Efficient H₂ production over Au/graphene/TiO₂ induced by surface plasmon resonance of Au and band-gap excitation of TiO₂

Yang Liu^a, Hongtao Yu^a, Hua Wang^{a,b}, Shuo Chen^a and Xie Quan^{a,*}

^a Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China. Fax: +86-411-84706263; Tel: +86-411-84706140; E-mail: quanxie@dlut.edu.cn

^b School of Fisheries and Life Science, Dalian Ocean University, Dalian 116023, China. E-mail: wanghua@dlou.edu.cn

10

Corresponding author's name: Xie Quan

Mail address: School of Environmental Science and Technology, Dalian University of Technology, Dalian, China, 116024.

15 Tel: +86-411-84706140; Fax: +86-411-84706263; E-mail: quanxie@dlut.edu.cn

Abstract: H₂ production over Au/Gr/TiO₂ composite photocatalyst induced by surface plasmon resonance of Au and band-gap excitation of TiO₂ using graphene (Gr) as an electron acceptor has been investigated. Electron paramagnetic resonance study indicated that, in this composite, Gr collected
20 electrons not only from Au with surface plasmon resonance but also from TiO₂ with band-gap excitation. Surface photovoltage and UV-vis absorption measurements revealed that compared with Au/TiO₂, Au/Gr/TiO₂ displayed more effective photogenerated charge separation and higher optical

absorption. Benefiting from these advantages, the H₂ production rate of Au/Gr/TiO₂ composite with Gr content of 1.0 wt% and Au content of 2.0 wt% was about 2 times as high as that of Au/TiO₂. This work represents an important step towards the efficient application of both surface plasmon resonance and band-gap excitation on the way to converting solar light into chemical energy.

5

Keywords: A. Composites, B. Chemical synthesis, B. Optical properties, D. Catalytic properties

1. Introduction

Since Fujishima and Honda reported the pioneering work of water splitting from a TiO₂ semiconductor electrode in 1972, this photocatalytic process appears to be an attractive strategy for H₂ production [1]. Unfortunately, TiO₂ only exhibited band-gap excitation under UV light irradiation which accounts for only 4% of the solar radiation energy. In order to extend the photoresponse of TiO₂ to visible region, considerable efforts have been made to develop available methods such as dye sensitization [2-4], metal and nonmetal doping [5-9] and surface plasmon resonance enhancement [10] and so on. Among these methods, the combination of plasmonic noble metal and semiconductor (especially Au/TiO₂) attracts the wide attention [11-14]. By loading plasmonic Au nanoparticles on the surface of TiO₂, researchers have observed plasmon-enhanced photocatalytic water splitting under visible illumination. However, in these work, TiO₂ only acts as a supporting material of Au under visible light which only induces the surface plasmon resonance of Au while cannot excite TiO₂. In fact, both Au and TiO₂ can be excited due to surface plasmon resonance and band-gap excitation under sunlight including both UV and visible light, which may lead to a more effective solar light utilization.

Theoretically, under UV and visible light irradiation, the electrons of Au induced by surface plasmon resonance with -1.3 eV (vs. NHE) of energy level will inject to the conduction band of TiO₂ (-0.5 eV vs NHE) [15, 16], and meanwhile, the valence electrons of TiO₂ will be excited to the conduction band leaving the holes in the valence band. In this situation, both electrons from Au and TiO₂ will accumulate on the surface of TiO₂. The following problem is that this accumulation may increase the probability of charge recombination. This is the intrinsic property of Au/TiO₂ that limits the energy conversion efficiency of Au/TiO₂. Therefore, it is of importance to find a way to break through this restriction and efficiently utilize both the surface plasmon resonance of Au and band-gap excitation of TiO₂ into solar-light-driven H₂ production.

In fact, if an electron acceptor is combined with Au/TiO₂ to induce a vectorial electron transport from Au/TiO₂ to the electron acceptor, the charge recombination of Au/TiO₂ aforementioned can be suppressed. Among the reported materials [17-20], graphene (Gr) has been regarded as not only a promising supporting platform for anchoring guest nanoparticles, but also excellent electron transfer mediator and acceptor to facilitate an efficient charge separation [21]. To the best of our knowledge, no report regarding the application of Gr as an acceptor of photogenerated electrons from both Au with surface plasmon resonance and TiO₂ with band-gap excitation for the photocatalytic H₂ production has been published. Here we report for the first time the surface plasmon resonance of Au and band-gap excitation of TiO₂ induced H₂ production over Au/Gr/TiO₂ composite photocatalyst using Gr as an electron acceptor.

