes of the anatase phase of TiO$_2$ (Figure 3d). The large AuNPs/TiO$_2$ and dual-particle size AuNPs/TiO$_2$ also displayed peaks at 38.2$^\circ$, 44.4$^\circ$, 64.6$^\circ$, and 77.5$^\circ$, which can be indexed to the (111), (200), (220), and (311) planes of Au. These observations were consistent with TEM results and provide additional evidence of successful fabrication of AuNPs onto TiO$_2$ [26,27]. Small AuNPs/TiO$_2$, however, exhibited no significant difference from TiO$_2$. We hypothesize this is due to the low content (0.1 wt%) of small AuNPs on TiO$_2$.

UV-vis diffuse reflectance spectra (DRS) and Photoluminescence (PL) spectra were collected to gain insight into the relationship between optical and photocatalytic properties of the synthesized materials. As shown in Figure 4a, the photocatalysts containing AuNPs exhibited a light absorption range significantly beyond the 390 nm absorption edge of pure TiO$_2$ [28–31]. In addition, a typical absorption peak around 580 nm can be observed from all three AuNPs/TiO$_2$ hybrids, corresponding to the SPR of AuNPs [32]. PL spectra displayed fluorescence quenching from all three AuNPs/TiO$_2$ hybrids (Figure 4b). These results suggest the deposition of AuNPs onto TiO$_2$ can efficiently restrain the electron-hole recombination [33,34], which leads to faster transfer of electrons between the TiO$_2$ and the AuNPs. In addition, the time-resolved fluorescence decay spectra of all samples were also
obtained (Figure 4c). The results suggest all four photocatalysts possessed similar fluorescence lifetimes; however, changes to the band gap of TiO$_2$ were observed after introducing different-sized AuNPs (Figure S4), indicating coupling AuNPs onto TiO$_2$ could increase the utilization of light [35]. The large AuNPs/TiO$_2$ and dual particle-size AuNPs/TiO$_2$ exhibited higher absorption intensity than that of small AuNPs/TiO$_2$. This observation can be attributed to the stronger electron-trapping effect caused by the SPR of large AuNPs populations. Additionally, obvious reduction in PL emission intensity was observed from both the large and dual particle-size AuNPs/TiO$_2$, likely resulting from the stronger electron-hole separation effect in these two photocatalysts. Both observations are consistent with the photocatalytic testing results, in which the large AuNPs/TiO$_2$ and dual particle-size AuNPs/TiO$_2$ composites exhibit higher photocatalytic efficiency than that of the small AuNPs/TiO$_2$ composites. However, no major optical property difference was observed between large AuNPs/TiO$_2$ and dual particle-sized AuNPs/TiO$_2$. As such, the improved photocatalytic properties of the dual particle-size AuNPs/TiO$_2$ must emerge from synergistic interactions between the two AuNPs populations on the TiO$_2$ surface.

![Figure 4.](image)

Figure 4. (a) UV-vis diffuse-reflectance spectra, (b) photoluminescence spectra, and (c) time-resolved luminescence decay spectra of pure TiO$_2$, small AuNPs/TiO$_2$, large AuNPs/TiO$_2$, and dual particle-size AuNPs/TiO$_2$ hybrids.

