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14. ABSTRACT Tandem catalysis represents a revolutionary catalysis philosophy. Rational design of heterogeneous nanocatalyst to incorporate photocatalysis with conventional catalytic system is of substantial potential in industrial applications. However, critical consideration in each catalyst component and their synergetic collaboration is necessary to achieve considerable improvement in activity and selectivity. In this work, TiO ₂ -Au/Pd nanocomposite composed of P25 TiO ₂ nanoparticles and Au/Pd nanowheels is applied in benzimidazole synthesis as plasmon-enhanced photocatalyst. This nanocatalyst system enables a green synthetic route with alcohol as starting material and a two					
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Report Title

Final Report: Biomolecular specificity regulated synthesis of nanocatalysts and heterointegration of photosynthesis nanodevices

ABSTRACT

Tandem catalysis represents a revolutionary catalysis philosophy. Rational design of heterogeneous nanocatalyst to incorporate photocatalysis with conventional catalytic system is of substantial potential in industrial applications. However, critical consideration in each catalyst component and their synergetic collaboration is necessary to achieve considerable improvement in activity and selectivity. In this work, TiO₂-Au/Pd nanocomposite composed of P25 TiO₂ nanoparticles and Au/Pd nanowheels is applied in benzimidazole synthesis as plasmon-enhanced photocatalyst. This nanocatalyst system enables a green synthetic route with alcohol as starting material and a two-step tandem approach; consequently it avoids involvement of aldehyde, acid or oxidant. (Scheme 1) The bimetallic surface of Au/Pd facilitates oxidation of alcohol and dehydrogenation of benzimidazoline intermediate, which renders significantly high conversion and selectivity. Also, Au/Pd nanowheels promote visible range photon utilization efficiency via the strong surface plasmon resonance absorption. The overall design features a multifunctional architecture and provides insights and opportunity towards high performance, low energy demand and sustainable catalytic process.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
09/03/2012 10.00	Yujing Li, Yu Huang. Low-temperature, seed-mediated synthesis of monodispersed hyperbranched PtRu nanoparticles and their electrocatalytic activity in methanol oxidation, <i>Journal of Materials Chemistry</i> , (02 2012): 12461. doi: 10.1039/c2jm30892d
09/12/2013 11.00	Lingyan Ruan, Hadi Ramezani-Dakhel, Chin-Yi Chiu, Enbo Zhu, Yujing Li, Hendrik Heinz, Yu Huang. Tailoring Molecular Specificity Toward a Crystal Facet: a Lesson From Biorecognition Toward Pt{111}, <i>Nano Letters</i> , (02 2013): 0. doi: 10.1021/nl400022g
