Coupling Plasmonic and Cocatalyst Nanoparticles on N–TiO₂ for Visible-Light-Driven Catalytic Organic Synthesis

Yannan Wang, Yu Chen, Qidong Hou, Meiting Ju and Weizun Li *

Received: 29 January 2019; Accepted: 1 March 2019; Published: 7 March 2019

Abstract: The use of the surface plasmon resonance (SPR) effect of plasmonic metal nanocomposites to promote photocarrier generation is a strongly emerging field for improving the catalytic performance under visible-light irradiation. In this study, a novel plasmonic photocatalyst, AuPt/N–TiO₂, was prepared via a photo-deposition–calcination technique. The Au nanoparticles (NPs) were used herein to harvest visible-light energy via the SPR effect, and Pt NPs were employed as a cocatalyst for trapping the energetic electrons from the semiconductor, leading to a high solar-energy conversion efficiency. The Au₂Pt₂/N–TiO₂ catalyst, herein with the irradiation wavelength in the range 460–800 nm, exhibited a reaction rate ~24 times greater than that of TiO₂, and the apparent quantum yield at 500 nm reached 5.86%, indicative of the successful functionalization of N–TiO₂ by the integration of Au plasmonic NPs and the Pt cocatalyst. Also, we investigated the effects of two parameters, light source intensity and wavelength, in photocatalytic reactions. It is indicated that the as-prepared AuPt/N–TiO₂ photocatalyst can cause selective oxidation of benzyl alcohol under visible-light irradiation with a markedly enhanced selectivity and yield.

Keywords: plasmonic photocatalyst; metal nanoparticle; N–TiO₂; nanocomposites; photocatalytic selective oxidation

1. Introduction

Titanium dioxide (TiO₂) was extensively studied in the past two decades as a photocatalyst because it can eliminate environmental pollutants, purify air, and produce clean hydrogen energy through the efficient utilization of solar energy [1]. Nevertheless, owing to the rapid recombination rate of the photogenerated electron–hole pairs and limited visible-light response, the application of pure TiO₂ is restricted. Appropriate modification, such as doping non-metals, is essential for TiO₂ to allow the further utilization of solar energy [2]. Nonetheless, the reported reactivity and quantum efficiency of TiO₂ derivative materials remains extremely low to meet the requirements of practical applications.

In order to sufficiently improve photocatalytic efficiency, both the visible-light absorption region and electron–hole separation of the photocatalyst should be optimized. Recently, semiconductor nanomaterials decorated with noble-metal nanoparticles (NPs) were recognized as a promising method for boosting the performance of photocatalysts [3–8]. Coupling semiconductors with noble metals (such as platinum and palladium) as the cocatalyst can form a Schottky barrier, serving as the “electron trapper” to improve charge migration and separation [9,10]. Plasmonic metals (gold and silver) nanoparticles with attractive SPR properties under visible-light excitation can be used as antennas for converting light energy into a local electric field [7,11,12], and improve the photocarrier generation/separation via plasmon-induced resonance energy transfer (PIRET) and the hot-electron
injection mechanism [13,14]. Consequently, the combination of multi-functional metal NPs in a noble metal/semiconductor nanostructure might effectively enhance the generation of photo-carriers and strengthen charge migration and separation.

For the hot-electron injection effect, the so-called SPR-sensitization effect, the plasmonic metal nanoparticles act as a dye molecule in dye-sensitized solar cells; as excited by the incident high-energy photon, the SPR effect of the plasmonic metal causes confined free electrons oscillating with incident light to generate excitation of hot electrons via non-radiative decay, so-called “plasmonic hot-electron generation”. Furthermore, these hot electrons with energy high enough to overcome the Schottky barrier can inject into the adjacent semiconductor’s conduction band [15–17]. To facilitate the PIRET process, the existence of intra-bandgap level-related defects can play a crucial role in the promotion of PIRET [18,19]. For instance, a TiO$_2$ photoanode based on N-doped exhibits enhanced photocurrent behavior induced by a PIRET water-splitting reaction [20]. N-doped TiO$_2$ introduces a new intra-bandgap level, which causes the absorption range of the semiconductor photocatalyst to overlap with the extinction wavelength of the plasmonic material, thereby obtaining a sufficient resonance interaction. In this case, the energy of the plasmonic oscillation is transferred from the plasmonic material to the semiconductor photocatalyst by an electromagnetic field or a dipole–dipole interaction.

In order to fully understand the excellent photocatalytic activity of the bifunctional noble-metal-modified N-doped TiO$_2$ under visible-light excitation, a detailed comparative study of light intensity and light wavelength is required. Herein, we integrated the plasmonic effect and a Schottky junction into one nanostructure by forming bifunctional plasmonic photocatalyst co-decorated with Au and Pt NPs and N–TiO$_2$. The activities of the AuPt/N–TiO$_2$ samples were evaluated by photocatalytic oxidation of benzyl alcohol. By strictly limiting the effects of other factors, we observed a direct correlation between photocatalytic activity and the irradiation parameter, which is essential for the design to improve the efficiency of the photocatalytic reaction. The results obtained in this paper are expected to contribute to the rational design and development of multifunctional metal nanoparticles for applications targeting solar energy conversion.

