Published in final edited form as:

J Am Chem Soc. 2011 October 26; 133(42): 16730–16733. doi:10.1021/ja204383q.

Plasmonic Enhancement of Photocatalytic Activity of Pt/n-Si/Ag Photodiodes Using Au/Ag Core/Shell Nanorods

Yongquan Qu[†], Rui Cheng[‡], Qiao Su[†], and Xiangfeng Duan^{†,§}

Xiangfeng Duan: xduan@chem.ucla.edu

[†]Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095

[‡]Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095

[§]California NanoSystems Institute, University of California, Los Angeles, CA 90095

Abstract

We report the plasmonic enhancement of the photocatalytic properties of the Pt/n-Si/Ag photodiode photocatalysts using Au/Ag core/shell nanorods. We show that Au/Ag core/shell nanorods can be synthesized with tunable plasmon resonance frequencies, and conjugated onto Pt/n-Si/Ag photodiodes using well-defined chemistry. Photocatalytic studies show that the conjugation with Au/Ag core/shell nanorods can significantly enhance the photocatalytic activity by more than 3 times. Spectral dependence studies further reveal the photocatalytic enhancement is strongly correlated with plasmonic absorption spectra of the Au/Ag core/shell nanorods, unambiguously demonstrating the plasmonic enhancement effect.

Photocatalysts can harness solar energy to drive useful redox chemistry, and therefore are of considerable interest for solar energy harvesting, conversion and storage, as well as environmental pollutant treatment.¹ We have recently reported the design and synthesis of a new generation of photocatalysts by integrating a nanoscale photodiode with two distinct redox nanocatalysts in a single nanowire heterostructure.^{2,3} Specifically, a nanoscale metal-semiconductor (e.g. Pt/n-Si) Schottky diode is encased in a protective insulating shell (silicon oxide) and integrated with two metallic nanocatalysts (e.g. Pt and Ag) in a heterojunction nanowire. The internal built-in potential across the Schottky diode promotes the efficient dissociation of photoexcited electron-hole pairs and directs the transportation of the separated charge carriers to the integrated redox catalysts for improved photocatalytic activity. The silicon oxide shell also prevents the direct electrochemical reactions on semiconductor surface and therefore ensures exceptional photochemical stability.

This rational design of photocatalytic nanosystems allows efficient charge separation, transportation and utilization to enable excellent photocatalytic quantum efficiency. However, the overall efficiency of the Pt/n-Si/Ag photodiodes can still be limited by relatively low optical absorption (<20%).^{2,3} Here we report a further enhancement of the photocatalytic performance of such photodiodes using Au and Au/Ag core/shell plasmonic nanorods. Coupling plasmonic metal nanostructures with semiconductor materials has the potential to significantly increase the absorption of semiconductors through a local field enhancement effect.^{4,5} The investigation on plasmonic enhanced photocatalytic properties is

Correspondence to: Xiangfeng Duan, xduan@chem.ucla.edu.

Supporting Information **Available:** Experimental details about synthesis of nanostructures and photocatalytic reactions. This materials is available free of charge via the internet at <http://pubs.acs.org>.

however less straightforward. Most studies carried out to date involve direct contact between metallic nanostructures with semiconductors.⁴ With this direct coupling, the enhanced photoactivity is often convoluted and has been attributed to the roles of the metal nanostructures as the electron trapping centers and/or the local surface plasmon resonance effect.⁴ It is often difficult to differentiate these two fundamentally different mechanisms. On the other hand, the direct contact between metal and semiconductor may also introduce interface trapping states that can increase electron-hole recombination and Fermi level pinning to degrade the photocatalytic activity.^{5c,6} Indeed, a reduced photocatalytic activity has also recently been reported for the photocatalysts with direct contact between metal nanostructures and semiconductor materials.⁵ Introducing a thin insulating shell to electrically isolate the metal nanostructures can avoid the interface defects and/or charge transfer between semiconductor and metal, while allow the propagation of optical field around the metal nanostructures, resulting in locally concentrated light for the enhancement of photocatalytic activity.⁷

