

**Zheng Li, Jonathan J. Foley IV, Sheng Peng, Cheng-Jun Sun, Yang Ren, Gary P. Wiederrecht, Stephen K. Gray, and Yugang Sun**

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# Reversible Modulation of Surface Plasmons in Gold Nanoparticles Enabled by Surface Redox Chemistry

Zheng Li,<sup>[a],⊥</sup> Jonathan J. Foley, IV,<sup>[a],⊥</sup> Sheng Peng,<sup>[a]</sup> Cheng-Jun Sun,<sup>[b]</sup> Yang Ren,<sup>[b]</sup> Gary P. Wiederrecht,<sup>\*,[a]</sup> Stephen K. Gray,<sup>\*,[a]</sup> and Yugang Sun<sup>\*,[a]</sup>

**Abstract:** We demonstrate switchable surface redox chemistry in gold@iron/iron-oxide core-shell nanoparticles with ambient oxidation and plasmon-mediated reduction to modulate the oxidation state of shell layers. The iron shell can be oxidized to iron oxide through ambient oxidation, leading to an enhancement and red-shift of the gold surface plasmon resonance (SPR). This enhanced gold SPR can drive reduction of the iron oxide shell under broadband illumination to reversibly blue-shift and significantly damp gold SPR absorption. The observed phenomena enable a unique mechanism for controlling the plasmonic properties and surface chemistry of small metal nanoparticles.

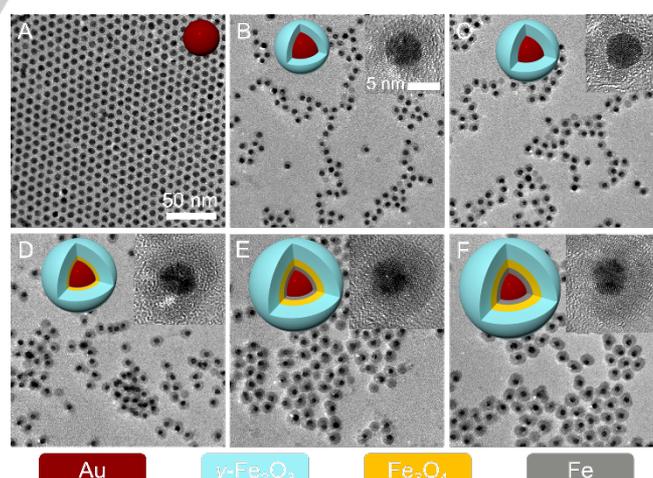
Collective oscillations of conduction electrons excited by incident light, known as surface plasmon resonance (SPR), are responsible for the extraordinary optical properties of noble metal nanostructures.<sup>[1]</sup> SPR enables extreme confinement of optical energy in the vicinity of a plasmonic structure, which can strongly enhance light-matter interactions in the near-field of the plasmon. This enhancement leads to the exceptional environmental sensitivity of the SPR and provides the foundation for a variety of sensing applications.<sup>[2]</sup> In addition, the near-field enhancement associated with SPR can enhance Rayleigh scattering, Raman scattering, and fluorescence efficiency of molecules adsorbed on plasmonic nanostructures,<sup>[3]</sup> enabling spectroscopic sensitivity down to the single-molecule limit.<sup>[4]</sup> Since the SPR characteristics of nanostructures are dependent on their size, shape, composition, and surrounding environment,<sup>[5]</sup> a plethora of methods have been developed to synthesize noble metal nanoparticles with tunable parameters to tailor their optical properties.<sup>[6]</sup> For instance, hybridization of plasmonic metal nanoparticles with ferromagnetic or semiconductor materials can effectively influence their optical properties through magneto-plasmonic interferometry and light-driven injection of charge carriers from semiconductors to metals, respectively.<sup>[7]</sup> Recent investigations also show the potential of surface plasmons (SPs) to drive chemical reactions,<sup>[8]</sup> e.g. the reduction of Cu<sub>2</sub>O to Cu in Cu@Cu<sub>2</sub>O core-shell particles.<sup>[9]</sup>