2. Materials and Methods

2.1. Synthesis

In a typical procedure, TiO$_2$-supported nanocrystals were prepared according to our previous paper [21]. The prepared TiO$_2$ product was mixed and ground with urea (1:4), and then the mixture was heated in air at 400 °C for two hours to obtain N–TiO$_2$ [22]. Finally, the noble metals were deposited on the N–TiO$_2$ via a typical photo-deposition calcination method, and the as-prepared catalysts were annealed in air for further use. All experimental methods are fully reported in the Supplementary Materials.

2.2. Sample Characterization

X-ray diffraction (XRD) patterns of the samples were recorded using a PANalytical X’pert MRD system (Almelo, Netherlands). Diffuse-reflectance ultraviolet–visible light (UV–Vis) spectra (DRS) of the samples were recorded on a Shimadzu 3600 UV–Vis spectrophotometer (Kyoto, Japan) in the air against BaSO$_4$. Transmission electron microscopy (TEM) images and scanning electron microscopy (SEM) images were taken by a FEI Tecnai F20 microscope (Hillsboro, OR, USA) and Hitachi S4800 microscope (Tokyo, Japan). X-ray photoelectron spectra (XPS) of the samples were recorded on a Thermo-Fisher Scientific ESCALAB 250XI system (Waltham, OR, USA). The steady-state photoluminescence (PL) spectrum was recorded by a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan). Photocurrent and electrochemical impedance spectroscopy measurements of the photocatalyst were performed on a CHI 760D workstation (Shanghai, China). All electrochemical measurements were made at room temperature.
3. Results and Discussion

SEM and TEM images (Figure 1 and Figure S1) were recorded to observe the morphology of as-prepared Au₂Pt₂/N–TiO₂. As shown in the TEM images, gold nanoparticles with an average size of ~25 nm can be observed instead of the presence of bimetallic Au–Pt alloy. It is suggested that the size of the metal nanoparticles is critical for modifying the chemical composition of the resulting nanomaterials, and the bimetallic alloy usually can be observed in the case of small gold (~7 nm) and platinum (~2 nm) nanoparticles [23]. Here, in this case, the gold nanoparticle size was larger than 20 nm, the formation of the bimetallic alloy NPs was not thermodynamically favored, and the segregation of gold and platinum nanoparticles was maintained. On the other hand, the platinum metal NPs was observed with a mean size of 2 nm (Figure 1h), which was uniformly decorated on the N–TiO₂ support. Furthermore, interplanar distances of 0.235 and 0.225 nm for gold and platinum nanoparticles were observed in the high-resolution TEM images (Figure 1f,g), which were indexed to the lattice spacings of Au(111) and Pt(111) planes of face-centered cubic (fcc) structures, respectively [24]. Another type of lattice fringe (~0.352 nm) can be indexed to the (101) plane of anatase TiO₂. The results obtained from the energy-dispersive X-ray (EDX) spectrum showed that the noble metal’s composition in Au₂Pt₂/N–TiO₂ (list in Table S1, Supplementary Materials) was consistent with the nominal load. Furthermore, the Brunauer–Emmett–Teller (BET) characterization results (Figure S2, Supplementary Materials) indicated that all catalysts exhibited similar surface areas, while pore volume and pore size decreased after the loading of noble-metal nanoparticles.

![Figure 1. SEM image of Au₂Pt₂/N–TiO₂ (a,b) and TEM and high-resolution TEM (HRTEM) images of N–TiO₂ (c,d) and Au₂Pt₂/N–TiO₂ (e–g). Nanoparticle size distributions of Au and Pt in Au₂Pt₂/N–TiO₂ (h). Scale bar (e,f): 2 nm.](image)

In the XRD characterization, all catalysts exhibited diffraction peaks dominated by TiO₂ (Figure 2a). Concerning the Au NPs, some additional weak peaks observed at 38° corresponded to Au; however, diffraction peaks for Pt were not found in the XRD patterns, possibly related to the line broadening caused by the quantum-size effects of small-sized Pt NPs [25]. Figure 2b shows the UV–Vis absorption spectra (DRS) of the as-prepared catalyst. The absorption band of the N–TiO₂ sample in the visible region of 400–500 nm corresponds to the presence of nitrogen. This effect is related to nitrogen doping, which possibly leads to the formation of hybridized states at the top of the valence band of the nitrogen 2p states and oxygen 2p states or an N-induced intermediate gap level [26]. XPS profiles were recorded to investigate the localization of nitrogen. N was mainly located at the interstitial atom on the Ti–O–N bonds (Figure S3, Supplementary Materials). By introducing impurity levels into the TiO₂ lattice, more overlapping portions of the absorption spectrum can be obtained between the TiO₂ and Au nanoparticles. In this way, the near-field electromagnetic resonance of the SPR...
These high-energy hot electrons then overcome the Schottky barrier and inject into the conduction band of the semiconductor. In this way, the SPR effect of the metal nanoparticles leads the photon energy transfer to the adjacent semiconductor or molecular complex, which in turn drives the chemical reaction.