09/12/2013 12.00	Xiaoqing Huang, Yongjia Li, Yu Chen, Hailong Zhou, Xiangfeng Duan, Yu Huang. Plasmonic and Catalytic AuPd Nanowheels for the Efficient Conversion of Light into Chemical Energy, <i>Angewandte Chemie International Edition</i> , (06 2013): 0. doi: 10.1002/anie.201301096
09/12/2013 13.00	Xiaoqing Huang, Yongjia Li, Yu Chen, Enbo Zhou, Yuxi Xu, Hailong Zhou, Xiangfeng Duan, Yu Huang. Palladium-Based Nanostructures with Highly Porous Features and Perpendicular Pore Channels as Enhanced Organic Catalysts, <i>Angewandte Chemie International Edition</i> , (02 2013): 0. doi: 10.1002/anie.201208901
09/12/2013 14.00	Yujing Li, Yongjia Li, Enbo Zhu, Tait McLouth, Chin-Yi Chiu, Xiaoqing Huang, Yu Huang. Stabilization of High-Performance Oxygen Reduction Reaction Pt Electrocatalyst Supported on Reduced Graphene Oxide/Carbon Black Composite, <i>Journal of the American Chemical Society</i> , (08 2012): 0. doi: 10.1021/ja3031449
09/12/2013 15.00	Xiaoqing Huang, Yu Chen, Chin-Yi Chiu, Hua Zhang, Yuxi Xu, Xiangfeng Duan, Yu Huang. A versatile strategy to the selective synthesis of Cu nanocrystals and the in situ conversion to CuRu nanotubes, <i>Nanoscale</i> , (05 2013): 6284. doi: 10.1039/c3nr01290e
09/12/2013 17.00	Xiaoqing Huang, Enbo Zhu, Yu Chen, Yongjia Li, Chin-Yi Chiu, Yuxi Xu, Zhaoyang Lin, Xiangfeng Duan, Yu Huang. A Facile Strategy to Pt ₃ Ni Nanocrystals with Highly Porous Features as Enhanced Oxygen Reduction Reaction Catalyst, <i>Advanced Materials</i> , (06 2013): 0. doi: 10.1002/adma.201205315
09/12/2013 18.00	Yongjia Li, Enbo Zhu, Yu Chen, Chinyi Chiu, Hang Yu, Xiaoqing Huang, Robert Hicks, Yu Huang. Gold Clusters Alloyed to Nanoporous Palladium Surfaces as Highly Active Bimetallic Oxidation Catalysts, <i>ChemSusChem</i> , (09 2013): 0. doi: 10.1002/cssc.201300477
09/12/2013 19.00	Xiaoqing Huang, Yujing Li, Yuxi Xu, Yang Wang, Enbo Zhu, Xiangfeng Duan, Yu Huang, Yongjia Li. Graphene-hemin hybrid material as effective catalyst for selective oxidation of primary C-H bond in toluene, <i>Scientific Reports</i> , (05 2013): 0. doi: 10.1038/srep01787
09/23/2014 21.00	Xiaoqing Huang, Yu Chen, Enbo Zhu, Yuxi Xu, Xiangfeng Duan, Yu Huang. Monodisperse Cu@PtCu nanocrystals and their conversion into hollow-PtCu nanostructures for methanol oxidation, <i>Journal of Materials Chemistry A</i> , (2013): 0. doi: 10.1039/c3ta13903d
09/23/2014 22.00	Lingyan Ruan, Hadi Ramezani-Dakhel, Chain Lee, Yongjia Li, Xiangfeng Duan, Hendrik Heinz, Yu Huang. A Rational Biomimetic Approach to Structure Defect Generation in Colloidal Nanocrystals, <i>ACS Nano</i> , (07 2014): 0. doi: 10.1021/nn501704k