Herein, we report self-modulation of the plasmonic properties of core-shell nanoparticles composed of Au, Fe, and iron-oxide (FeO<sub>x</sub>). Alternating the oxidation states of iron through plasmon-mediated reduction and ambient oxidation enables the reversible damping and recovery of the SPR signal of the Au core

nanoparticles. To our knowledge, this work represents a novel approach and the first demonstration of utilizing external stimuli (i.e., SPR mediated photo-illumination and oxidizing atmosphere) to reversibly switch the oxidation states of shell materials, and reciprocally the SPR properties of hybrid core-shell nanostructures.

The Au@Fe@FeO<sub>x</sub> core-shell nanoparticles are synthesized through a seed-mediated approach<sup>[10]</sup> in which uniform Au nanoparticles are used as seeds (see Supporting Information (SI) for details).<sup>[11]</sup> The thickness of the shells monotonically increases with increasing reaction time, as shown in Figure 1B-F. Iron is readily oxidized to magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) once the samples are exposed to the ambient atmosphere.<sup>[12]</sup> The outermost Fe atoms tend to be converted to Fe<sub>2</sub>O<sub>3</sub>, which has a higher oxidation state than the Fe<sub>3</sub>O<sub>4</sub> layer that tends to reside closer to the Au core.<sup>[13]</sup> As a result, particles with a thick shell coating formed at long reaction times consist of Au cores, Fe shells, and FeO<sub>x</sub> shells (see Figure 1 graphics). The detailed compositions of the core-shell nanoparticles are analyzed using X-ray absorption near edge structure (XANES) spectroscopy, and the results are presented in Table S1 in the SI.

Ultraviolet-visible (UV-Vis) absorption spectroscopy is employed to elucidate the variation of optical properties of the Au@Fe@FeO<sub>x</sub> core-shell nanoparticles with different shell compositions. As shown in Figure 2A, the bare Au nanoparticles (Figure 1A) dispersed in toluene exhibit a well-defined absorption peak with a maximum at 520 nm. The core-shell nanoparticles formed at short deposition times (e.g., 1 min and 2 min with the corresponding