Also, the photoluminescence emission (PL) of the samples was recorded to understand the behavior of the electrons and holes generated by light in catalysts. Here, the steady-state fluorescence emission spectrum (Figure 2c) showed a substantial attenuation of the PL signal owing to the deposition of noble metal (Pt), indicating that Pt NPs effectively form the Schottky barrier at the metal/N–TiO$_2$ heterojunction. This Schottky barrier, in turn, reduces electron–hole ($e^−$–$h^+$) pair recombination and increases the number of photoreactive photo-carriers available for photoreaction [32]. To further determine the role of the noble-metal nanoparticles in illumination, the photoelectrochemical properties of catalyst were characterized (Figure 2d), and it is demonstrated that the photocurrent intensity of Au$_2$Pt$_2$/N–TiO$_2$ is considerably higher than that of N–TiO$_2$. Such an apparent transient photocurrent enhancement is primarily associated with the available gold NPs, which absorb visible light and promote photocarrier generation through the SPR effect. Subsequently, we used the electrochemical impedance spectra (EIS) experiments to investigate the generation of the electron. The results of charge transport characteristics (Figure 2d inset) revealed that the radius of Au$_2$Pt$_2$/N–TiO$_2$ in the middle-frequency region is smaller than the radius of N–TiO$_2$, which demonstrates that the photoinduced electron–hole separation efficiency is higher, and the interface charge can be transferred to the electron donor more quickly.

Figure 2. X-ray diffraction (XRD) patterns (a), ultraviolet–visible light (UV–Vis) diffuse reflectance spectra (DRS) (b), and photoluminescence spectra (c) of prepared photocatalysts. Photocurrent transient response (d) and electrochemical impedance spectroscopy (EIS) Nyquist plots (inset) of the sample electrodes of TiO$_2$, N–TiO$_2$, Au$_2$Pt$_2$/TiO$_2$, Au$_2$Pt$_2$/N–TiO$_2$ under visible-light irradiation.
For investigating the photocatalytic performance, we used the selective oxidation of benzyl alcohol as a probe reaction to study the photocatalytic activity of Au$_2$Pt$_2$/N–TiO$_2$ catalyst for visible-light-driven organic catalytic synthesis [33–35]. Figure 3a summarizes the reaction parameters such as conversion, yield, and selectivity data. After 2.5 h, benzaldehyde formed over bare TiO$_2$ (yield: 3.37%) under visible-light irradiation. Considering that bare TiO$_2$ does not absorb visible light, this visible-light catalytic reactivity can be ascribed to the ligand-to-metal charge transfer resulting from the surface complex formed by the adsorption of benzyl alcohol on the surface of TiO$_2$ [36–38]. Moreover, N–TiO$_2$ does not significantly increase the activity, and the selectivity in TiO$_2$ and N–TiO$_2$ cases was low (~70%). Hence, the loading of metal NPs can significantly improve reaction efficiency compared with TiO$_2$. Among all samples, the Au$_2$Pt$_2$/N–TiO$_2$ composite presented the highest photocatalytic performance, and its yield was 24 times that of TiO$_2$. On the contrary, the yield of the Au$_2$Pt$_2$/TiO$_2$ photocatalyst was only 70% of the Au$_2$Pt$_2$/N–TiO$_2$, which suggests that the overlapped intrinsic absorption of N–TiO$_2$ with plasmonic material may boost the PIRET process. Moreover, the yields over Au$_2$/N–TiO$_2$ and Pt$_2$/N–TiO$_2$ increased by 5.5 and 19 times, respectively, indicating that the Schottky barrier formed between Pt nanoparticles and TiO$_2$ is crucial for the improvement in the catalyst efficiency. It is interesting to note that, after the loading of noble-metal nanoparticles, the selectivity increased from 73.8% to greater than 95%, which means that, when noble-metal nanoparticles are used as photocatalysts for selective oxidation of benzyl alcohol, the photolysis of the reaction is negligible.

To better understand the factors affecting the performance of Au$_2$Pt$_2$/N–TiO$_2$ photocatalyst, we tuned and investigated the light-source wavelength and intensity in the photocatalytic reaction. The most significant enhancement in the yield of the reaction was observed by irradiation of 460–560 nm over Au$_2$Pt$_2$/N–TiO$_2$ photocatalyst (Figure 3b), accounting for 81.26% of the strengthening of the total light irradiation. Also, we used a multiple-wavelength laser light source to confirm the effect of illumination wavelength (Figure 3d and Figure S4, Supplementary Materials). Au$_2$Pt$_2$/N–TiO$_2$ exhibited an exceptionally high apparent quantum yield at two wavelengths (500 nm and 532 nm), with 5.86% at 500 nm and 4.57% at 532 nm. Moreover, it is believed that there are two possible mechanisms that may affect the performance of the photocatalytic activity, namely hot-electron injection and PIRET. Upon irradiation of visible light, following light absorption and SPR excitation in these nanostructures, electromagnetic decay takes place on a femtosecond timescale non-radiatively by transferring the energy to hot electrons; then, these “hot enough” electrons with high energy would inject into the N–TiO$_2$ conduction band. In this manner, the apparent quantum yield will fit well with the pattern of the plasmonic metal absorption spectrum, which is consistent with an observation reported in previous literature [39]. On the other hand, in this case, nitrogen doping introduces a new intra-bandgap level above the TiO$_2$ valence band, which can resonate with the electromagnetic field generated by the gold SPR effect, and the electromagnetic field is then able to improve the generation of photocarriers from intra-bandgap levels to the TiO$_2$ conduction band through the PIRET process. As a result, it will further increase the photocatalytic efficiency. Therefore, a high apparent quantum yield (AQY) was observed in the band that was contributed by the hot-electron injection mechanism caused by plasmonic absorption and the PIRET mechanism. Subsequently, further analysis (Figure 3c) showed that the correlation between the dependence of light enhancement on optical irradiance of all photocatalysts indicates that photoexcitation intensity is a crucial factor for the photo-enhancing activity, which is consistent with previously published literature [40,41]. The above analysis suggested that the enhanced activity on the Au$_2$Pt$_2$/N–TiO$_2$ catalyst is dominated by the specific illumination wavelength and irradiation intensity. Through the analysis of PL and photoelectrochemical tests, we believe the following two factors can describe this: (1) through the loading with Au NPs (plasmonic nanoparticles), on the one hand, plasmonic photocatalysts can utilize a specific wavelength of photons (especially in the visible-light range) to extract hot electrons from the plasmonic metals and more efficiently generate electron–hole pairs. On the other hand, due to the strong near-field electromagnetic resonance caused by the surface plasmons, the rate of generation of photocarriers in TiO$_2$ is enhanced.
by the PIRET between the electromagnetic field and the resonance electronic energy levels of TiO$_2$; (2) the integration of a cocatalyst such as Pt NPs can result in the formation of a Schottky barrier that acts as an “electron trapper” for improving photoinduced charge transport and separation.