- 09/23/2014 23.00 Lingyan Ruan, Enbo Zhu, Yu Chen, Zhaoyang Lin, Xiaoqing Huang, Xiangfeng Duan, Yu Huang. Biomimetic Synthesis of an Ultrathin Platinum Nanowire Network with a High Twin Density for Enhanced Electrocatalytic Activity and Durability, *Angewandte Chemie International Edition*, (11 2013): 0. doi: 10.1002/anie.201304658
- 09/23/2014 24.00 Zipeng Zhao, Yu Chen, Enbo Zhu, Mufan Li, Xiangfeng Duan, Yu Huang, Xiaoqing Huang. A rational design of carbon-supported dispersive Pt-based octahedra as efficient oxygen reduction reaction catalysts, *Energy & Environmental Science*, (07 2014): 0. doi: 10.1039/C4EE01082E
- 09/23/2014 20.00 Xiaoqing Huang, Zipeng Zhao, Yu Chen, Chin-Yi Chiu, Lingyan Ruan, Yuan Liu, Mufan Li, Xiangfeng Duan, Yu Huang. High Density Catalytic Hot Spots in Ultrafine Wavy Nanowires, *Nano Letters*, (07 2014): 0. doi: 10.1021/nl501137a

TOTAL: 14

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

- 08/31/2012 7.00 Xiangfeng Duan, Yu Huang, Xiaoqing Huang, Yujing Li, Hailong Zhou, Xing Zhong. Simplifying the Creation of Dumbbell-Like Cu-Ag Nanostructures and Their Enhanced Catalytic Activity, Chemistry - A European Journal (07 2012)
- 08/31/2012 8.00 Yujing Li, Yongjia Li, Hailong Zhou, Xiangfeng Duan, Yu Huang, Xiaoqing Huang. Synthesis of PtPd Bimetal Nanocrystals with Controllable Shape, Composition, and Their Tunable Catalytic Properties, Nano Letters (08 2012)
- 09/03/2012 9.00 Richard E. Palmer, Yujing Li, Yu Huang, Chin-Yi Chiu, Lingyan Ruan, Wenbing Yang, Zhi Wei Wang, Yang Yang. Synthesis of bimetallic Pt-Pd core-shell nanocrystals and their high electrocatalytic activity modulated by Pd shell thickness, Nanoscale (09 2011)
- 11/16/2011 3.00 Chin-Yi Chiu, Yujing Li, Lingyan Ruan, Xingchen Ye, Christopher B. Murray, Yu Huang. Platinum nanocrystals selectively shaped using facet-specific peptide sequences, Nature Chemistry (4 2011)
- 11/16/2011 2.00 Yujing Li, Yu Huang. Morphology-Controlled Synthesis of Platinum Nanocrystals with Specific Peptides, Advanced Materials (03 2010)
- 11/16/2011 5.00 Lingyan Ruan, Chin-Yi Chiu, Yujing Li, Yu Huang. Synthesis of Platinum Single-Twinned Right Bipyramid and {111}-Bipyramid through Targeted Control over Both Nucleation and Growth Using Specific Peptides, Nano Letters (07 2011)
- 11/16/2011 6.00 Yujing Li, Yu Huang, Chin-Yi Chiu. Size-controlled synthesis of Pd nanocrystals using a specific multifunctional peptide, Nanoscale (05 2010)

TOTAL: 7

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

2011 Kavli Fellow
2010 Sloan Research Fellowship (Chemistry)
2010 National Institute of Health Director's New Innovator Award
2010 DARPA Young Faculty Award
2009 UCLA Faculty Career Development Award

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Yongjia Li	1.00	
Enbo Zhu	0.30	
FTE Equivalent:	1.30	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Xiaoqing Huang	0.10
FTE Equivalent:	0.10
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Yu Huang	0.10	
FTE Equivalent:	0.10	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment.

Technology Transfer

Title: Biomolecular specificity regulated synthesis of nanocatalysts and heterointegration of photosynthesis nanodevices

W911NF0910433S Final Report (9/1/14-8/25/15)

Yu Huang, UCLA. (Program Officer: John Prater)

1. Objectives and Approaches

With exceedingly fast population and economic growth, twenty-first century is featured by enormous energy requirement. Meeting these needs is only possible with development of new energy resources, or utilization of existing energy resources. To this specific point of view, catalysis becomes a key issue in solving our energy challenges. The ultimate objective of the project is to bio-assemble a practical photocatalytic water splitting device for hydrogen generation. The main sub-objectives are to engineer highly active and selective nanocatalysts and to create reliably interfaces between the co-catalysts. Within this context, over the past funding years, we have successfully explored synthetic approaches to various nanocatalysts and investigated the structure and composition enhanced properties of these nanocatalysts. (1-21) In this report, we will highlight the accomplishment of a tandem catalyst design with incorporated plasmonic photocatalysis.