2. Experimental Section

2.1 Materials Preparation

In order to obtain the Au/Gr/TiO₂ composite, three steps were involved including graphene oxide (GO) fabrication, Gr/TiO₂ hydrothermal synthesis and photodeposition of Au on Gr/TiO₂. In the first

step, GO was produced from natural graphite powder by a modified Hummers method [22]. In the second step, to prepare Gr/TiO₂, P25 and GO (weight ratio, 100:0.5, 100:1 and 100:2, respectively) were mixed homogeneously in 60 mL deionized water. The obtained solution was transferred to a Teflon-lined stainless steel autoclave (100 mL) followed by sonication for 1 h. Then, the autoclave was heated in an air blowing thermostatic oven at 160 °C for 3 h. After the hydrothermal reaction, the obtained precipitate was washed with deionized water, and dried overnight at room temperature. In the third step, to synthesize Au/Gr/TiO₂, 0.4 g Gr/TiO₂ was added to 100 mL mixed liquid of alcohol and water (volume ratio of 1:1) containing a varying amount of HAuCl₄ (0.8 mM, 1.6 mM and 3.2 mM). Subsequently, the solution was sonicated for 5 min. After that, the solution was irradiated under Xe lamp with vigorous stirring for 1 h. Finally, the obtained precipitate was rinsed with deionized water and dried overnight at room temperature.

2.2 Characterization

The morphology of the samples was observed by transmission electron microscopy (TEM, FEI Tecnai G² F30). The crystal structures of the samples were investigated by an X-ray diffractometer (XRD, Shimadzu LabX XRD-6000) employing Cu K α radiation accelerating voltage of 40 kV and current of 30 mA over the 2θ range of 20-80°. Raman spectra measurements were performed on a Renishaw Micro-Raman system 2000 spectrometer with He-Ne laser excitation (wavelength 633.8 nm). The electron paramagnetic resonance (EPR) spectrum was recorded on a Bruker A200 EPR spectrometer (90 K, 9064 MHz, 0.998 mW, X-band). Surface photovoltage (SPV) was tested by a lock-in based surface photovoltage measurement system, which consisted of a monochromator (model Omni- λ 3005) and a lock-in amplifier (model SR830-DSP) with an optical chopper (model SR540) running at a frequency of 20 Hz. The UV-vis diffuse spectra (DRS) were measured by a Shimadzu

UV-2450 spectrophotometer with the scanning range from 200 to 800 nm.

2.3 Photocatalytic H_2 Production

H_2 production experiments were conducted at 10 °C in a closed top-irradiation gas-circulation system under Xe lamp (wavelength range from 320 nm to 800 nm) irradiation. 0.1 g photocatalyst powder was placed in a Pyrex top-irradiation glass reactor containing 100 mL pure water (or methanol). The suspension was irradiated from the top of the reactor. The amount of evolved H_2 gas was monitored by an on-line gas chromatograph (Shimadzu, GC-14C) with a TCD detector and a packed column (5Å molecular sieves, 2 m × 4 mm). High purity nitrogen gas was used as a carrier gas.

3. Results and discussion

3.1 Morphology and Structure of Au/Gr/TiO₂

From the TEM image of Au/Gr/TiO₂, it can be observed that nanoparticles were deposited on the Gr sheets (Fig. 1a). These nanoparticles with different sizes occupied almost the whole surface of Gr sheets and were differentiated in the HRTEM image in Fig. 1b. They were highly crystallized with clear lattice fringes, and a lattice spacing of 0.235 nm was consistent with the lattice of Au (111) plane (JCPDS 04-0784). Meanwhile, the lattice spacing of 0.350 nm could be indexed as the (101) lattice plane of anatase TiO₂ (JCPDS 21-1272).