Figure 3. (a) Conversion, yield, and selectivity for the photo-oxidation of benzyl alcohol to benzaldehyde over prepared photocatalysts. (b) The dependence of yield and irradiation wavelength over photocatalysts for the selective oxidation of benzyl alcohol. (c) The rate of photocatalytic reaction over TiO$_2$, N–TiO$_2$, Au$_2$Pt$_2$/TiO$_2$, and Au$_2$Pt$_2$/N–TiO$_2$ as a function of irradiance intensity. (d) Diffuse-reflectance UV–Vis spectra of Au$_2$Pt$_2$/N–TiO$_2$ photocatalyst and the quantum yield for the formation of benzaldehyde under a multiple-wavelength laser light source. The apparent quantum yield was calculated using the equation $\Phi_{AQY} = (Y_{vis} - Y_{dark})/N \times 100\%$, where $Y_{vis}$ and $Y_{dark}$ are the yields of photocatalytic reaction under irradiation or dark conditions, and $N$ is the number of incident photons in the reaction vessel.

The reaction mechanism involved in the photocatalytic oxidation of benzyl alcohol on Au$_2$Pt$_2$/N–TiO$_2$ was inspected by a control experiment using different radical scavengers and by electron spin resonance (ESR) spectroscopy measurement using spin trapping and labeling [42]. As shown in Figure 4a, there was no significant change in the reaction process for the hydroxyl (·OH) radicals scavenged by TBA. However, when ammonium oxalate, silver nitrate, and benzoquinone were separately added to capture photogenerated holes, electrons, and superoxide (·O$_2^-$) radicals, the yield of the reaction was significantly reduced. This observation indicated that, in addition to the hydroxyl (·OH) radicals, radicals such as photogenerated holes, electrons, and superoxide radicals are involved in the process of visible-light photooxidation of benzyl alcohol. Furthermore, ESR measurement using spin trapping and labeling (Figure 4b) indicated that oxygen can be used to capture photogenerated electrons, providing superoxide (·O$_2^-$) radicals, which played a vital role in the photocatalytic process. It is a known fact that the ·OH radical is a highly reactive intermediate which can oxidize substrate molecules indiscriminately without selectivity [43]; however, superoxide (·O$_2^-$) radicals are well-known oxidants for selective oxidation reactions [44,45]. Thus, the specific oxidation behavior of the superoxide species in the system and the absence of hydroxyl (·OH) radicals can advantageously favor the selective oxidation of benzyl alcohol and can be a significant cause of high reaction selectivity.
The possible reaction mechanism is illustrated in Figure 4c. Under specific wavelength and intensive visible-light irradiation, the incident photons excite the SPR of the gold nanoparticles. The electrons collectively oscillating by localized surface plasmons decay non-radiatively through intraband or interband excitations on Au NPs, generating hot electrons with high enough energy, then finally transfer into the N–TiO2 conduction band. Meanwhile, in this case, N-doping introduces a new intra-bandgap level above the TiO2 valence band, which can resonate with the electromagnetic field generated by the gold SPR effect, and the electromagnetic field is then able to improve the generation of photocarriers from intra-bandgap levels to the TiO2 conduction band through the PIRET process. After the contact of Pt and N–TiO2, a Schottky junction can be established at the interface, wherein the conduction and valence band are bent upward to the N–TiO2 interface. The electrons on the N–TiO2 conduction band are enriched by the Pt NPs via the Schottky barrier between cocatalyst and N–TiO2 and then captured by oxygen molecules, affording superoxide (·O2−) species [11,46]. The superoxide (·O2−) species may attract the hydrogen atom of the substrate (benzyl alcohol) to form an alkoxide intermediate; after that, the transient alkoxide intermediate undergoes rapid hydride transfer, resulting in the elimination of proton hydrogen, and ultimately resulting in benzaldehyde. The local electromagnetic field generated by the gold nanoparticles under visible light enhances the excitation probability of the photogenerated electron and hole pairs of the N–TiO2 support material, resulting in more photogenerated carriers, and then these photogenerated electrons migrate to the cocatalyst nanoparticles across the Schottky barrier between Pt–TiO2 and react with oxygen to form superoxide radicals.