Herein we report an unambiguous investigation of plasmonic modulation of photocatalyst properties by coupling plasmonic nanostructures (Au nanorods and Au/Ag core/shell nanorods) and Pt/n-Si/Ag photodiode photocatalysts with ~15 nm thick silicon oxide shell. The Au/Ag core/shell nanorods are selected here due to their broad plasmon resonance tunability from near UV to IR range to allow for wide spectral dependence studies. The 15 nm silicon oxide shell can serve several purposes: (1) it protects the semiconductor materials from direct photoelectrochemical corrosion to improve the stability; without this protection, the photoelectrochemical corrosion could lead to degradation/dissolution of the semiconductors and/or cause the metal nanostructures to break away from the semiconductors; (2) it avoids direct charge exchange between semiconductor and metal to avoid the formation of interface defects and Fermi level pinning; (3) it prevents the metal nanostructures function as an additional co-catalyst for photocatalytic reactions that could complicates the interpretation of the results. Therefore, the coupling of silicon oxide insulated Pt/n-Si/Ag photodiodes with Au/Ag nanorods provides an interesting and clean system to investigate the plasmonic effect on photocatalysis.

Au/Ag core/shell nanorods are synthesized by adding gold nanorod seeds (Fig. 1a) into a silver coating solution containing the silver nitrate (AgNO_3), ascorbic acid (AA) and sodium hydroxide (NaOH).⁸ For a fixed amount of gold nanorod seeds, increasing the amount of AgNO_3 leads to a strong color change from light brown to green, orange and yellow, suggesting a change of plasmonic absorption due to the formation of silver coating. Transmission electron microscopy (TEM) studies clearly show Au/Ag core/shell nanorod structures (Fig. 1b, 1c). The images also confirm the expected increase of silver shell thickness with increasing concentration of AgNO_3 in the coating solution. UV-vis absorption spectroscopic studies clearly show the obvious tunability of the spectral features. With increasing silver ion concentrations and consequently increasing silver shell thickness, the resulting plasmonic absorption peaks are progressively blue-shifted in relative to the spectrum of the starting gold nanorods (Fig. 1d).

The synthetic method for the Pt/n-Si/Ag nanowire photodiodes is summarized in our previous report and online supporting materials.³ In brief, the silicon nanowire arrays are prepared by electroless wet chemical etching and followed by baking at 900 °C under ambient conditions to form a ~ 15 nm silicon oxide shell. The Pt/Si heterojunction nanowires are prepared through partial silicon dry etching followed by electrodeposition of Pt. Silver metal is deposited on the silicon end of Pt/Si heterojunction nanowires through a self-catalyzed photoreduction process. TEM image clearly shows the interface of silicon/platinum heterostructures with a silver particle anchored at the silicon end of the nanowire

(Fig. 2a). Energy-dispersive X-ray (EDX) studies further confirm the three distinct sections of Pt, Si and Ag in the heterojunction nanowire.

Three Au or Au/Ag plasmonic nanorods are then loaded on the surface of photodiodes using (3-mercaptopropyl)trimethoxysilane (MPTMS) as the coupling agent. To this end, MPTMS is first used to modify the Au nanorods and Au/Ag core/shell nanorods. The silane modified nanorods are then conjugated onto the silicon oxide shell of the photodiodes in ethanol solution. Coupling photodiodes with Au nanorods (Fig. 1a), Au/Ag core/shell nanorods-A (Fig. 1b) and Au/Ag core/shell nanorods-B (Fig. 1c), three photocatalysts are obtained and named as Au NRs-Diodes (Fig. 2b), Au/Ag NRs-A-Diodes (Fig. 2c) and Au/Ag NRs-B-Diodes (Fig. 2d), respectively. The average number of metallic nanorods per micron length of photodiode nanowires is about 200, 175 and 115 for AuNRs, Au/Ag core/shell nanorods-A and Au/Ag core/shell nanorods-B, respectively.

The photocatalytic degradation of organic dyes or toxic pollutants is of great significance in environmental pollutant treatment, and represents a commonly used approach to characterize the activity of photocatalysts. To this end, photocatalytic degradation of nitrobenzene (NB) is performed to evaluate the photocatalytic activity of the photodiodes and plasmonic resonance effect of the metal nanorods. NB has an absorption peak at 267 nm (Fig. S1) and will not interfere with the light absorption of plasmonic nanostructures. For photocatalytic studies, photocatalysts containing 2 mg of photodiodes are dispersed in 10 ml of 300 μ M NB aqueous solution. The reactions are exposed to light irradiation from a 300 W xenon light (power density ~ 0.56 W/cm²) under vigorous stir. The experimental parameters are identical for all reactions. The reaction system was cooled by air flow. Small aliquots are taken out at different reaction time. The nanowire photodiodes are centrifuged off and the concentration of the NB aqueous solution is monitored by UV-vis absorption spectroscopy.