XRD patterns of TiO₂, Gr/TiO₂, Au/TiO₂ and Au/Gr/TiO₂ were compared in Fig. 2a. The peaks in the XRD pattern of TiO₂ at 2θ of 25.5°, 37.1°, 38.1°, 48.3°, 54.1° and 55.3° could be indexed respectively to the (101), (103), (004), (200), (105) and (211) crystal faces of anatase TiO₂ (JCPDS 21-1272). Compared with that of TiO₂, the XRD pattern of Au/TiO₂ showed four additional peaks at 2θ of 38.2°, 44.2°, 64.8°, and 78.0° corresponding to the (111), (200), (220), and (311) planes of Au, respectively. All these characteristics peaks of TiO₂ and Au coexisted in the XRD pattern of Au/Gr/TiO₂. These results agreed well with that of TEM measurements, meaning the good crystallinity

of TiO₂ and Au nanoparticles. No peaks belonging to Gr were detected in the patterns of Gr/TiO₂ and Au/Gr/TiO₂ due to the low amount of Gr. In order to get more detail information with regard to Gr, Raman spectra of GO, TiO₂, Gr/TiO₂ and Au/Gr/TiO₂ were shown in Fig. 2b. Two characteristic peaks at 1333 cm⁻¹ (D band) and 1596 cm⁻¹ (G band) were observed in GO sample. The D mode suggested the presence of sp³ defects due to intervalley scattering and G mode raised from the first order scattering of the E_{2g} phonon of sp² carbon forms. Compared with GO, there were a slightly downshift of D bands (1326 cm⁻¹) and G bands (1591 cm⁻¹) as well as an increment in D/G intensity ratio in Gr/TiO₂, which indicated the increased defects originated from the reduction of GO. Further downshift of D bands (1324 cm⁻¹) and G bands (1587 cm⁻¹) in Au/Gr/TiO₂ could be attributed to the surface-enhanced Raman scattering effect arising from surface plasmon resonance field induced by Au nanoparticles. The peaks at 143, 400, 516, and 638 cm⁻¹ were observed in Gr/TiO₂ and Au/Gr/TiO₂ samples, respectively, which corresponded to the E_{g(1)}, B_{1g(1)}, A_{1g} + B_{1g(2)}, and E_{g(2)} modes of anatase TiO₂. These observations, together with the results of TEM and XRD, provided evidences for the successful fabrication of the Au/Gr/TiO₂ composite.

3.2 EPR studies

In order to reveal the charge transport process of Au/Gr/TiO₂, EPR spectra of the samples were recorded in dark and under Xe lamp irradiation with and without cut-filter (400 nm). As shown in Fig. 3a, no signal was observed in the spectra of TiO₂ and Au/TiO₂ in dark. Compared with those of Gr free samples, the spectra of Gr containing samples (Gr/TiO₂ and Au/Gr/TiO₂) showed the isotropic signal at about g = 2.005 corresponding to the oxygen vacancy [14], which revealed that the introduction of Gr resulted in the emergence of oxygen vacancy due to the chemical combination between Gr and TiO₂ [23]. Theoretically, under Xe lamp irradiation, the oxygen vacancy could trap the electrons not

only from the surface plasmon resonance of Au but also from the **band-gap excitation** of TiO₂ [14] followed by a corresponding signal increase. This increase, as expected, was found in Fig. 3b. Specifically, the signal increase in the spectrum of Au/Gr/TiO₂ under Xe lamp with cut-filter (400 nm) corresponded to the surface plasmon resonance induced electrons trapping on oxygen vacancy. Further signal increase under Xe lamp without cut-filter could be indexed to the **band-gap excitation** electrons of TiO₂ trapping on the oxygen vacancy.

Based on the EPR results, considering that Gr was an ultimate electron acceptor according to the energy level gradient [24, 25], there was a vectorial electron transport from Au/TiO₂ to Gr in Au/Gr/TiO₂ under Xe lamp irradiation. This electron transport may suppress the charge recombination by extracting excited electrons of Au/TiO₂ to Gr before they recombined with photogenerated holes of TiO₂ and thus was expected to facilitate the charge separation.

3.3 Charge Separation and Optical Absorption

Based on the EPR results, the vectorial electron transport from Au/TiO₂ to Gr may facilitate the charge separation in Au/Gr/TiO₂. The better the charge separation is, the higher the surface photovoltage (SPV) is. Among all the samples, Au/Gr/TiO₂ exhibited the highest SPV response (Fig. 4a), indicating the enhanced charge separation in Au/Gr/TiO₂. This result provided evidence of the promotion role of Gr for the charge separation of Au/Gr/TiO₂.

The optical absorption of TiO₂, Gr/TiO₂, Au/TiO₂ and Au/Gr/TiO₂ were studied by UV-vis diffuse spectroscopy to evaluate their light absorption ability. As shown in Fig. 4b, TiO₂ only absorbed UV light while Gr/TiO₂, Au/TiO₂ and Au/Gr/TiO₂ responded to both UV and visible light. In particular, compared with Gr/TiO₂ and Au/TiO₂, Au/Gr/TiO₂ exhibited enhanced absorption in the visible region, which could be attributed to the combination of Gr and the surface plasmon resonance absorption of Au nanoparticles. These results indicated that surface plasmon resonance of Au, band-gap excitation of TiO₂ and Gr simultaneously contributed to the light absorption in Au/Gr/TiO₂.