**Figure 4.** (a) Controlled experiment using different radical scavengers; (b) ESR spectra collected using 5,5-dimethyl-1-pyrroline-N-oxide ((DMPO–·O2−)) as the spin trap. (c) A plausible mechanism for the photo-oxidation of benzyl alcohol over Au2Pt2/N–TiO2 under visible-light irradiation.

As listed in Table 1, we further investigated the photocatalytic oxidation of various aromatic alcohols over Au2Pt2/N–TiO2. As expected, Au2Pt2/N–TiO2 has not only high activity for oxidation of aromatic alcohols, but also has excellent selectivity for carbonyl compounds. Furthermore, the conversions of different aromatic alcohol substrates were significantly different; for example, the substitution of para-substituted benzyl alcohol with an electron-donating group (–OCH3 and –CH3) can increase the efficiency of the reaction, while substitution with an electron-withdrawing group (–Cl) lowers the activity. Furthermore, the durability of the photocatalyst is also a crucial parameter.
for its further application. As shown in Figures S5 and S6 (Supplementary Materials), no significant decrease in the photocatalytic activity was observed after five cycles, indicating that Au2Pt2/N–TiO2 maintained highly durability in the photocatalytic reaction.

Table 1. Photocatalytic selective oxidation of various aromatic alcohols on Au2Pt2/N–TiO2.

| Entry | Substrate | Product | Yield (%) | Selectivity (%) |
|-------|-----------|---------|-----------|-----------------|
| 1     | ![Image](image1.png) | ![Image](image2.png) | 80.9 | 97.7 |
| 2     | ![Image](image3.png) | ![Image](image4.png) | 78.1 | 79.6 |
| 3     | ![Image](image5.png) | ![Image](image6.png) | 87.9 | 97.9 |
| 4     | ![Image](image7.png) | ![Image](image8.png) | 63.8 | 76.9 |
| 5     | ![Image](image9.png) | ![Image](image10.png) | 91.2 | 100 |
| 6     | ![Image](image11.png) | ![Image](image12.png) | 50.1 | 54.2 |
| 7     | ![Image](image13.png) | ![Image](image14.png) | 52.2 | 75.1 |

*Solvent: 1.5 mL of trifluorotoluene; substrate: 0.1 mmol aromatic alcohol; photocatalyst: 10 mg of Au2Pt2/N–TiO2; 1 atm of O2, reaction temperature was maintained at 30 °C, for 2.5 h of reaction time. Yield of aromatic aldehyde; selectivity of aldehyde or ketone; h 1 h of reaction time.*

4. Conclusions

In this study, we successfully synthesized the plasmonic photocatalyst Au2Pt2/N–TiO2 and investigated its catalytic performance for photo-oxidation of aromatic alcohol. A combination of bifunctional metal NPs was demonstrated for their dual properties related to plasmonic absorption, as well as efficient electron trapping. Coupling a semiconductor with Pt NPs as the cocatalyst can form a Schottky barrier interface, serving as the “electron trapper” to improve charge migration and separation. The Au nanoparticles can be used as an antenna for converting light energy into a local electric field, and hot-electron injection and PIRET mechanisms improve photocarrier generation. The intra-bandgap states of N-doped TiO2 take a crucial part in improving both hot-electron injection and PIRET from plasmonic metal nanoparticles to the semiconductor. As a result, the reaction rate of the Au2Pt2/N–TiO2 catalyst, herein, is ~24 times than that of TiO2, and the AQY at 500 nm reaches 5.86%, indicative of the successful functionalization of N–TiO2 via the integration of Au plasmonic NPs and the Pt cocatalyst. Furthermore, it is indicated that the intensity and wavelength of the illumination source and the choice of the light source have a significant impact on the activity of photocatalytic...
reaction. This modification of multifunctional metal NPs demonstrates promise for visible-light-driven catalytic applications.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2079-4991/9/3/391/s1: Figure S1: TEM images of Au$_2$Pt$_2$/N–TiO$_2$ photocatalyst; Figure S2: (a) N$_2$ adsorption/desorption isotherm of as-prepared catalysts; (b) the corresponding Barrett-Joyner-Halenda (BJH) desorption pore size distribution; Figure S3: Fine XP spectra of (a) Au 4f; (b) Pt 4f; (c) N 1s, and (d) O 1s obtained from Au$_2$Pt$_2$/N–TiO$_2$; Figure S4: (a–d) Diffuse-reflectance UV–Vis spectra of TiO$_2$, N–TiO$_2$, Au$_2$Pt$_2$/TiO$_2$, and Au$_2$Pt$_2$/N–TiO$_2$ catalysts and the quantum yield for the formation of benzaldehyde under laser irradiation of different wavelengths, such as 405 nm, 450 nm, 500 nm, 532 nm, and 635 nm. The apparent quantum yield was calculated using the equation \[ \Phi_{\text{aqy}} = \left( \frac{Y_{\text{vis}} - Y_{\text{dark}}} {Y_{\text{vis}}} \right) \times 100\% ] where \( Y_{\text{vis}} \) and \( Y_{\text{dark}} \) denote the yield of benzaldehyde under light and dark conditions, respectively. \( N \) denotes the number of incident photons in the reaction vessel; Figure S5: Recyclability tests of Au$_2$Pt$_2$/N–TiO$_2$ for the selective oxidation of benzyl alcohol; Figure S6: (a,b) TEM images of Au$_2$Pt$_2$/N–TiO$_2$ catalyst after photocatalysis reaction; (c,d) the EDX analysis of photocatalysis before and after photocatalysis reaction; Table S1: Summarized physical and chemical data for TiO$_2$, N–TiO$_2$, Au$_2$Pt$_2$/TiO$_2$, and Au$_2$Pt$_2$/N–TiO$_2$ photocatalysts.