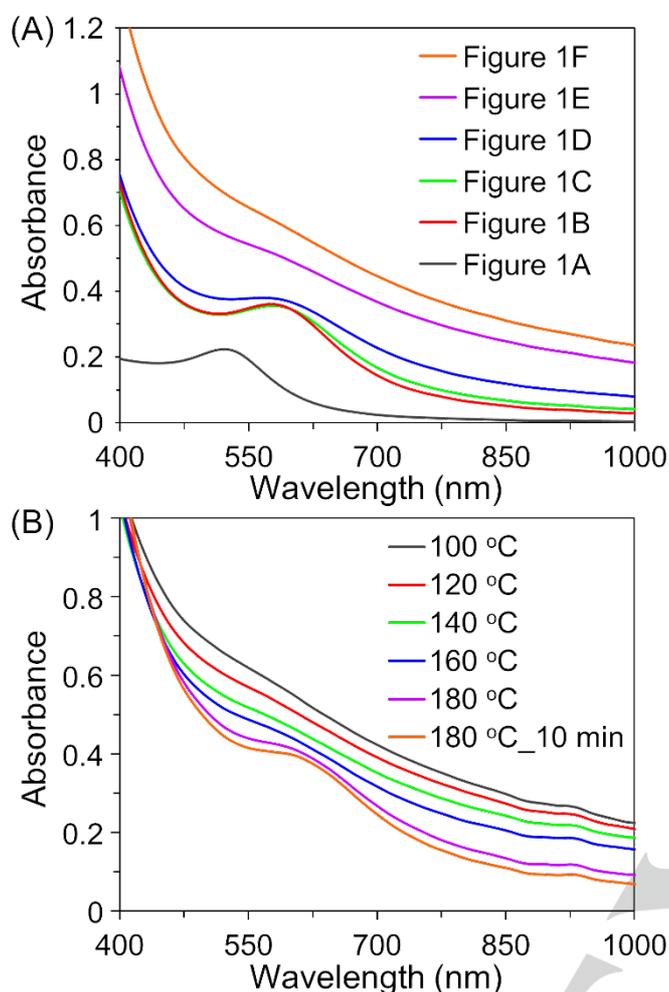


**Figure 1.** TEM and HRTEM (inset) images of Au nanoparticles (A) before and after their surfaces were coated with iron-containing shells grown for different times: (B) 1 min, (C) 2 min, (D) 5 min, (E) 20 min, and (F) 30 min. The inset schematic illustrations highlight the compositional construction of different core-shell nanoparticles. The thicknesses of layers with different iron-containing compositions can be found in the Supporting Information (SI) in Table S1. Scale bars in the image of Figure 1A and inset of Figure 1B apply to all the other images and insets, respectively.

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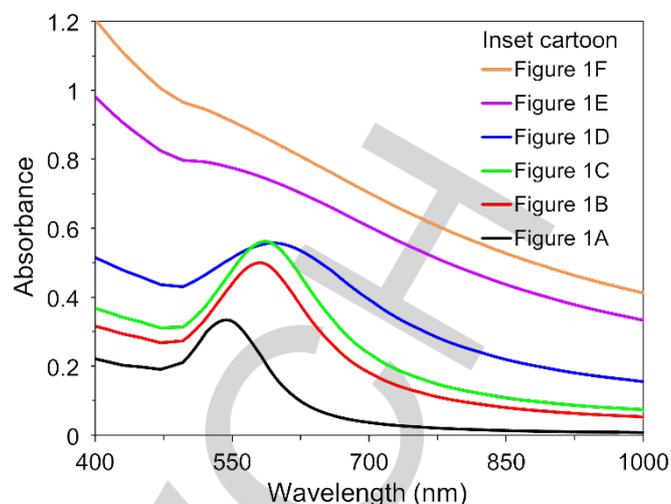
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**Figure 2.** Quantitative UV-Vis spectra of (A) Au nanocrystals during the deposition of iron-containing shells at different times and (B) oxidation of Au@Fe@FeO<sub>x</sub> nanoparticles, which grew for 30 min in Figure 2A, through air bubbling oxidation, in which the sample was heated at 180 °C in ODE with controlled air bubbling speed at 80 mL/min.

samples shown in Figure 1B and C) are composed of Au cores and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> shells, and their absorption spectra exhibit red-shifted SPR. The core-shell nanoparticles formed at deposition times beyond 5 min (Figure 1D-F) are composed of shells containing metallic Fe in direct contact with the Au cores. The corresponding absorption spectra show a significant damping of the peak feature. The Au SPR absorption band becomes completely featureless for core-shell nanoparticles formed at long deposition times (e.g., 30 min).

Rigorous electrodynamics calculations are performed to correlate the observed changes in the absorption spectra with the changes in composition and oxidation state of the iron-containing shells in the Au@Fe@FeO<sub>x</sub> nanoparticles (See Figure 3). Mie theory analysis in the quasi-static limit is used to write an expression for the SPR condition of an Au@Fe core-shell particle in terms of the radii and permittivity of the core and shell layers, as well as the permittivity of the surrounding media.<sup>[14]</sup> This analysis reveals that the strong broadband absorption of metallic Fe is responsible for the dramatic damping of the Au SPR feature. It can be seen that a Fe layer as thin as 0.5 nm around an Au nanoparticle completely destroys the condition for SPR in the core-shell structures (see SI, Figure S1). Significantly lower near-field intensity is also observed at the Au SPR frequency in the Fe coated particles (see Figure S2). The ratio of the shell thickness to the core particle radius is important to determine the SPR