Figure 3a shows the concentration of the NB solution as a function of reaction time. The blue up-triangles, red circles, olive diamonds and purple right-triangles represent the NB dye photodegradation catalyzed by photodiodes, Au NRs-Diodes, Au/Ag NRs-A-Diodes and Au/Ag NRs-B-Diodes, respectively. The degraded percentages of NB by pure photodiodes are 34.6 % within 40 minutes of light irradiation. In contrast, the light irradiation on NB alone and the mixture of NB and 1 mg Au/Ag core/shell nanorods-B results in a slow photodegradation of NB (*ca.* 7% within 40 min.), confirming the photocatalytic activity is indeed originated from Pt/Si/Ag photodiodes. A significantly larger percentage of NB is degraded with the Au NRs-Diodes, Au/Ag NRs-A-Diodes and Au/Ag NRs-B-Diodes. The apparent photodegradation rates of NB catalyzed by Au NRs-Diodes, Au/Ag NRs-A-Diodes and Au/Ag NRs-B-Diodes during the first 20 min linear degradation region are 1.61, 2.20 and 3.30 times of the reaction catalyzed by photodiodes alone. The experiments were repeated three times to confirm the plasmonic enhancement effect. Compared with photodiodes alone, the average enhancement factors are 1.68 ± 0.08 , 2.09 ± 0.09 and 3.18 ± 0.11 for Au NRs-Diodes, Au/Ag NRs-A-Diodes and Au/Ag NRs-B-Diodes, respectively. Due to the existence of silicon oxide shell on the surface of photodiodes, the accelerated photodegradation rate of IC is not a result of metal nanorods acting as the electron traps to aid electron-hole separation or additional co-catalytic effect by the metal nanostructures. It can therefore be attributed to the plasmonic resonance effect of metal nanostructures.

To further confirm the enhancement is due to plasmonic resonance effect, we have investigated the spectral dependence of the photocatalytic activity. In this case, a monochromator (Corner 260, Newport) is used to modulate the wavelength of the incident light. All experiments were repeated for three times to ensure the consistency between experiments. Figure 3b shows the photoactivity enhancement factor for the Au NRs-Diode composites compared to that of photodiodes alone as a function of the irradiation

wavelength. The results clearly demonstrate the enhancement shows a strong spectral dependence qualitatively matching well with the intensity of the Au nanorods UV-vis extinction spectra. The same phenomena are also observed for Au/Ag NRs-A-Diodes and Au/Ag NRs-B-Diodes (Fig. 3c and 3d). Since gold or silver extinction is a consequence of the excitation of their local surface plasmon resonance, the qualitative match between the metal nanorods plasmon resonance intensity and the enhancement factors unambiguously demonstrates plasmon resonance of the metal nanorods is the primary factor responsible for the enhanced photocatalytic activity of the photodiodes. Parallel studies on photodegradation of indigo carmine (IC) also show qualitatively similar results (Fig. S2), further confirming the strong plasmonic enhancement of the plasmonic enhanced photoactivity of the Pt/Si/Ag photodiodes.

We have also used finite-difference time-domain (FDTD) approach to simulate of plasmon resonance enhancement of local optical field. The simulation shows more than one order of magnitude enhancement of optical field can be achieved in the very proximity of the plasmonic nanostructures, and the enhancement quickly decays to a much smaller enhancement factor of 1.5-5 at 15 nm distance from the plasmonic nanostructures (Fig. S3). The overall enhancement factors observed in our experiment are comparable to or slightly better than the simulation results. A few factors may contribute to the additional enhancement. First, the existence of aggregated plasmonic nanorods and the local field coupling between plasmonic nanorods could increase the enhancement depth. Secondly, the enhancement within the 15 nm SiO₂ could also contribute to the overall enhancement of absorption due to an optical trapping effect (i.e. the photon can be trapped within the nanowires due to a wave-guiding effect)⁹.

In summary, we have designed and synthesized a model system to provide a definitive investigation of the plasmonic resonanace enhanced photocatalytic properties by coupling Pt/n-Si/Ag photodiodes with Au nanorods or Au/Ag core/shell nanorods. Our studies show that the local surface plasmon resonance of metal nanostructures can be employed to enhance light absorption of semiconductor materials to result in a greatly enhanced photoactivity. The overlap between UV-vis absorption of metal nanorods and spectral dependent enhancement factors for each photocatalyst demonstrates strongly that the enhanced photoactivity can be attributed the local surface plasmon resonance of metal nanorods. It is well known that the plasmonic enhancement effect is highly localized to the surface of metal nanostructures with a roughly exponentially decay of the strength in space (Fig. S3).⁷ With the continued optimization of the heterostructures (e.g. reduce the oxide layer thickness), it is possible to further improve the enhancement effect.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We acknowledge support by the NIH Director's New Innovator Award Program, part of the NIH Roadmap for Medical Research, through Grant 1DP2OD004342-01. We acknowledge Electron Imaging Center for Nanomachines (EICN) at UCLA for support for TEM.