**Author Contributions:** W.L. and M.J. guided the project and designed the experiments; Y.W. and Y.C. performed (a–d) Diffuse-reflectance UV–Vis spectra of TiO$_2$, N–TiO$_2$, Au$_2$Pt$_2$/TiO$_2$, and Au$_2$Pt$_2$/N–TiO$_2$ catalysts and the quantum yield for the formation of benzaldehyde under laser irradiation of different wavelengths, such as 405 nm, 450 nm, 500 nm, 532 nm, and 635 nm. The apparent quantum yield was calculated using the equation. \[ \Phi_{\text{aqy}} = \left( \frac{Y_{\text{vis}} - Y_{\text{dark}}} {Y_{\text{vis}}} \right) \times 100\% ] where \( Y_{\text{vis}} \) and \( Y_{\text{dark}} \) denote the yield of benzaldehyde under light and dark conditions, respectively. \( N \) denotes the number of incident photons in the reaction vessel; Figure S5: Recyclability tests of Au$_2$Pt$_2$/N–TiO$_2$ for the selective oxidation of benzyl alcohol; Figure S6: (a,b) TEM images of Au$_2$Pt$_2$/N–TiO$_2$ catalyst after photocatalysis reaction; (c,d) the EDX analysis of photocatalysis before and after photocatalysis reaction; Table S1: Summarized physical and chemical data for TiO$_2$, N–TiO$_2$, Au$_2$Pt$_2$/TiO$_2$, and Au$_2$Pt$_2$/N–TiO$_2$ photocatalysts.

**Funding:** This research was supported by the National Natural Science Foundation of China (21878163), the National key Research Project (2018YFD0800103), the Fundamental Research Funds for the Central Universities, and the Natural Science Foundation of Tianjin, China (17JCZDJC39500).

**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**

1. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38. [CrossRef] [PubMed]
2. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* **2001**, *293*, 269–271. [CrossRef] [PubMed]
3. Linic, S.; Aslam, U.; Boerigter, C.; Morabito, M. Photochemical transformations on plasmonic metal nanoparticles. *Nat. Mater.* **2015**, *14*, 567–576. [CrossRef] [PubMed]
4. Chen, Y.; Wang, Y.; Li, W.; Yang, Q.; Hou, Q.; Wei, L.; Liu, L.; Huang, E.; Ju, M. Enhancement of photocatalytic performance with the use of noble-metal-decorated TiO$_2$ nanocrystals as highly active catalysts for aerobic oxidation under visible-light irradiation. *Appl. Catal. B Environ.* **2017**, *210*, 352–367. [CrossRef]
5. Zhang, N.; Han, C.; Fu, X.; Xu, Y.-J. Function-Oriented Engineering of Metal-Based Nanohybrids for Photoredox Catalysis: Exerting Plasmonic Effect and Beyond. *Chem* **2018**, *4*, 1832–1861. [CrossRef]
6. Sarina, S.; Zhu, H.; Jaatinen, E.; Xiao, Q.; Liu, H.; Jia, J.; Chen, C.; Zhao, J. Enhancing catalytic performance of palladium in gold and palladium alloy nanoparticleics for organic synthesis reactions through visible light irradiation at ambient temperatures. *J. Am. Chem. Soc.* **2013**, *135*, 5793–5801. [CrossRef] [PubMed]
7. Fang, C.; Jia, H.; Chang, S.; Ruan, Q.; Wang, P.; Chen, T.; Wang, J. (Gold core)/(titania shell) nanostructures for plasmon-enhanced photon harvesting and generation of reactive oxygen species. *Energy Environ. Sci.* **2014**, *7*, 3431–3438. [CrossRef]
8. Zhang, N.; Han, C.; Xu, Y.-J.; Foley Iv, J.J.; Zhang, D.; Codrington, J.; Gray, S.K.; Sun, Y. Near-field dielectric scattering promotes optical absorption by platinum nanoparticles. *Nat. Photonics* **2016**, *10*, 473–482. [CrossRef]
9. Tanaka, A.; Nakanishi, K.; Hamada, R.; Hashimoto, K.; Kominami, H. Simultaneous and stoichiometric water oxidation and Cr(VI) reduction in aqueous suspensions of functionalized plasmonic photocatalyst Au/TiO$_2$-Pt under irradiation of green light. *ACS Catal.* **2013**, *3*, 1886–1891. [CrossRef]
10. Zhang, P.; Wang, T.; Chang, X.; Gong, J. Effective Charge Carrier Utilization in Photocatalytic Conversions. *Acc. Chem. Res.* **2016**, *49*, 911–921. [CrossRef] [PubMed]
11. Christopher, P.; Xin, H.; Linic, S. Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat. Chem.* **2011**, *3*, 467–472. [CrossRef] [PubMed]
12. Li, B.; Gu, T.; Ming, T.; Wang, J.; Wang, P.; Wang, J.; Yu, J.C. (Gold Core)@(Ceria Shell) Nanostructures for Plasmon-Enhanced Catalytic Reactions under Visible Light. *ACS Nano* **2014**, *8*, 8152–8162. [CrossRef] [PubMed]
Cushing, S.K.; Li, J.; Meng, F.; Senty, T.R.; Suri, S.; Zhi, M.; Li, M.; Bristow, A.D.; Wu, N. Photocatalytic activity enhanced by plasmonic resonant energy transfer from metal to semiconductor. *J. Am. Chem. Soc.* 2012, 134, 15033–15041. [CrossRef] [PubMed]  

