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Abstract: The mesoporous Au-TiO₂ nanocomposites with different Au concentrations were prepared via a co-polymer assisted sol-gel method. The structures have been characterized by powder X-Ray diffraction, N₂ adsorption-desorption isotherms, diffuse reflectance UV-Vis spectroscopy, X-ray photoemission spectroscopy, transmission electron microscopy. Most generated Au nanoparticles were embedded in the mesoporous TiO₂ matrix. The prepared Au-TiO₂ nanocomposites exhibit remarkable visible-light activity for H₂ evolution from photocatalytic water reduction in the presence of ascorbic acid as the electron donor. By comparing with Pt-TiO₂ samples, we found that the visible-light activity of the Au-TiO₂ nanocomposites could be partially contributed by the defects/impurity states in the TiO₂ matrix, while the gold surface plasmons could significantly enhance the weak visible-light excitation of TiO₂ matrix. In addition, further studies by controlling irradiation wavelengths suggest that some plasmon-excited electrons could transfer from Au nanoparticles to the contacting TiO₂ to reduce water for H₂ generation. We believe that these Au-TiO₂ nanocomposites as well as the mechanistic studies would have considerable impact on future development of metal-semiconductor hybrid photocatalysts for efficient solar hydrogen production.

Mesoporous Plasmonic Au-TiO₂ Nanocomposites for Efficient Visible-Light-Driven Photocatalytic Water Reduction

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Keywords: Photocatalyst; Surface plasmon resonance; Au-TiO₂ nanocomposites; Hydrogen

1. Introduction

Energy and environmental issues at a global level are receiving more and more attention. Hence, tremendous research efforts have been made to abate environment pollution and explore renewable energy resources. Hydrogen gas as an ultimate clean fuel is environmental friendly and has been considered as one of the most important alternative energy sources to replace fossil fuels. During the past decades, TiO₂-based semiconductor materials have been widely applied in environmental remediation and solar-driven hydrogen production due to their low cost, non-toxicity, and high chemical stability[1-4]. However, TiO₂ can only be excited by UV light with the wavelength less than ~385nm because of the wide band gap (E_g : ~3.2 eV)[5]. The high rate of electron-hole recombination in excited TiO₂ often results in a low quantum yield and poor efficiency for photocatalytic reactions, which also restricts the practical application of TiO₂-based materials[6]. To date, many efforts such as doping and surface modification have been employed to improve the photocatalytic activity of TiO₂, especially in the visible light region[7-13]. Loading TiO₂ with noble metals (e.g. Pt, Au, and Pd) has been demonstrated as an effective way to enhance the photocatalytic efficiency of TiO₂ by reducing the fast recombination of the photogenerated charge carriers[14-18]. The metal-loading process was usually implemented by depositing Au nanoparticles over pre-synthesized TiO₂ or commercial P25 titania through photodeposition under UV light irradiation or deposition-precipitation processes[19-25].

In Au-TiO₂ nanocomposites, the gold particle size is a key factor that could significantly influence their catalytic efficiencies. Although it is well known that small gold nanoparticles with the diameter less than 5 nm usually show high catalytic activities[26,27], Idriss et al. found that the Au-TiO₂ hybrids exhibited increasing hydrogen production rate as the loading Au particle size increases up to 12 nm[28]. Recently, many researchers have found that the excitation of gold nanoparticles can also contribute significantly to the photocatalytic performance of Au-TiO₂ nanocomposites, especially under visible-light irradiation. This is mainly attributed to the excitation of surface plasmon resonance (SPR) on gold nanoparticles. For an individual gold nanoparticle, after SPR excitation the plasmon decay usually

completes within a few picoseconds[29]. However, when the gold nanoparticle is contacting with TiO_2 , the plasmon-excited electrons can be injected into the TiO_2 within ~ 250 fs with yield up to 50%[30]. Consequently, the decay process of these excited electrons can be prolonged up to 1.5 ns though it is also dependent on TiO_2 particle size. By this way, an instant charge separation can be achieved on the gold nanoparticle that is able to accept electrons from external electron-donors. As a result, in recent years people have reported the plasmon-induced photocatalytic oxidation of alcohols over Au- TiO_2 nanocomposites[31]. Although it has been proposed that some of the energetic electrons from SPR-excitation should have sufficient potential to drive water reduction[32], there are still very few reports to demonstrate SPR-driven hydrogen evolution by using hybrid materials of gold nanoparticles and metal oxide semiconductors.