3.4 Photocatalytic H_2 production.

Gr and Au played different but important roles in the Au/Gr/TiO₂ composite photocatalyst and they could strongly influence the H_2 production over Au/Gr/TiO₂. As shown in Fig. 5a, there was a higher H_2 production rate over Gr/TiO₂ than TiO₂ in methanol. With the increase in the amount of Gr, the amount of H_2 produced increased and reached to the maximum value when the content of Gr in Gr/TiO₂ reached 1.0 wt%. This enhanced performance benefited from the enhancement of the light absorption as well as charge transfer and separation by the introduction of Gr. The driving force of the efficient charge transfer and separation was initiated by the different energy levels between the conduction band of TiO₂ and the work function of Gr [26]. However, when the Gr content was further increased exceed 1.0 wt%, the amount of H_2 decreased because an excess of Gr may block the incident light.

Fig. 5b correlated the H_2 production over Au/Gr/TiO₂ photocatalyst with the ratio of Au. After loading Au on Gr/TiO₂, the amount of evolved H_2 was sharply increased and reached to the maximum value when the content of Au in Au/Gr/TiO₂ was 2 wt%. In this photocatalyst, excited electrons from Au nanoparticles with surface plasmon resonance could be trapped by the oxygen vacancy of TiO₂ and then injected to the surface of Gr. Both processes promoted the charge transfer and separation, thus enhanced the H_2 production activity. However, overloading of Au resulted in the blocking of the light absorption of Au/Gr/TiO₂, and hence diminished the H_2 production rates. Based on the above results, the optimum Gr and Au contents in Au/Gr/TiO₂ composite were 1.0 and 2.0 wt%, respectively.

To evaluate the photocatalytic H_2 production activity of Au/Gr/TiO₂, H_2 production tests were carried out not only in methanol but also in pure water. As shown in Fig. 6a, compared with that over TiO₂, the H_2 production rate was enhanced over Gr/TiO₂ and Au/TiO₂ samples. The maximum H_2 production rate which was about 2 times as high as that of Au/TiO₂ was observed over Au/Gr/TiO₂ in

methanol. In particular, efficient photocatalytic H₂ production over Au/Gr/TiO₂ (44 μmol·h⁻¹) in pure water could be achieved while no H₂ was detected on TiO₂ and Gr/TiO₂ (Fig. 6b). As mentioned above, in Au/Gr/TiO₂, Gr was a good platform for Au and TiO₂ nanoparticles assembling. Besides, Gr could guide the charge transport and acted as an electron acceptor for trapping the excited electrons not only from TiO₂ but also from surface plasmon resonance of Au, which led to an improved charge transport and separation. In this situation, these trapped electrons on Gr could efficiently reduce protons to H₂. As a result, enhanced H₂ production was achieved on the Au/Gr/TiO₂ photocatalyst. The stability of Au/Gr/TiO₂ was tested by cycle photocatalytic hydrogen production experiments (Fig. 6c). After the third cycle, no obvious change was observed on the photocatalytic activity, suggesting that Au/Gr/TiO₂ had a good stability.

Based on these results, the mechanisms of photocatalytic H₂ production over Au/Gr/TiO₂ photocatalyst was shown in the scheme (Fig. 7). The Gr sheet served as a huge 2D platform for the grafting of TiO₂ and Au nanoparticles on its surface. Under Xe lamp irradiation, the electrons (e⁻) on the valence band of TiO₂ were excited to its conduction band. Meanwhile, the excited electron by surface plasmon resonance of Au could be injected to the conduction band of TiO₂, and then these electrons transferred to Gr to reduce protons to H₂.

4. Conclusions

We have demonstrated that solar-light-driven H₂ production over Au/Gr/TiO₂ can be induced by surface plasmon resonance of Au and band-gap excitation of TiO₂ using Gr as an electron acceptor. Deposition of Au and TiO₂ on Gr realized an efficient light absorption in the UV and visible region, enhanced the charge separation and thus improved the H₂ production rate. This study paves the way to efficiently utilize the noble metal with surface plasmon resonance, semiconductor with band-gap excitation and Gr to form highly active photocatalyst for converting solar light into chemical energy.