Li, J.; Cushing, S.K.; Meng, F.; Senty, T.R.; Bristow, A.D.; Wu, N. Plasmon-induced resonance energy transfer for solar energy conversion. *Nat. Photonics* 2015, 9, 601–607. [CrossRef]  

Mubeen, S.; Lee, J.; Singh, N.; Krämer, S.; Stucky, G.D.; Moskovits, M. An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. *Nat. Nanotechnol.* 2013, 8, 247–251. [CrossRef] [PubMed]  

Zhang, Y.; He, S.; Guo, W.; Hu, Y.; Huang, J.; Mulchay, J.R.; Wei, W.D. Surface-Plasmon-Driven Hot Electron Photochemistry. *Chem. Rev.* 2018, 118, 2927–2954. [CrossRef] [PubMed]  

Zhang, P.; Wang, T.D.; Gong, J. Mechanistic Understanding of the Plasmonic Enhancement for Solar Water Splitting. *Adv. Mater.* 2015, 27, 5328–5342. [CrossRef] [PubMed]  

Usón, L.; Sebastian, V.; Mayoral, A.; Hueso, J.L.; Eguizabal, A.; Arruebo, M.; Santamaria, J. Spontaneous formation of Au–Pt alloyed nanoparticles using pure nano-counterparts as starters: A ligand and size dependent process. *Nanoscale* 2015, 7, 10152–10161. [CrossRef] [PubMed]  

Liu, L.; Dao, T.D.; Kodiyath, R.; Kang, Q.; Abe, H.; Nagao, T.; Ye, J. Plasmonic janus-composite photocatalyst comprising Au and C-TiO$_2$ for enhanced aerobic oxidation over a broad visible-light range. *Adv. Funct. Mater.* 2015, 24, 7754–7762. [CrossRef]  

Al-Azri, Z.H.N.; Chen, W.T.; Chan, A.; Jovic, V.; Ina, T.; Idriss, H.; Waterhouse, G.I.N. The roles of metal co-catalysts and reaction media in photocatalytic hydrogen production: Performance evaluation of M/TiO$_2$ photocatalysts (M = Pd, Pt, Au) in different alcohol-water mixtures. *J. Catal.* 2015, 329, 355–367. [CrossRef]  

Li, X.; Liu, P.; Mao, Y.; Xing, M.; Zhang, J. Preparation of homogeneous nitrogen-doped mesoporous TiO$_2$ spheres with enhanced visible-light photocatalysis. *Appl. Catal. B Environ.* 2015, 164, 352–359. [CrossRef]  

Murdock, M.; Waterhouse, G.I.N.; Nadeem, M.A.; Metson, J.B.; Keane, M.A.; Howe, R.F.; Llorca, J.; Idriss, H. The effect of gold loading and particle size on photocatalytic hydrogen production from ethanol over Au/TiO$_2$ nanoparticles. *Nat. Chem.* 2011, 3, 489–492. [CrossRef] [PubMed]  

Pan, X.; Xu, Y.J. Defect-mediated growth of noble-metal (Ag, Pt, and Pd) nanoparticles on TiO$_2$ with oxygen vacancies for photocatalytic redox reactions under visible light. *J. Phys. Chem. C* 2013, 117, 17996–18005. [CrossRef]  

Sakamoto, H.; Ohara, T.; Yasumoto, N.; Shiraishi, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T. Hot-Electron-Induced Highly Efficient O$_2$ Activation by Pt Nanoparticles Supported on Ta$_2$O$_5$ Driven by Visible Light. *J. Am. Chem. Soc.* 2015, 137, 9324–9332. [CrossRef] [PubMed]  

Jiang, D.; Wang, W.; Sun, S.; Zhang, L.; Zheng, Y. Equilibrating the plasmonic and catalytic roles of metallic nanostructures in photocatalytic oxidation over Au-modified CeO$_2$. *ACS Catal.* 2015, 5, 613–621. [CrossRef]  