Herein, we report a simple one-pot synthetic method to prepare mesoporous Au- TiO_2 nanocomposites which exhibit remarkable visible-light activity for hydrogen evolution from photocatalytic water reduction. Our studies reveal that such visible-light-driven photocatalytic activities come from SPR excitation of the gold nanoparticles that are well dispersed in the mesoporous TiO_2 matrix. The conclusion is further supported by the investigation on the effect from irradiation wavelengths and comparison results with Pt-loaded TiO_2 nanocomposites.

2. Experimental Section

2.1 Sample preparation

The mesoporous Au- TiO_2 nanocomposites were prepared through a co-polymer assisted sol-gel method[33]. In a typical synthesis, 1.0 g Pluronic P123 (Triblock co-polymers, poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol), Sigma-Aldrich), 3.0 g tetrabutyl titanate (Sigma-Aldrich), 1.7 g TiCl_4 (Sinopharm Chemical Reagent), and various amount of AuCl_3 (Sigma-Aldrich) were mixed in 20 mL ethanol and kept stirring for 2 h. Then the sol was cast into a Petri-dish and dried at 40°C for 24 h. The dried gel was calcined at 350°C for 4 h with a temperature ramping of $0.5^\circ\text{C}/\text{min}$. The acquired catalyst is denoted as xAu- TiO_2 in which x is the molar concentration (x%) of Au to TiO_2 in

the mixed precursors. The control samples, 2Pt-TiO₂ and 2Pt-P25 (2% Pt in mole), were synthesized via photo-deposition. Briefly, quantitative H₂PtCl₆•6H₂O was added into 100mg support catalyst (TiO₂ or P25) suspension mixed with 16 mL deionized water and 4 mL methanol. The suspension was exposed under UV-vis light (300-Watt xenon lamp) for 2h to photo-deposit Pt onto the catalyst surfaces. Then the suspension was centrifuged, and the collected powder was washed with deionized water for several times and then dried at 60°C over night.

2.2 Sample Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 X-Ray diffractometer (Cu-K_α source) at a scanning rate of 1° /min with the scanning range from 20° to 80°. N₂ adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020M⁺C system. The sample was degassed at 200 °C for 4 h in N₂ before the measurement. The pore size distribution of mesopores in the samples was analyzed by BJH method. Diffuse reflectance UV-Vis spectra were acquired on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). Transmission Electron Microscopy (TEM) images were obtained on JEOL JEM-2010 with 200 kV accelerating voltage. Dark-field TEM images were acquired on FEI Titan under STEM mode. X-ray Photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific Theta Probe XPS with monochromatized Al K_α ($h\nu=1486.7$ eV) source. The likely charging of samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 285 eV.

2.3 Photocatalytic activity measurement

The prepared nanocomposites were tested for H₂ evolution from photocatalytic water reduction in the presence of L-ascorbic acid as the electron donor. For the visible-light-driven H₂ evolution by various Au-TiO₂ samples and Pt-loaded TiO₂ samples, 10 mg composite photocatalysts were dispersed into 10 ml aqueous solution of L-ascorbic acid (0.1 M, pH=6) in a quartz bottle. The bottle was sealed and purged with pure nitrogen gas for 30 min to drive away oxygen. Then the suspension was exposed under the 300-Watt Xe lamp (MAX-302, Asahi Spectra Co. Ltd.) coupling with a UV cutoff filter ($\lambda > 420$ nm)

to evaluate the photocatalytic efficiencies under visible light (see the supporting information for the details of reactor setup). The sampling gas composition from the upper space above the liquid suspension in the quartz bottle was periodically analyzed quantitatively by an Agilent 7890A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). In the control experiments which test the H₂ evolution activity of 2Au-TiO₂ and Pt-loaded TiO₂ samples under UV-vis light, the UV cutoff filter ($\lambda > 420$ nm) was taken away, and all other experimental settings and parameters were the same with those experiments for the visible-light-driven H₂ evolution.