Acknowledgements

This work was supported by the National Basic Research Program of China (2011CB936002), National Natural Science Foundation of China (NSFC-JST 21261140334), and Program for Changjiang Scholars and Innovative Research Team in University (IRT_13R05). Thanks are due to
5 Shahzad Afzal for the English corrections.

References

- [1] A. Fujishima, K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 238 (1972) 37-38.
- 10 [2] R. Abe, K. Hara, K. Sayama, K. Domen, H. Arakawa, Steady Hydrogen Evolution from Water on Eosin Y-Fixed TiO₂ Photocatalyst Using a Silane-Coupling Reagent under Visible Light Irradiation. J. Photochem. Photobiol. A 137 (2000) 63-69.
- [3] R. Abe, K. Sayama, H. Arakawa, Significant Influence of Solvent on Hydrogen Production from Aqueous I₃⁻/I⁻ Redox Solution Using Dye-Sensitized Pt/TiO₂ Photocatalyst under Visible Light
15 Irradiation. Chem. Phys. Lett. 379 (2003) 230-235.
- [4] J. R. Swierk, T. E. Mallouk, Design and Development of Photoanodes for Water-Splitting Dye-Sensitized Photoelectrochemical Cells. Chem. Soc. Rev. 42 (2013) 2357-2387.
- [5] A. Kudo, H. Kato, Effect of Lanthanide-Doping into NaTaO₃ Photocatalysts for Efficient Water Splitting. Chem. Phys. Lett. 331 (2000) 373-377.
- 20 [6] H. M. Luo, T. Takata, Y. G. Lee, J. F. Zhao, K. Domen, Y. S. Yan, Photocatalytic Activity Enhancing for Titanium Dioxide by Co-Doping with Bromine and Chlorine. Chem. Mater. 16 (2004) 846-849.

-
- [7] G. Liu, P. Niu, C. H. Sun, S. C. Smith, Z. G. Chen, G. Q. Lu, H. M. Cheng, Unique Electronic Structure Induced High Photoreactivity of Sulfur-Doped Graphitic C₃N₄. *J. Am. Chem. Soc.* 132 (2010) 11642-11648.
- [8] Z. S. Li, W. J. Luo, M. L. Zhang, J. Y. Feng, Z. G. Zou, Photoelectrochemical Cell for Solar Hydrogen Production: Current State of Promising Photoelectrodes, Methods to Improve Their Properties, and Outlook. *Energy. Environ. Sci.* 6 (2013) 347-370.
- [9] X. B. Chen, S. H. Shen, L. J. Guo, S. S. Mao, Semiconductor-Based Photocatalytic Hydrogen Generation. *Chem. Rev.* 110 2010 6503-6570.
- [10] S. Linic, P. Christopher, D. B. Ingram, Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat. Mater.* 10 (2011) 911-921.
- [11] H. Zhang, X. J. Lv, Y. M. Li, Y. Wang, J. H. Li, Plasmonic Gold Nanocrystals Coupled with Photonic Crystal Seamlessly on TiO₂ Nanotube Photoelectrodes for Efficient Visible Light Photoelectrochemical Water Splitting. *Nano Lett.* 13 (2013) 14-20.
- [12] Y. Tian, T. Tatsuma, Mechanisms and Applications of Plasmon-Induced Charge Separation at TiO₂ Films Loaded with Gold Nanoparticles. *J. Am. Chem. Soc.* 127 (2005) 7632-7637.
- [13] A. Furube, L. C. Du, K. Hara, R. Katoh, M. Tachiya, Ultrafast Plasmon-Induced Electron Transfer from Gold Nanodots into TiO₂ Nanoparticles. *J. Am. Chem. Soc.* 129 (2007) 14852-14853.
- [14] J. B. Priebe, K. Michael, H. Junge, M. Beller, D. Hollmann, A. Brückner, Water Reduction with Visible Light: Synergy between Optical Transitions and Electron Transfer in Au-TiO₂ Catalysts Visualized by In situ EPR Spectroscopy. *Angew. Chem. Int. Ed.* 52 (2013) 11420-11424.
- [15] J. Y. Zhang, Y. H. Wang, J. Zhang, L. Zhang, F. Huang, J. G. Yu, Enhanced Photocatalytic Hydrogen Production Activities of Au-Loaded ZnS Flowers. *ACS Appl. Mater. Interface* 5 (2013) 1031-1037.