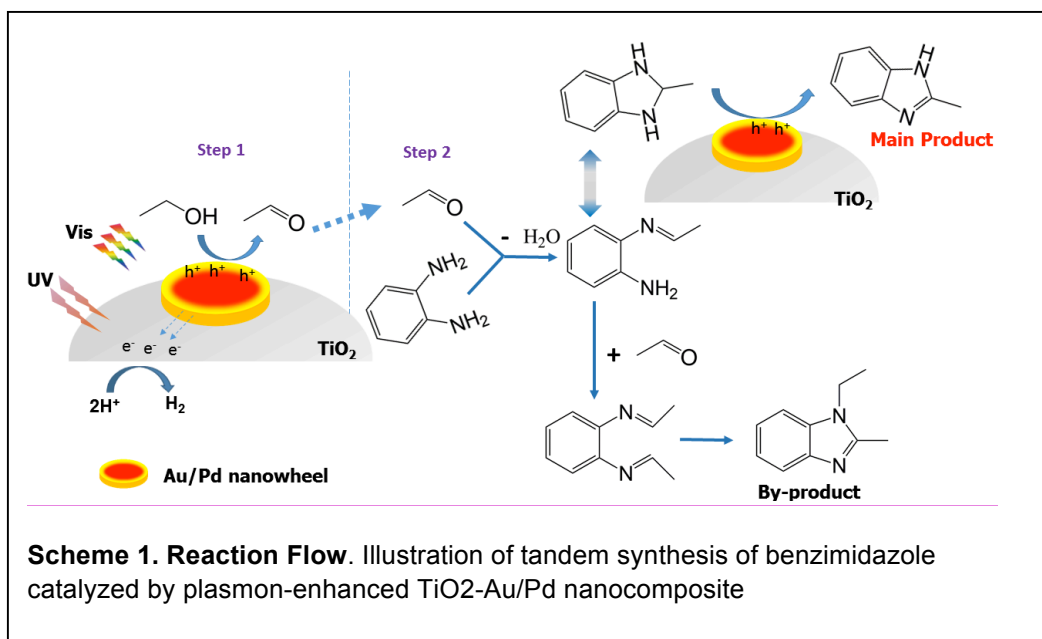
2. Accomplishments for the last year

Plasmon-enhanced TiO₂-Au/Pd Nanocomposite Photocatalyst for Tandem Synthesis of Benzimidazole

2.1 Approaches: Wet-chemical synthetic routes are explored to create nanocatalysts, and tandem catalysts systems were created through physical mixture and annealing. XRD, XPS, TEM, and STEM are used to characterized the detailed structures. Energy dispersion spectroscopy, UV-vis spectroscopy and ICP-AES and elemental micro-mapping are used for composition analysis. Catalytic reactions are carried out to evaluate the performance of the created nanocatalyst systems.

2.2 Overall Design

Tandem catalysis represents a revolutionary catalysis philosophy. Rational design of heterogeneous nanocatalyst to incorporate photocatalysis with conventional catalytic system is of substantial potential in industrial applications. However, critical consideration in each catalyst component and their synergetic collaboration is necessary to achieve considerable improvement in activity and selectivity. In this work, TiO₂-Au/Pd nanocomposite composed of P25 TiO₂ nanoparticles and Au/Pd nanowheels is applied in benzimidazole synthesis as plasmon-enhanced photocatalyst. This nanocatalyst system enables a green synthetic route with alcohol as starting material and a two-step tandem approach; consequently it avoids involvement of aldehyde, acid or oxidant. (Scheme 1) The bimetallic surface of Au/Pd facilitates oxidation of alcohol and dehydrogenation of benzimidazoline intermediate, which renders significantly high conversion and selectivity. Also, Au/Pd nanowheels promote visible range photon utilization efficiency via the strong surface plasmon resonance absorption. The overall design features a multifunctional architecture and provides insights and opportunity towards high performance, low energy demand and sustainable catalytic process.



Benzimidazole ring is an important pharmacophore in modern drug discovery, which has significant activity against several viruses such as HIV, HSV-1, RNA, influenza and human cytomegalovirus. Traditionally, it is produced by coupling *1,2*-diaminobenzenes with carboxylic acids under harsh dehydrating acidic environment and high temperature. Direct reaction of phenylenediamine substrates with aldehydes offers a relatively mild reaction condition, but is restricted by unstable aldehyde reactant and excessive oxidant. Besides, aldehyde is generally less favored than alcohol because of its volatility, pungent odor, and easy degradation via autoxidation in air. Moreover, catalysts used in most aforementioned synthetic routes are homogenous, which adds difficulty in purification and catalyst recycling. In terms of heterogeneous catalysis, transition metal catalyzed preparation of *N*-alkylbenzimidazoles from *o*-haloanilines provides an alternative route, however preparation of the starting material anilides is onerous. Hence, the design of an alternative heterogeneous catalyst which allows mild reaction conditions and stable reactants like alcohol is highly desirable.