3. Results and discussion

3.1 XRD analysis

The XRD patterns of the pure TiO₂ sample and Au-TiO₂ nanocomposites with various gold ratios are presented in Fig. 1. For pure TiO₂, all peaks are well indexed as the anatase phase (JCPDS card No. 83-2243), and the average crystallite size is estimated as 8.29 nm based on calculation from the Debye-Scherrer equation. The Au-TiO₂ nanocomposites did not show any peak shift, indicating that the TiO₂ matrix was well maintained as the anatase phase. As listed in Table 1, the average TiO₂ crystallite sizes of all samples are quite similar, indicating that the introduced gold does not alter the crystalline properties of the TiO₂ matrix. The samples with 0.5%Au, 1%Au and 2%Au showed two characteristic peaks of metallic gold (JCPDS card. No. 01-1174) at 38.3° (111) and 44.5° (200). But when the Au concentration is too low (< 0.5%), the gold peaks were not observed due to the weak signal beyond the instrument detection limit.

3.2 Surface area analysis

Fig. 2A shows the N₂ adsorption-desorption isotherm of the Au-TiO₂ samples with different Au ratio. The isotherms of all samples exhibit a hysteresis loop at relative high pressure, indicating the presence of mesopores (type IV). The observed type H3 hysteresis loop suggested narrow necks and wider bodies (ink-bottle pores) in the pores[34]. The surface area of 0.5Au-TiO₂ and 2Au-TiO₂ were characterized as 187.0 m²/g and 157.0 m²/g, which are still close to the value of pure TiO₂ (168.2 m²/g). This means that

the surface area of nanocomposites was not greatly influenced by the introduced gold. The mesopore size distribution of these samples was analyzed by BJH method (Fig. 2B), and the average pore volume and pore size are listed in Table 2.

Pluronic P123, a non-ionic amphiphilic triblock copolymer, is believed as the key reagent for large surface area from high porosity[35,36]. The surface area and average pore volume of 2Au-TiO₂ nanocomposite are nearly twice larger than that of the control sample (2Au-TiO₂ without P123). This confirmed that the P123 copolymer acts as the porosity promoter to create more mesopores when it is removed at elevated temperature in the post-synthesis thermal treatment. The Au-TiO₂ samples exhibit smaller pore volume and pore size than the pure TiO₂ sample probably due to the blockage of some pores in the TiO₂ matrix by the generated gold nanoparticles.

3.3 TEM analysis

Fig. 3 shows the TEM and HRTEM images of a typical 2Au-TiO₂ sample. The nanocomposites are composed by loosely packed nanoparticles that are agglomerated into a mesoporous network. The HRTEM image (Fig. 3B) shows well resolved (101) lattice fringes ($d=0.35$ nm) of anatase TiO₂, and Au (200) lattice ($d= 0.20$ nm) features. The quantitative EDX analysis indicates the molar concentration of Au as 1.97% which is close to the theoretical value 2% in the precursor mixtures. This also indicates negligible Au loss in the sample preparation process. The dark-field TEM image (Fig. 4) at STEM mode reveals that the Au nanoparticles were well dispersed in the TiO₂ matrix with a mean particle size of 12.9 nm. The other Au-TiO₂ samples also show similar mean size of gold nanoparticles in the TiO₂ matrix.

3.4 Optical properties of the Au-TiO₂ nanocomposites

The UV-Vis diffuse reflectance spectra of the Au-TiO₂ nanocomposites with various Au concentrations are shown in Fig. 5. The band gaps of all samples are calculated according to the modified Kubelka-Munk function $[F(R)E]^{1/2}$ vs the energy of absorbed light E [37], which are plotted in Fig. S2, and the band gap values of all samples are listed in Table 3. The values are all in the range of

experimental error (± 0.2 eV), thereby the introducing of Au has almost no influence on the band gap energy of the TiO_2 matrix. However in contrast to the pure TiO_2 sample, the Au- TiO_2 nanocomposites have significantly enhanced light absorption in the visible region with a broadband peak located at around 590 nm arising from the SPR of gold nanoparticles in the TiO_2 matrix[30]. It should be noted that this SPR wavelength has a relatively red-shift comparing to that of free gold particles of similar sizes (e.g. 520~530 nm for 15 nm Au nanoparticles in aqueous suspension)[38]. This might be due to the high refractive index of anatase TiO_2 ($n=2.49$) comparing to water ($n=1.33$).