References

1. (a) Hagfeldt A, Gratzel M. *Acc Chem Res.* 2000; 33:269–277. [PubMed: 10813871] (b) Gomez-Romero P. *Adv Mater.* 2001; 13:163–174.(c) Goetzberger A, Hebling C, Schock HW. *Mater Sci Eng R.* 2003; 40:1–46.(d) Lewis NS. *Science.* 2007; 315:798–801. [PubMed: 17289986] (e) Tian B, Kempa TJ, Lieber CM. *Chem Soc Rev.* 2009; 38:16–24. [PubMed: 19088961] (f) Law M, Greene

- LE, Johnson JC, Saykally R, Yang PD. *Nat Mater.* 2005; 4:455–459. [PubMed: 15895100] (g) Tian BZ, Zheng XL, Kempa TJ, Fang Y, Yu NF, Yu GH, Huang JL, Lieber CM. *Nature.* 2007; 449:885–890. [PubMed: 17943126] (h) Qu YQ, Liao L, Li YJ, Zhang H, Huang Y, Duan XF. *Nano Lett.* 2009; 9:4539–4543. [PubMed: 19807130] (i) Qu YQ, Zhong X, Li YJ, Liao L, Huang Y, Duan XF. *J Mater Chem.* 20:3590–3594. (j) Xu S, Qin Y, Xu C, Wei YG, Yang RS, Wang ZL. *Nat Nanotechnol.* 2010; 5:366–373. [PubMed: 20348913] (k) Wang ZL. *Nano Today.* 2010; 5:540–552. (l) Li JH, Zhang JZ. *Coord Chem Rev.* 2009; 253:3015–3041.
2. Qu YQ, Liao L, Cheng R, Wang Y, Lin YC, Huang Y, Duan XF. *Nano Lett.* 2010; 10:1941–1949. [PubMed: 20373781]
3. Qu YQ, Xue T, Zhong X, Lin YC, Liao L, Choi JN, Duan XF. *Adv Funct Mater.* 2010; 20:3005–3011. [PubMed: 21629399]
4. (a) Chandrasekharan N, Kamat PV. *J Phys Chem B.* 2000; 104:10851–10857. (b) Jakob M, Levanon H, Kamat PV. *Nano Lett.* 2003; 3:353–358. (c) Subramanian V, Wolf EE, Kamat PV. *J Am Chem Soc.* 2004; 126:4943–4950. [PubMed: 15080700] (d) Hirakawa T, Kamat PV. *Langmuir.* 2004; 20:5645–5647. [PubMed: 16459570] (e) Kamat PV. *J Phys Chem C.* 2008; 112:18737–18753. (f) Hirakawa T, Kamat PV. *J Am Chem Soc.* 2005; 127:3928–3934. [PubMed: 15771529] (g) Wu XF, Song HY, Yoon JM, Yu YT, Chen YF. *Langmuir.* 2009; 25:6438–6447. [PubMed: 19341284] (h) Silva CC, Juárez R, Marino T, Molinari R, García H. *J Am Chem Soc.* 2011; 133:595–602. (i) Chen WT, Yang TT, Hsu YJ. *Chem Mater.* 2008; 20:7204–7206. (j) Yang TT, Chen WT, Hsu YJ, Wei KH, Lin TY, Lin TW. *J Phys Chem C.* 2010; 114:11414–11420. (k) Khon E, Mereshchenko A, Tarnovsky AN, Acharya K, Klinkova A, Hewa-Kasakarage NN, Nemitz I, Zamkov M. *Nano Lett.* 2011; 11:1792–1799. [PubMed: 21417253]
5. (a) Awazu K, Fujimaki M, Rockstuhl C, Tominaga J, Murakami H, Ohki Y, Yoshida N, Watanabe T. *J Am Chem Soc.* 2008; 130:1676–1680. [PubMed: 18189392] (b) Mori K, Kawashima M, Che M, Yamashita H. *Angew Chem Int Ed.* 2010; 49:8598–8601. (c) Thimsen E, Le Formal F, Grätzel M, Warren SC. *Nano Lett.* 2011; 11:35–43. [PubMed: 21138281] (d) Brown MD, Suteewong T, Kumar RSS, D'Innocenzo V, Petrozza A, Lee MM, Wiesner U, Snaith HJ. *Nano Lett.* 2011; 11:438–445. [PubMed: 21194204] (e) Liu LP, Wang GM, Li Y, Li YD, Zhang JZ. *Nano Res.* 2011; 4:249–258.
6. Nakato Y, Tsubomura H. *J Photochem.* 1985; 29:257–266.
7. (a) Camden JP, Dieringer JA, Zhao J, Van Duyne RP. *Acc Chem Res.* 2008; 41:1653–1661. [PubMed: 18630932] (b) Anker JN, Hall WP, Lyandres O, Shah NC, Zhao J, Van Duyne RP. *Nat Mater.* 2008; 7:442–453. [PubMed: 18497851] (c) Ferry VE, Munday JN, Atwater HA. *Adv Mater.* 2010; 22:4794–4808. [PubMed: 20814916] (d) Li JF, Huang YF, Ding Y, Yang ZL, Li SB, Zhou XS, Fan FR, Zhang W, Zhou ZY, Wu DY, Ren B, Wang ZL, Tian ZQ. *Nature.* 2010; 464:392–395. [PubMed: 20237566]
8. (a) Park K, Vaia RA. *Adv Mater.* 2008; 20:3882–3886. (b) Cardinal MF, Rodriguez-Gonzalez B, Alvarez-Puebla RA, Perez-Juste J, Liz-Marzan LM. *J Phys Chem C.* 2010; 114:10417–10423. (c) Becker J, Zins I, Jakab A, Khalavka Y, Schubert O, Sonnichsen C. *Nano Lett.* 2008; 8:1719–1723. [PubMed: 18454558] (d) Lee YH, Chen H, Xu QH, Wang JF. *J Phys Chem C.* 2011; 115:7997–9004. (e) Okuno Y, Nishioka K, Kiya A, Nakashima N, Ishibashi A, Niidome Y. *Nanoscale.* 2010; 2:1489–1493. [PubMed: 20820740]
9. (a) Soller BJ, Hall DG. *J Opt Soc Am A.* 2001; 18:2577–2584. (b) Pala RA, White J, Barnard E, Liu J, Brongersma ML. *Adv Mater.* 2009; 21:3504–3509.