Electrochemical measurements of photocurrent responses were collected for all four samples to further probe the enhanced photocatalytic activity of the dual particle-size AuNPs/TiO$_2$ composite (Figure 5a). Both 2 wt% large AuNPs/TiO$_2$ and 0.1 wt% small AuNPs/TiO$_2$ composites demonstrated enhanced photocurrent density than that of pure TiO$_2$, implying a higher separation efficiency of photogenerated charge carriers from large AuNPs/TiO$_2$ and small AuNPs/TiO$_2$ [36]. Significantly, the photocurrent density observed from 2.1 wt% dual particle-size AuNPs/TiO$_2$ was almost three times greater than the photocurrent observed from the 2 wt% large AuNPs/TiO$_2$ sample. This result strongly suggests that the co-existence of dual particle-size AuNPs on TiO$_2$ streamlines charge separation and photogenerated electron transfer. EIS measurements were also carried out under light irradiation (350–780 nm) to provide additional evidence in support of this observation. EIS Nyquist plots of pure TiO$_2$, 0.1 wt% small AuNPs/TiO$_2$, 2 wt% large AuNPs/TiO$_2$, and 2.1 wt% dual particle-size AuNPs/TiO$_2$ displayed gradually decreased semicircle radius (Figure 5b). Since the resistance of charge transfer was directly proportional to the semicircle radius of the Nyquist plot [36,37], the introduction of 2.1 wt% dual particle-size AuNPs onto TiO$_2$ could enhance the charge transfer separation and inhibit the recombination of photogenerated electron-hole pairs. Taken together, it appears the population of small AuNPs dispersed on TiO$_2$ can readily capture electrons generated from the conduction band of TiO$_2$; this phenomenon leads to the generation of more electron-hole pairs (narrower band gap) and much easier electron migration [16,38]. Secondly, the large AuNPs offer intensive local electric fields through SPR [39]. Hot electrons formed can be injected into the conduction band of TiO$_2$, which greatly facilitates electron transfer and light use efficiency.
Figure S5 shows the N$_2$ adsorption-desorption isotherms of all four samples. All isotherms featured typical type-IV curves; however, the pure TiO$_2$ sample was found to have a specific surface area of 17.09 m$^2$ g$^{-1}$. The small AuNPs/TiO$_2$, large AuNPs/TiO$_2$, and dual particle-size AuNPs/TiO$_2$ exhibited BET surface areas of 58.82 m$^2$ g$^{-1}$, 43.23 m$^2$ g$^{-1}$, and 11.77 m$^2$ g$^{-1}$, respectively. Surface area results suggest the photocatalytic activity enhancement of dual particle-sized AuNPs/TiO$_2$ did not originate from a change in surface area [40]. XPS measurements were also employed to analyze the surface electron states in the dual particle-size AuNPs/TiO$_2$ composites. The survey XPS spectrum of the dual particle-size AuNPs/TiO$_2$ and pure TiO$_2$ is shown in Figure 6a. The weak Au signal was mainly due to the low content of AuNPs on the TiO$_2$ surface. The peak position of Ti 2p (458.6 and 464.3 eV) in AuNPs/TiO$_2$ composites shows no shift compared to pure TiO$_2$ (Figure 6b). A 0.3 eV negative shift in the O 1s peaks at 532.9 and 530.2 eV (Figure 6c), as well as a 0.8 eV negative shift from standard Au 4f$^{0,5/2}$ and Au 4f$^{0,7/2}$ (Figure 6d), were observed in the dual particle-size AuNPs/TiO$_2$ composites. These perturbations were consistent with an increase in electron density for Au and O$^{2-}$. XPS results can be taken as direct evidence for the formation of a Schottky barrier between the AuNPs and TiO$_2$ [36,41,42].

Based on the results described above, we wondered if analogous H$_2$ evolution rates could be observed for dual-particle sized AuNPs/TiO$_2$ composites prepared by a different synthetic method. Such a result would provide evidence that dual-particle fabrication may be beneficial for AuNPs/TiO$_2$ composites regardless of the chosen synthetic strategy. With this in mind, we prepared a 2.1 wt% dual-sized AuNPs/TiO$_2$ composite by introducing GDCs onto the TiO$_2$ matrix. TEM images of the as-prepared GDCs revealed a uniform spherical structure (diameter ~450 nm) with homogenous incorporation of 3–5 nm AuNPs (Figure S6a). After annealing GDCs to TiO$_2$, both large-sized AuNPs and small-sized AuNPs were observed on the TiO$_2$ surface (Figure 7). AuNP size distributions were determined to be 45.7 ± 2.9 nm and 16.3 ± 2.8 nm by measuring 100 individual AuNPs (Figure S7). Notably, these two size distributions were very similar to the size distributions of AuNPs on the previously synthesized dual particle-size AuNPs/TiO$_2$ composites. XRD experiments (Figure S8) revealed characteristic Au peaks of (111), (200), (220), and (311) crystal planes, which confirms the successful incorporation of AuNPs onto the TiO$_2$ matrix. Photocatalytic H$_2$ experiments using GDC-directed dual particle-size AuNPs/TiO$_2$ photocatalysts revealed a H$_2$ evolution rate slightly higher (6150 µmol h$^{-1}$ g$^{-1}$) than that observed from the previously prepared dual particle-size AuNPs/TiO$_2$ photocatalysts (Figure 8a). All additional characterization experiments indicated both dual particle-size AuNPs/TiO$_2$ composites have analogous electrochemical properties (Figure 8b,c). BET surface area measurements of the 2.1 wt% GDC-directed AuNPs/TiO$_2$ composite indicated no alternation of specific surface area after AuNPs incorporation, similar to that of 2.1 wt% dual particle-size AuNPs/TiO$_2$ (Figure S9). Binding energy shifts and intensity changes observed from XPS
spectra (Figure S10) showed strong interactions between AuNPs and TiO$_2$ in the 2.1 wt% GDC-directed AuNPs/TiO$_2$ composite for photocatalytic enhancement, consistent with the result obtained from the 2.1 wt% dual particle-size AuNPs/TiO$_2$ photocatalysts.