3.5 XPS analysis

The XPS spectra of pure TiO_2 and 2Au- TiO_2 are shown in Fig. 6. For both samples, Ti 2p, O 1s, C 1s and Au 4f were recorded, deconvoluted, and analyzed. The Ti 2p XPS spectra shown in Fig. 6A display only two components with the binding energy at 459.0eV and 464.7eV, respectively, which could be assigned to Ti 2p_{3/2} and Ti 2p_{5/2} spin-orbit components of Ti^{4+} [39]. The binding energy located at 530.3eV for O1s XPS spectra could be assigned to O^{2-} in TiO_2 lattice. The O 1s shoulder with the binding energy at 531.6eV is attributed to surface hydroxyl groups on TiO_2 [39]. These results suggest that the introducing of gold did not affect the chemical state of Ti and O in the TiO_2 matrix.

Fig. 6C indicates the binding energy of Au 4f_{7/2} at 83.2 eV and Au 4f_{5/2} at 86.8 eV with no indication of Au^+ (4f_{7/2} at 84.6 eV) and Au^{3+} (4f_{7/2} at 86.5 eV)[7,21,40]. This result suggests that the Au species in the Au- TiO_2 nanocomposites are in metallic Au^0 state. The relative negative shift (0.8 eV) of Au 4f_{7/2} peak in comparison of bulk Au (4f_{7/2} at 84.0eV)[39] can be attributed to electron redistribution (from TiO_2 to Au) at the Au- TiO_2 contact interfaces when their Fermi levels are aligned[41]. This also indicates that the Au nanoparticles were embedded into the mesoporous TiO_2 network with large Au surface area in contacting with TiO_2 .

3.6 Photocatalytic hydrogen evolution by Au- TiO_2 nanocomposites

The Au- TiO_2 nanocomposites with different Au molar concentration were evaluated for visible-light-driven hydrogen evolution from photocatalytic water reduction under visible light irradiation ($\lambda > 420$

nm). Many different types of organic compounds, such as alcohols[42,43], aldehydes[44,45], and organic acids[46-48], have been used as electron donors for photocatalytic hydrogen generation. In our experiment, ascorbic acid (0.1 M, pH=6) was used as the sacrificial reagent to quench the photogenerated holes. Fig. 7 shows the hydrogen evolution amount of various Au-TiO₂ samples, by which the H₂ production rates are calculated and listed in Table 4. It indicates that the hydrogen evolution rate becomes higher as the Au concentration increases up to 2%. This means that the gold nanoparticles are responsible to the visible-light-induced photocatalytic activities. Higher content of gold nanoparticles leads to more light absorption via SPR, and thereby higher photocatalytic activity. However, excess gold nanoparticles in the nanocomposites could act as the recombination center of photo-generated charges to reduce the photocatalytic activity, which is evidenced by the lower H₂ evolution rate on 5Au-TiO₂ than that on 2Au-TiO₂. In addition, the stability of the Au-TiO₂ photocatalyst during the photocatalytic H₂ evolution reaction was tested. As shown the Fig. S3, the 2Au-TiO₂ photocatalyst showed steady H₂ evolution even for 24 hours with no dropping in the photocatalytic activity.

3.7 The roles of Au nanoparticle excitation for hydrogen evolution

The visible light absorption of gold nanoparticles is contributed by surface plasmon resonance and interband (5d to 6sp) transition[49]. Nevertheless, the visible-light induced interband transition can not provide sufficient potential to reduce water, although it may leave oxidative holes in the d-band, which are capable for the oxidation of dyes and alcohols[50]. Therefore we attribute the visible-light-induced hydrogen evolution to the SPR excitation of gold nanoparticles. In literatures, two major roles have been proposed for the Au nanoparticle SPR in Au-loaded TiO₂ composites. One is the SPR-induced field enhancement on the excitation of defects or impurity states in the TiO₂ matrix. Another is direct transfer of SPR-excited Au surface electrons into TiO₂. In order to clarify the SPR roles in our Au-TiO₂ nanocomposites, we carried our several comparison experiments.