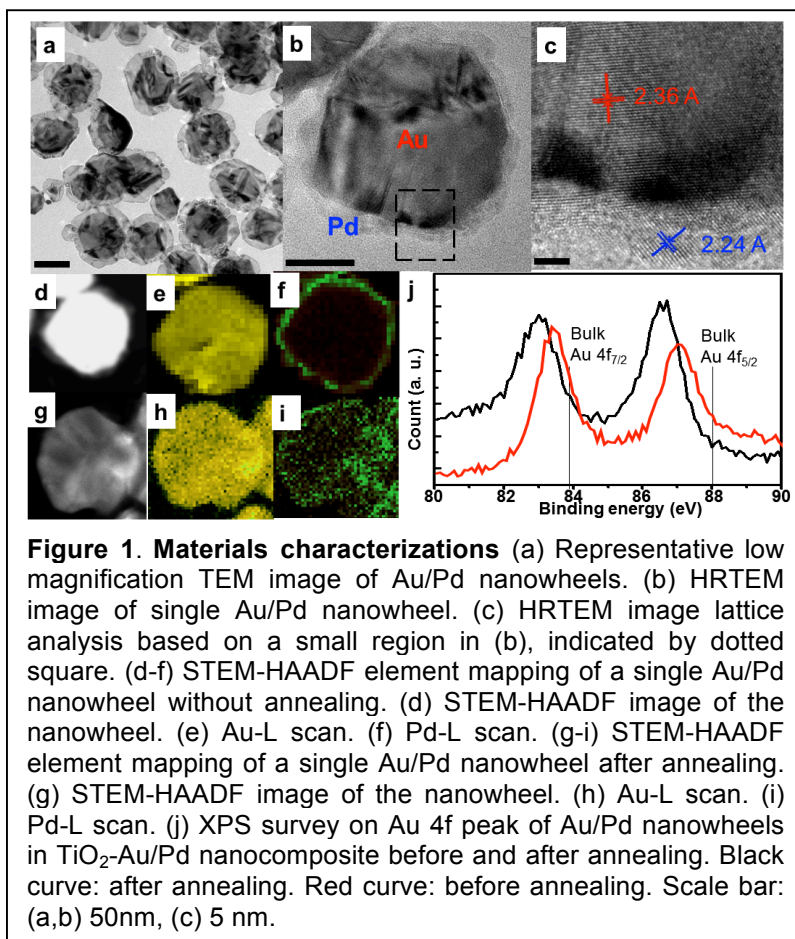
To address the above-mentioned challenges in benzimidazole production, we designed a highly efficient plasmon-enhanced tandem catalysis system, which allows alcohols to participate in reaction directly with phenylenediamine substrates at room temperature, in absence of strong acids or oxidants. The heterogeneous nanocatalyst is composed of commercially available Degussa P25 TiO₂ nanoparticles and plasmonic Au/Pd nanowheels. It features following four aspects. First, the system embarks tandem catalytic enhancement in reaction flow and overall catalytic performance (Scheme 1). Ethanol is used directly as starting material, which is oxidized to acetaldehyde on Au/Pd nanowheel surface (1st step). Then, acetaldehyde reacts *in situ* with *o*-phenylenediamine substrate to form final products (2nd step). Through this, we expect a substantial improvement in overall kinetics while avoiding aldehyde introduction in the beginning. Second, the surface composition of Au/Pd nanowheel is well tailored to improve its synergetic effect. Through annealing treatment, the metallic surface previously of segregated Au and Pd domains transforms to Au-Pd alloy. Since Au-Pd bimetallic surface is generally considered more active or selective than pure Au or Pd surface, a more

prompt oxidative catalysis behavior can be anticipated. Third, apart from the overall conversion, the selectivity is closely related to this alloy surface. *o*-phenylenediamine may either take one acetaldehyde molecule to form main product 2-methylbenzimidazole via a dehydrogenation step, or two acetaldehyde molecules to form 1-ethyl-2-methyl-1*H*-benzimidazole as by-product (Scheme 1). Hence the selectivity is heavily affected by the dehydrogenation of benzimidazoline intermediate. On the other hand, the alloy surface on Au/Pd nanowheel as effective oxidative catalyst can substantially promote the dehydrogenation reaction, therefore guarantee preferential formation of main product. Last, the system adopts environmental friendly photocatalysis approach, in which the oxidation of ethanol in 1st step and dehydrogenation of benzimidazoline intermediate in 2nd step is facilitated by photo-generated holes. More significantly, Degussa P25 TiO₂, although widely acknowledged a cost-effective and active photocatalyst, lacks visible range absorption. The Au/Pd nanowheel with strong plasmonic adsorption near 550 nm can raise the overall photon utilization efficiency.