Figure 1.

Structure and spectroscopic characterization of Au and Au/Ag core/shell nanorods. (a) TEM image of Au nanorods. (b) TEM image of Au/Ag core/shell nanorods-A with a 0.86 molar ratio of Ag/Au. (c) TEM image of Au/Ag core/shell nanorods-B with a 2.58 molar ratio of Ag/Au. The scale bars in A, B and C are all 50 nm. (d) Absorption spectra of gold nanorods and Au/Ag core/shell nanorods as shown in a, b and c. Black line represents Au nanorods. Red line represents Au/Ag core/shell nanorods-A. Blue line represents Au/Ag core/shell nanorods-B.

Figure 2.

(a) TEM image of a Pt/n-Si/Ag photodiodes. (b) TEM image of photodiode photocatalyst with Au nanorods on loaded surface. (c) TEM image of photodiode photocatalyst with Au/Ag core/shell nanorods-A on surface. (d) TEM image of photodiode photocatalyst with Au/Ag core/shell nanorods-B on surface. The insets of b, c and d are the images of individual nanorods on the surface of the photodiodes. The scale bar of insets is 30 nm.

Figure 3.

(a) Photocatalytic activity of four catalysts in NB degradation reaction. Black squares represent the NB alone. Magenta stars represent the mixture of NB and Au/Ag core/shell nanorods-B. Blue triangles represent the activity of the Pt/n-Si/Ag photodiodes alone. Red circles represent activity of the Au NRs-Diodes. Olive diamonds represent activity of the Au/Ag NRs-A-Diodes. Violet right-triangles represent activity of the Au/Ag NRs-B-Diodes. (b) Photoactivity enhancement factor (black square symbols) for Au NRs-Diodes as a function of excitation wavelength. Solid curve is the absorption spectrum of Au nanorods. (c) Photoactivity enhancement factor (black square symbols) for Au/Ag NRs-A-Diodes as a function of excitation wavelength. Solid curve is the absorption spectrum of Au/Ag core/shell nanorods. (d) Photoactivity enhancement factor (black square symbols) for Au/Ag NRs-B-Diodes as a function of excitation wavelength. Solid curve is the absorption spectrum of Au/Ag core/shell nanorods.