-
- [16] Y. C. Pu, G. M. Wang, K. D. Chang, Y. C. Ling, Y. K. Lin, B. C. Fitzmorris, C. M. Liu, Y. H. Lu, Y. X. Tong, J. Z. Zhang, Y. J. Hsu, Y. Li, Au Nanostructure-Decorated TiO₂ Nanowires Exhibiting Photocativity Across Entire UV-visible Region for Photoelectrochemical Water Splitting. *Nano. Lett.* 13 (2013) 3817-3823.
- ⁵ [17] S. Sakthivel, M. V. Shankar, M. Palanichamy, B. Arabindoo, D. W. Bahnemann, V. Murugesan, Enhancement of Photocatalytic Activity by Metal Deposition: Characterisation and Photonic Efficiency of Pt, Au and Pd Deposited on TiO₂ Catalyst. *Water Res.* 38 (2004) 3001-3008.
- [18] H. Tada, T. Ishida, A. Takao, S. Ito, Drastic Enhancement of TiO₂-Photocatalyzed Reduction of Nitrobenzene by Loading Ag Clusters. *Langmuir*, 20 (2004) 7898-7900.
- ¹⁰ [19] K. Woan, G. Pyrgiotakis, W. Sigmund, Photocatalytic Carbon-Nanotube-TiO₂ Composites. *Adv. Mater.* 21 (2009) 2233-2239.
- [20] X.Y. Zhang, H.P. Li, X.L. Cui, Y. J. Lin, Graphene/TiO₂ Nanocomposites: Synthesis, Characterization and Application in Hydrogen Evolution from Water Photocatalytic Splitting. *Mater. Chem.* 20 (2010) 2801-2806.
- ¹⁵ [21] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, Graphene-Based Composite Materials. *Nature*, 442 (2006) 282-286.
- [22] W. S. Hummers, R. E. Offeman, Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 80 (1958) 1339-1339.
- [23] H. Zhang, X. J. Lv, Y. M. Li, Y. Wang, J. h. Li, P25-Graphene Composite as a High Performance
²⁰ Photocatalyst. *ACS Nano.* 4 (2010) 380-386.
- [24] J. Zhou, G. H. Tian, Y. J. Chen, X. Y. Meng, Y. H. Shi, X. R. Cao, K. Pan, H. Q. Fu, In Situ Controlled Groth of ZnIn₂S₄ Nanosheets on Reduced Graphene Oxide for Enhanced Photocatalytic Hydrogen Production Performance. *Chem. Commun.* 49 (2013) 2237-2239.

-
- [25] W. G. Wang, J. G. Yu, Q. J. Xiang, B. Cheng, Enhanced Photocatalytic Activity of Hierarchical Macro/Mesoporous TiO₂-Graphene Composites for Photodegradation of Acetone in Air. *Appl. Catal. B: Environ.* 119-120 (2012) 109-116.
- [26] X. Wu, X. C. Zeng, Periodic Graphene Nanobuds. *Nano Lett.*, 9 (2008) 250-256.

5

10

15

20

Figure Captions:

Figure 1

TEM (a) and HRTEM (b) images of Au/Gr/TiO₂.

Figure 2

5 (a) XRD patterns and (b) Raman spectra of Au/Gr/TiO₂.

Figure 3

EPR spectra of (a) TiO₂, Au/TiO₂, Gr/TiO₂, and Au/Gr/TiO₂ in dark. (b) Au/Gr/TiO₂, in dark, under Xe lamp irradiation with and without cut-filter (400nm).

Figure 4

10 SPV (a) and DRS (b) of TiO₂, Gr/TiO₂, Au/TiO₂ and Au/Gr/TiO₂.

Figure 5

Photocatalytic H₂ production over Gr/TiO₂ with different amount of Gr in methanol (a), Au/Gr/TiO₂ with different content of Au in methanol (b).

Figure 6

15 Photocatalytic H₂ production over TiO₂, Gr/TiO₂, Au/TiO₂ and Au/Gr/TiO₂ in methanol (a) and in pure water (b); Three consecutive cycling H₂ production experiments of Au/Gr/TiO₂ (c). Reaction conditions: 0.1g catalyst, 300 W Xe lamp.

Figure 7

Schematic diagram for the solar H₂ production mechanisms on Au/Gr/TiO₂.

Fig. 1

5

10

Fig. 2

Fig. 3

Fig. 4

Fig. 5

5

10

15

Fig. 6

5

Fig. 7

5

10

15