3.7.1 Comparison of 2Au-TiO₂ and 2Pt-TiO₂

It is well known that Pt is an excellent co-catalyst from water splitting and has a low overpotential and better activity than Au for hydrogen evolution[51,52]. The comparison samples, 2Pt-TiO₂ and 2Pt-P25, were synthesized via photodeposition of Pt precursors onto the surface of support TiO₂. The H₂ evolution plots and corresponding calculated reaction rates are presented in Fig. 8 and Table 5, respectively. Under UV-vis light irradiation, the TiO₂ matrix is excited by UV-light and those excited electrons in the conduction band can transfer to the contacting metal nanoparticles for H₂ evolution. Due to the lower overpotential on Pt, it is thereby indubitable that the Pt-loaded TiO₂ samples exhibit much higher H₂ evolution activity than 2Au-TiO₂, which is also in agreement with previous reports[51]. However, when the reaction was carried out under visible light ($\lambda > 420$ nm) irradiation, highly reversed activities were observed. The H₂ evolution rate of 2Au-TiO₂ is more than three times higher than that of 2Pt-TiO₂. This result confirms the tremendous effect from gold excitation since the small Pt nanoparticles do not exhibit SPR in the visible light region.

We note that the 2Pt-TiO₂ sample still exhibits slight visible-light activity for H₂ evolution as comparing to Pt-loaded commercial P25 that shows negligible activity. Consistently, the absorption spectrum does indicate that the TiO₂ sample prepared with P123 exhibit a slight absorption edge above 420 nm as compared to the commercial P25 that shows no absorption in the visible region (Fig. S4). It is known that the extended absorption of TiO₂ in the visible region is caused by excitation of valence electrons into defects or impurity states that locate below the TiO₂ conduction band[10]. Thus these observations suggest that the pure TiO₂ sample produced by this P123-assisted sol-gel method contains some defects or impurity states, causing slight visible-light absorption near 420 nm. Furthermore, this weak visible-light excitation of TiO₂ can be promoted by the Au SPR excitation (> 500 nm) which induces strongly enhanced localized electric field and improves the charge separation process on the adjacent TiO₂ surface[32]. By this way, the 2Au-TiO₂ sample could exhibit much higher photocatalytic activity than 2Pt-TiO₂.

In addition, as shown in Table 2 the surface area of the standard 2Au-TiO₂ sample is only twice than that of the control sample 2Au-TiO₂ without P123 assist. However, the former showed hydrogen evolution rate (7.0 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) more than four times higher than the latter (1.6 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). This indicates that surface area difference has considerably minor effect on the photocatalytic activity comparing to the P123-induced visible-light absorption and its coupling with surface plasmon of gold nanoparticles.

3.7.2 Effect of Excitation Wavelengths

In order to differentiate the SPR excitation of Au nanoparticles with defect/impurity excitation of TiO₂ matrix, we have carried out further comparison test by controlling the irradiation wavelengths at 500 $\pm$ 20 nm and 550 $\pm$ 20 nm. The 2Pt-TiO₂ sample showed no H₂ evolution even after 12h irradiation at both wavelengths, indicating that the photons with energy in these ranges are not able to excite defect/impurity states of the TiO₂ matrix. In comparison, under irradiation at 500 $\pm$ 20 nm, the 2Au-TiO₂ sample still exhibits steady hydrogen evolution with a rate of 1.35 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ (Fig. 9). However, we observed much less hydrogen evolution rate (0.04 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) when the 2Au-TiO₂ sample was irradiated at 550 $\pm$ 20 nm which is even closer to the SPR peak of the gold nanoparticles. This result suggests that the transfer of plasmon-excited energetic electrons from gold to TiO₂ should be responsible to water reduction, nevertheless stronger plasmon excitation does not ensure more efficient water reduction.

Zhu et al. proposed that plasmon-excited electrons would have an energy distribution, and only a small portion of electrons can reach high energy level[50]. Our results also suggest that the photon energy for plasmon-excitation may still determine the potential and energy distribution of those excited electrons as well as their ability of transferring to contacting semiconductors. Comparing the excitation at 550 $\pm$ 20 nm, the excitation by higher energy photons (500 $\pm$ 20 nm) would allow more electrons to possess sufficient high reduction potential to jump into TiO₂ conduction band, thereby result in higher hydrogen evolution rate.