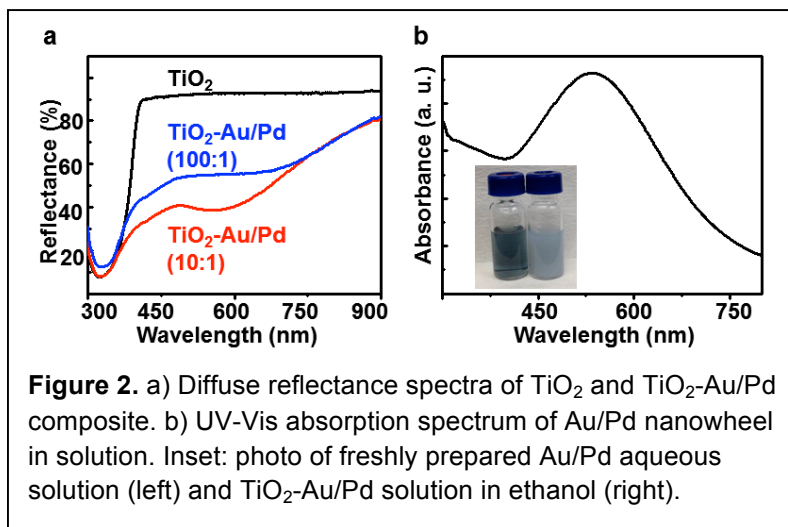
2.3 Results and Discussion

Structures: The TiO₂-Au/Pd composite was formed by physically mixing commercially available Degussa P25 TiO₂ and Au/Pd nanowheel ~80

+/- 15 nm in size, followed by annealing in inert environment. (Figure 1a-c). Specifically, Au/Pd nanowheel samples before and after annealing are analyzed by STEM-HAADF element mapping and line-scan to track the surface composition change. Before annealing, the nanowheel is a typical core/shell (Au/Pd) structure with little Pd element in core region (Figure 1d-f). After annealing, significant inter-diffusion of Au and Pd atoms results in a more uniform, mixed element distribution (Figure 1g-i). Hence the nanowheel itself displays core/shell composition before annealing, and forms Au-Pd alloy surface after annealing. X-ray photoelectron spectroscopy (XPS) characterization on Au 4f peak in TiO₂-Au/Pd sample identifies that Au 4f_{7/2} and Au 4f_{5/2} peaks both blue-shift after annealing (Figure 1j), confirming alloy formation and close contact with TiO₂.

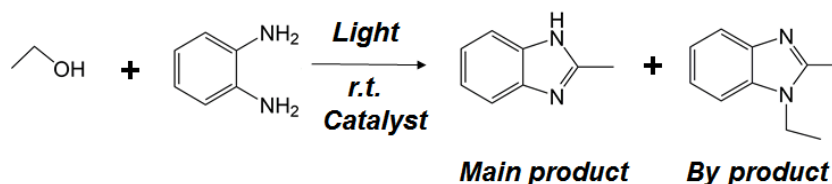


Diffuse reflectance UV-Vis-IR spectroscopy was used to study optical property of TiO₂-Au/Pd nanocomposite (Figure 2a). While the P25 TiO₂ absorbs mostly below 400 nm, apparent enhancement of absorption in visible light range can be noticed once Au/Pd is introduced. Interestingly, with increasing amount of Au/Pd (TiO₂:Au/Pd mass ratio decreases from 100:1 to 10:1), the spectrum trough deepens in visible range with obvious minima at ~560 nm. This value is close to absorption



peak of Au/Pd nanowheel (~540 nm) measured in solution form (Figure 2b), therefore can be ascribed to SPR of Au/Pd nanowheel. The 20 nm red shift is attributed to high refractive index of TiO₂, as discussed in earlier literatures. These results prove our assumption that Au/Pd will facilitate visible range absorption.