Lu, D.; Ouyang, S.; Xu, H.; Li, D.; Zhang, X.; Li, Y.; Ye, J. Designing Au Surface-Modified Nanoporous-Single-Crystalline SrTiO$_3$ to Optimize Diffusion of Surface Plasmon Resonance-Induce Photoelectron toward Enhanced Visible-Light Photoactivity. *ACS Appl. Mater. Interfaces* 2016, 8, 9506–9513. [CrossRef] [PubMed]
32. Shiraishi, Y.; Tsukamoto, D.; Sugano, Y.; Shiro, A.; Ichikawa, S.; Tanaka, S.; Hirai, T. Platinum nanoparticles supported on anatase titanium dioxide as highly active catalysts for aerobic oxidation under visible light irradiation. *ACS Catal.* 2012, 2, 1984–1992. [CrossRef]
33. Verma, S.; Baig, R.B.N.; Nadagouda, M.N.; Varma, R.S. Selective Oxidation of Alcohols Using Photoactive VO@g-C3N4. *ACS Sustain. Chem. Eng.* 2016, 4, 1094–1098. [CrossRef]
34. Sugano, Y.; Shiraishi, Y.; Tsukamoto, D.; Ichikawa, S.; Tanaka, S.; Hirai, T. Supported Au-Cu bimetallic alloy nanoparticles: An aerobic oxidation catalyst with regenerable activity by visible-light irradiation. *Angew. Chem. Int. Ed.* 2013, 52, 5295–5299. [CrossRef] [PubMed]
35. Jiang, T.; Jia, C.; Zhang, L.; He, S.; Sang, Y.; Li, H.; Li, Y.; Xu, X.; Liu, H. Gold and gold-palladium alloy nanoparticles on heterostructured TiO$_2$ nanobelts as plasmonic photocatalysts for benzyl alcohol oxidation. *Nanoscale* 2015, 7, 209–217. [CrossRef] [PubMed]
36. Higashimoto, S.; Kitao, N.; Yoshida, N.; Sakura, T.; Azuma, M.; Ohue, H.; Sakata, Y. Selective photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes by molecular oxygen on titanium dioxide under visible light irradiation. *J. Catal.* 2009, 266, 279–285. [CrossRef]
37. Higashimoto, S.; Suetsugu, N.; Azuma, M.; Ohue, H.; Sakata, Y. Efficient and selective oxidation of benzylic alcohol by O$_2$ into corresponding aldehydes on a TiO$_2$ photocatalyst under visible light irradiation: Effect of phenyl-ring substitution on the photocatalytic activity. *J. Catal.* 2010, 274, 76–83. [CrossRef]
38. Kobayashi, H.; Higashimoto, S. DFT study on the reaction mechanisms behind the catalytic oxidation of benzyl alcohol into benzaldehyde by O$_2$ over anatase TiO$_2$ surfaces with hydroxyl groups: Role of visible-light irradiation. *Appl. Catal. B Environ.* 2015, 170–171, 135–143. [CrossRef]
39. Tanaka, A.; Sakaguchi, S.; Hashimoto, K.; Kominami, H. Preparation of Au/TiO$_2$ with metal cocatalysts exhibiting strong surface plasmon resonance effective for photoinduced hydrogen formation under irradiation of visible light. *ACS Catal.* 2013, 3, 79–85. [CrossRef]
40. Tanaka, A.; Hashimoto, K.; Kominami, H. Preparation of Au/CeO$_2$ exhibiting strong surface plasmon resonance effective for selective or chemoselective oxidation of alcohols to aldehydes or ketones in aqueous suspensions under irradiation by green light. *J. Am. Chem. Soc.* 2012, 134, 14526–14533. [CrossRef] [PubMed]
41. Xiao, Q.; Liu, Z.; Bo, A.; Zavahir, S.; Sarina, S.; Bottle, S.; Riches, J.D.; Zhu, H. Catalytic transformation of aliphatic alcohols to corresponding esters in O$_2$ under neutral conditions using visible-light irradiation. *J. Am. Chem. Soc.* 2015, 137, 1956–1966. [CrossRef] [PubMed]
42. Fu, H.; Zhang, L.; Zhang, S.; Zhu, Y.; Zhao, J. Electron spin resonance spin-trapping detection of radical intermediates in N-doped TiO$_2$-assisted photodegradation of 4-chlorophenol. *J. Phys. Chem. B* 2006, 110, 3061–3065. [CrossRef] [PubMed]
43. Li, A.; Wang, T.; Chang, X.; Cai, W.; Zhang, P.; Zhang, J.; Gong, J. Spatial separation of oxidation and reduction co-catalysts for efficient charge separation: Pt@TiO$_2$@MnO$_x$ hollow spheres for photocatalytic reactions. *Chem. Sci.* 2016, 7, 890–895. [CrossRef] [PubMed]
44. Salmistraro, M.; Schwartzberg, A.; Bao, W.; Depero, L.E.; Weber-Bargioni, A.; Cabrini, S.; Alessandri, I. Triggering and monitoring plasmon-enhanced reactions by optical nanoantennas coupled to photocatalytic beads. *Small* 2013, 9, 3301–3307. [CrossRef] [PubMed]
45. Primo, A.; Corma, A.; Garcia, H. Titania supported gold nanoparticles as photocatalyst. *Phys. Chem. Chem. Phys.* 2011, 13, 886–910. [CrossRef] [PubMed]
46. Christopher, P.; Xin, H.; Marimuthu, A.; Linic, S. Singular characteristics and unique chemical bond activation mechanisms of photocatalytic reactions on plasmonic nanostructures. *Nat. Mater.* 2012, 11, 1044–1050. [CrossRef] [PubMed]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).