4. Conclusion

The mesoporous plasmonic Au-TiO₂ nanocomposites with different Au concentration were prepared via a co-polymer assisted sol-gel method. These Au-TiO₂ nanocomposites exhibit remarkable visible-light activities for hydrogen evolution from photocatalytic water reduction when ascorbic acid is used as the electron donor. Among them, the 2% Au-TiO₂ shows the highest photocatalytic activity. Our studies reveal that such visible-light-driven photocatalytic activities can be attributed to three major reasons. First, the copolymer-induced defect/impurity states in the TiO₂ matrix lead to weak visible-light absorption near 420 nm; Second, the plasmon-excitation of gold nanoparticles at longer wavelengths enhances this weak visible light excitation through strong localized electric field and improves charge separation on TiO₂; Third, some plasmon-excited electrons with sufficient high energy can transfer from Au nanoparticles to the contacting TiO₂ to generate hydrogen by reducing water. The overall proposed mechanism is illustrated as Fig.10. We believe that our investigation results would have considerable impact on the future development of more efficient plasmonic metal-semiconductor photocatalysts for hydrogen production.

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Table 1 - The main crystallite size of the various Au-TiO₂ photocatalysts.

Catalyst	TiO ₂	0.1Au-TiO ₂	0.2Au-TiO ₂	0.5Au-TiO ₂	1Au-TiO ₂	2Au-TiO ₂
$d_{\text{XRD}}(\text{nm})$	8.29	7.99	8.15	7.64	7.53	8.34

Table 2 - The BET surface area and pore distribution of various Au-TiO₂ photocatalysts.

Catalyst	BET surface area(m ² /g)	Average pore volume(cm ³ /g)	Average pore size(nm)
TiO ₂	168.16	0.235	3.92
0.5Au-TiO ₂	186.95	0.230	3.56
2Au-TiO ₂ without P123	77.14	0.079	3.28
2Au-TiO ₂	156.97	0.165	3.30

Table 3 - The calculated band gap $E_g(\text{eV})$ of various Au-TiO₂ photocatalysts.

Catalyst	TiO ₂	0.1Au-TiO ₂	0.2Au-TiO ₂	0.5Au-TiO ₂	1Au-TiO ₂	2Au-TiO ₂
$E_g(\text{eV})$	3.15	3.25	3.28	3.29	3.28	3.29

Table 4 - Photocatalytic H₂ evolution rate ($\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ catalyst) over various Au-TiO₂ photocatalysts.

Catalyst	0.1Au-TiO ₂	0.2Au-TiO ₂	0.5Au-TiO ₂	1Au-TiO ₂	2Au-TiO ₂	5Au-TiO ₂
R	0.37	0.95	1.68	3.70	7.00	2.88

Table 5-Photocatalytic H₂ evolution rate ($\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$) over 2Au-TiO₂, 2Pt-TiO₂, and 2Pt-P25catalysts.

Catalyst	Light source	
	Uv-vis light	Visible light ($\lambda > 420\text{nm}$)
2Au-TiO ₂	57.02	7
2Pt-TiO ₂	300.63	2.39
2Pt-P25	223.90	0.23

Fig. 1 - XRD patterns of prepared TiO₂ and various Au-TiO₂ samples.

Fig. 2 - (A) The N₂ adsorption-desorption isotherms of pure TiO₂ and various Au-TiO₂ samples. (B) The pore size distributions of pure TiO₂ and various Au-TiO₂ samples.

Fig. 3 - (A) TEM and (B) HRTEM images of 2Au-TiO₂; (C) EDX spectrum of 2Au-TiO₂.

Fig. 4 - (Left) Dark field TEM image of 2Au-TiO₂ catalyst. The white dots represent Au nanoparticles. (Right) Size distribution of Au nanoparticles incorporated in TiO₂ matrix for the 2Au-TiO₂ sample.

Fig. 5 - UV-Vis absorption spectra of various Au-TiO₂ samples after conversion from diffuse reflectance spectra.

Fig. 6 - The (A) Ti 2p, (B) O 1s spectra of pure TiO₂ and 2Au-TiO₂; (C) Au 4f XPS spectrum of 2Au-TiO₂

Fig. 7 - Plots of photocatalytic H₂ evolution amount versus visible light ($\lambda > 420$ nm) irradiation time by using different Au-TiO₂ photocatalysts.

Fig. 8 - The photocatalytic H₂ evolution over 2Au-TiO₂ under irradiation at 500 ± 20 nm.

Fig. 9 - The photocatalytic H₂ evolution over 2Au-TiO₂, 2Pt-TiO₂, and 2Pt-P25 photocatalysts under visible light (Left) and UV-Vis (Right) irradiation.

Fig. 10 - Schematic illustration of the proposed mechanism for photocatalytic hydrogen evolution over Au-TiO₂ photocatalysts under visible light irradiation.