2.4. Catalysis: Catalytic performance of TiO₂-Au/Pd is assessed in reaction of *o*-phenylenediamine and ethanol with white light irradiation. All experiments were under N₂ protection to avoid ambient oxygen interference. The overall reaction is shown in Scheme 1, where ethanol is photo-oxidized to acetaldehyde, which subsequently reacts with *o*-phenylenediamine. The monoimine intermediate, after transferring to benzimidazole reversibly, undergoes dehydrogenation to form final product 2-methylbenzimidazole. The major by-product in this reaction is 1-ethyl-2-methyl-1*H*-benzimidazole, as a result of second acetaldehyde addition and rearrangement of imidazole ring. In dark control experiments, none of the catalysts create detectable products (Table 1, Entries 1-4), suggesting photo-initiated nature of the reaction. With white light irradiation, TiO₂-Au/Pd helps converting >99.9% reactants after three hours, equivalent to turn over number (TON) of 3,850 (Table 1, Entry 7). It exceeds TiO₂ trial result of 25.8% conversion, as well as Au/Pd trial of 2.6% conversion (Table 1, Entries 5,6). These results clearly indicate the high catalytic activity is a synergetic outcome contributed by both TiO₂ and Au/Pd. Next, impact of Au/Pd nanowheel dosage is examined. When mass ratio of TiO₂ to Au/Pd is 100:1, it demonstrates best catalytic performance (Table 1, Entry 7). Reducing metal nanoparticle dosage results in lower conversions (Table 1, Entries 9-11), while further increasing Au/Pd dosage to 10:1 also leads to reduction in conversion (Table 1, Entry 8). These phenomena can be explained as the following: Au/Pd nanowheel serves as plasmon absorber and provides catalytic sites. Larger Au/Pd dosage means increased reaction kinetics and number of active sites. However, excessive metal component increases exciton recombination occurrence, which is eventually reflected by inversely changed conversion. Moreover, we tested physical mixture of TiO₂ and Au/Pd to compare its catalytic effect with integrated nanocomposite (Table 1, Entry 12). The physical mixture only gives 34.6% conversion, probably due to lack of synergetic collaboration, and restricted exciton transfer across interface between semiconductor and metal domains. Lastly, TiO₂-Au and TiO₂-Pd are used as reference. The conversion obtained from TiO₂-Au is only 50.6%, and from TiO₂-Pd is 70.5%, which demonstrates the advantage of bimetallic Au/Pd over its singular metal components.

Table 1. Conversion and selectivity results by various catalysts and reaction conditions*Overall reaction*

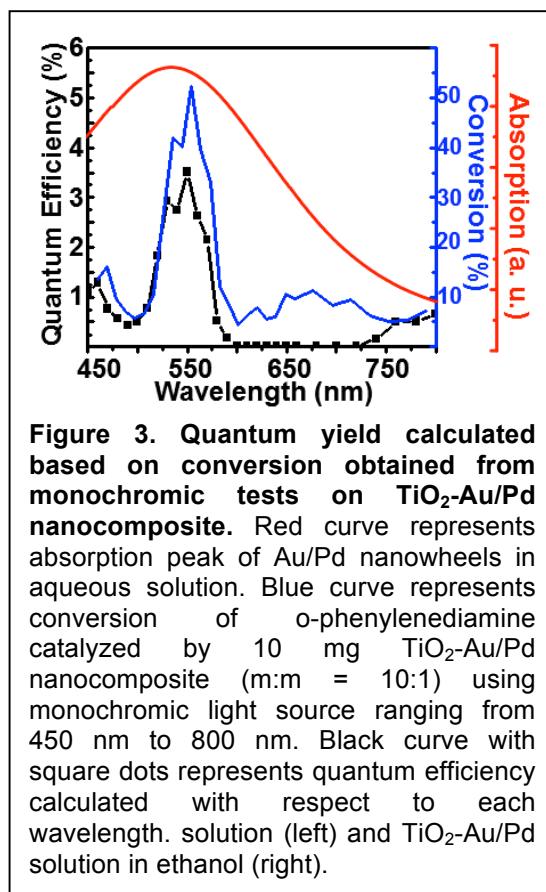
Entry	Catalyst	Dosage (mg)	TiO ₂ :metal mass ratio	Light	Conversion (%)	Selectivity (%)
1	-	-	-	Dark	-	-
2	TiO ₂	10	-	Dark	-	-
3	Au/Pd	1	-	Dark	0.6	-
4	TiO ₂ -Au/Pd	10	100:1	Dark	0.4	-
5	TiO ₂	10	-	White	25.8	84.6
6	Au/Pd	1	-	White	2.6	96.4
7	TiO ₂ -Au/Pd	10	100:1	White	>99.9	98.9
8	TiO ₂ -Au/Pd	10	10:1	White	86.7	99.4
9	TiO ₂ -Au/Pd	10	250:1	White	72.3	93.8
10	TiO ₂ -Au/Pd	10	500:1	White	69.5	90.1
11	TiO ₂ -Au/Pd	10	1000:1	White	61.4	79.6
12	TiO ₂ +Au/Pd *	10	100:1	White	34.6	86.2
13	TiO ₂ -Au	10	100:1	White	50.6	82.3
14	TiO ₂ -Pd	10	100:1	White	70.5	93.6