A feasible mechanism for the enhanced H$_2$ evolution performance from both dual particle-size AuNPs/TiO$_2$ composites is presented in Figure 9. Initially, photo-excited electron-hole pairs are generated from the conduction and valence band of TiO$_2$ under light irradiation. The generated electrons are then readily captured and transferred to AuNPs [34,43], which contributes to the formation of a Schottky barrier between AuNPs and TiO$_2$. Specifically, small-sized AuNPs dispersed on TiO$_2$ can promote the capture of electrons generated in the TiO$_2$ conduction band, which forms more electron-hole pairs and facilitate the charge transfer [44,45]. Concurrently, an intensive local electric field near large-sized AuNPs can be formed though SPR [15]. Consequently, the hot electrons can be injected into the conduction band of TiO$_2$ and significantly boost the charge transfer [19]. As a result, the captured electrons in small sized AuNPs, as well as the transferred electrons from large sized AuNPs to TiO$_2$, can both synergistically promote the reduction of H$_2$O to H$_2$ (holes are consumed by sacrificial agent TEOA).
Nanomaterials 2019, 9, x 10 of 14

Figure 7. (a–c) TEM and (d) HRTEM photographs of 2.1 wt% gold-dicyanodiamine composite (GDC)-directed dual particle-size AuNPs/TiO$_2$ composite.

Figure 8. (a) Photocatalytic H$_2$ generation rates, (b) transient photocurrent responses, and (c) electrochemical impedance spectroscopy Nyquist plots of pure TiO$_2$, 2.1 wt% dual particle-size AuNPs/TiO$_2$, and 2.1 wt% GDC-directed dual particle-size AuNPs/TiO$_2$ photocatalysts under light irradiation (350–780 nm).

Figure 9. Schematic diagram for possible mechanism of dual particle-size AuNPs/TiO$_2$ composites for H$_2$ evolution.
4. Conclusions

In summary, we successfully synthesized a 2.1 wt% dual particle-size AuNPs/TiO$_2$ composite and investigated the synergistic effects of the two different AuNPs size distributions on photocatalytic H$_2$ production enhancement. The 2.1 wt% dual particle-size AuNPs/TiO$_2$ composites not only display a H$_2$ evolution efficiency 281 times greater than TiO$_2$ alone, but also outperform the AuNPs/TiO$_2$ composites containing small or large AuNPs at a total concentration of 2.1 wt% AuNPs. These synergistic effects appear to be attributed to increased electron-hole pairs promoted by small sized AuNPs, as well as the enhanced electron transfer facilitated through the SPR of large AuNPs. Significantly, a comparable photocatalytic efficiency enhancement can be also observed from dual particle-size AuNPs/TiO$_2$ photocatalysts synthesized through a different GDC-directed synthetic method. The synergistic effects observed here from dual particle-size AuNPs composites may open a new pathway for designing other efficient photocatalysts in the future.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-4991/9/4/499/s1, Figure S1: (a–c) TEM images of large AuNPs/TiO$_2$ and (d) Diameter distribution of large sized AuNPs determined by measuring 100 individual AuNPs on TiO$_2$. Figure S2: (a) TEM image of small AuNPs/TiO$_2$ and (b) Diameter distribution of small sized AuNPs determined by measuring 100 individual AuNPs on TiO$_2$. Figure S3: (a–c) TEM images of dual particle-size AuNPs/TiO$_2$ and (d) Diameter distribution of dual particle-size AuNPs determined by measuring 100 individual AuNPs on TiO$_2$. Figure S4: Transformed Kubelka-Munk function vs. the light energy curves of (a) pure TiO$_2$, (b) small AuNPs/TiO$_2$, (c) large AuNPs/TiO$_2$ and (d) dual particle-size AuNPs/TiO$_2$. Figure S5: Nitrogen adsorption of pure TiO$_2$, large AuNPs/TiO$_2$, small AuNPs/TiO$_2$ and dual particle-size AuNPs/TiO$_2$. Figure S6: (a) TEM and (b,c) HRTEM images of gold-dicyanodiamine composites (GDCs). Figure S7: (a–c) TEM images of 2.1 wt% GDC-directed dual particle-size AuNPs/TiO$_2$ and (d) Diameter distribution of 2.1 wt% GDC-directed dual particle-size AuNPs determined by measuring 100 individual AuNPs on TiO$_2$. Figure S8: XRD patterns of pure TiO$_2$ and 2.1 wt% GDC-directed dual particle-size AuNPs/TiO$_2$. Figure S9: Nitrogen adsorption of 2.1 wt% dual particle-size AuNPs/TiO$_2$ and 2.1 wt% GDC-directed dual particle-size AuNPs/TiO$_2$. Figure S10: (a) Survey XPS spectrum and high-resolution spectra of (b) Ti 2p, (c) O 1s and (d) Au 4f for pure TiO$_2$ and 2.1 wt% GDC-directed dual particle-size AuNPs/TiO$_2$.

Author Contributions: S.Y. conceived and designed the experiments. Q.Z. (Qian Zhao) and Q.Z. (Qiaoli Zhang) performed the experiments. Q.Z. (Qian Zhao), C.D., S.S., J.D.S., S.Y. and C.Z. analyzed the data and wrote the manuscript.

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