Experiment condition: 2 mmol of *o*-phenylenediamine, 10 ml ethanol, N₂ gas (1 atm), reaction time 3 hours.

* Physical mixture of TiO₂ nanoparticles and Au/Pd nanowheels (without annealing).

2.5. Mechanism: The plasmon-enhanced photocatalysis is another advantageous feature of this catalytic system. Previous studies revealed hot carrier transfer and local electrical field enhancement can both contribute to the activity enhancement. To reveal the main mechanism in our catalytic results, we carried out monochromic irradiation experiment based on both TiO₂-Au/Pd nanocomposite and TiO₂. Monochromic test on TiO₂-Au/Pd shows both the conversion and the quantum efficiency rise sharply when irradiation wavelength is near 550 nm (Figure 3). The highest conversion and quantum efficiency are obtained at 560 nm, which is identical to maximum absorption of TiO₂-Au/Pd nanocomposite (Figure 2a) and close to Au/Pd nanowheel's SPR peak (Figure 2b). Once the wavelength used shifts away, these conversion and quantum yield increments disappear quickly (Figure 3). This is consistent with previous observations from TiO₂-Au,

that once the excitation wavelength corresponds to metal SPR band, hot electrons could be generated on metal surface and injected into conduction band of adjacent semiconductor, leaving photo-generated holes on metal surface. The holes are responsible for the oxidation reaction, which in our case is ethanol oxidation and benzimidazoline dehydrogenation. Nonetheless, we could not entirely rule out the possibility of local field enhancement mechanism, because our result also indicated abnormal rise in visible-range photoresponse from 500 nm to 575 nm catalyzed by TiO₂ alone. This might be attributed to the increased sub-band transition via local electrical field enhancement mechanism. Once the incident wavelength is close to metal SPR peak, intense electrical field from metal SPR absorption can boost sub-band transition in semiconductor domain nearby. However, we suggest local field enhancement is not the main cause of photocatalytic enhancement here due to the following reasons. Firstly, local electrical field enhancement leads to photo-oxidation occurrence on semiconductor surface, which is contradictory to the inactive catalytic performance of TiO₂ observed (Table 1). Secondly, if this mechanism indeed played a dominant role, the wavelength to obtain best conversion and quantum yield catalyzed by TiO₂-Au/Pd should follow that of TiO₂ at around 525 nm, rather than 560 nm (Figure 3). Thereafter, we suggest the hot electron injection is the leading enhancement mechanism in our system.



3. In summary, during entire funding period, we have successfully explored synthetic approaches to various nanocatalysts and investigated the structure and composition enhanced properties of these nanocatalysts. (1-x). At the later stage, we started to explore the integration of catalytic components to create more efficient and green tandem catalytic system that mimics the superior catalytic functions like those observed in biological entities.

4. Publications

1. Li, Y.; Whyburn, G. P.; Huang, Y. Specific peptide regulated synthesis of ultrasmall platinum nanocrystals. *Journal of the American Chemical Society* **2009**, *131*, 15998-15999.
2. Chiu, C.-Y.; Li, Y.; Huang, Y. Size-controlled synthesis of Pd nanocrystals using a specific multifunctional peptide. *Nanoscale* **2010**, *2*, 927-930.
3. Li, Y.; Huang, Y. Morphology-controlled synthesis of platinum nanocrystals with specific peptides. *Advanced Materials* **2010**, *22*, 1921-1925.

4. Chiu, C.-Y.; Li, Y.; Ruan, L.; Ye, X.; Murray, C. B.; Huang, Y. Platinum nanocrystals selectively shaped using facet-specific peptide sequences. *Nature chemistry* **2011**, *3*, 393-399.
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