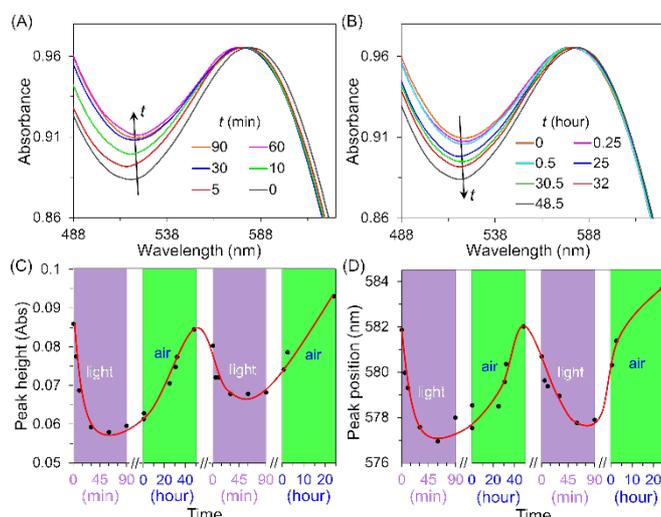


**Figure 3.** Theoretical calculation results of UV-Vis spectra based upon the composition evolution during the growth of iron-containing shells on Au nanoparticle core.

damping efficiency, and so thicker Fe shells would be required to produce such dramatic damping for larger Au particles (see Figure S3). A more detailed discussion of the damping mechanism is provided in SI. This result is fully consistent with the experimental observation of extreme damping of the absorption peak in the core-shell particles formed at long deposition times, which contain metallic Fe in the shells. Calculations on all Au@FeO<sub>x</sub> structures reveal that the SPR peak position is red-shifted in the presence of the oxide layer, consistent with the experimentally-observed evolution of the absorption spectra taken at short deposition times.

The profound damping effect of metallic Fe on the Au SPR peak can be reversed by deeply oxidizing the sample to convert the Fe into FeO<sub>x</sub>, leading to the regeneration of the Au SPR peak. For example, heating the Au@Fe@FeO<sub>x</sub> core-shell nanoparticles (Figure 1F) under air bubbling oxidation (see SI for details), can transform the innermost Fe into FeO<sub>x</sub>. Corresponding XANES analysis (SI, Table S1) over the samples confirms a complete conversion of Fe into FeO<sub>x</sub> and the formation of Au@FeO<sub>x</sub> core-shell particles. TEM images of the sample formed after oxidation (SI, Figure S4) indicate that the original morphology remains. As shown in Figure 2B, the characteristic Au SPR feature reemerges after the solution is heated and held at 180 °C. Besides, the complete transformation of Fe into FeO<sub>x</sub> coincides with the recovery of the Au SPR peak. The experimental measurements in Figure 2 and the calculated results in Figure 3 are consistent with our conjecture that formation of the Fe layer around the Au core plays a fundamental role in triggering the damping of the Au SPR feature, and that the SPR damping can be reversed by transforming Fe to FeO<sub>x</sub>.

To demonstrate plasmon-mediated reduction of iron oxide, we start with Au@FeO<sub>x</sub> core-shell nanoparticles that are composed of a thin iron oxide layer and exhibit a typical Au SPR peak with strong intensity (see SI for details). Decay of the Au SPs results in a distribution of hot electrons that can drive the reduction of FeO<sub>x</sub> adjacent to the Au surfaces to form Fe.<sup>[8],[9],[14],[15]</sup> In order to prevent re-oxidation or hot-electron scavenging, experiments demonstrating this effect are carried out with a freeze-pump-thaw (FPT) cell (SI, Figure S5) to remove the dissolved oxygen. As shown in Figure 4A, illumination with a bright white light source leads to a reduction in the SPR peak height (see definition in Figure 4 caption), with longer illumination times leading to greater reduction in the peak intensity. The SPR peak recovers when the FPT cell is opened to ambient oxidation. As shown in Figure 4B, with the Au SPR peak maximum at the same absorbance, the

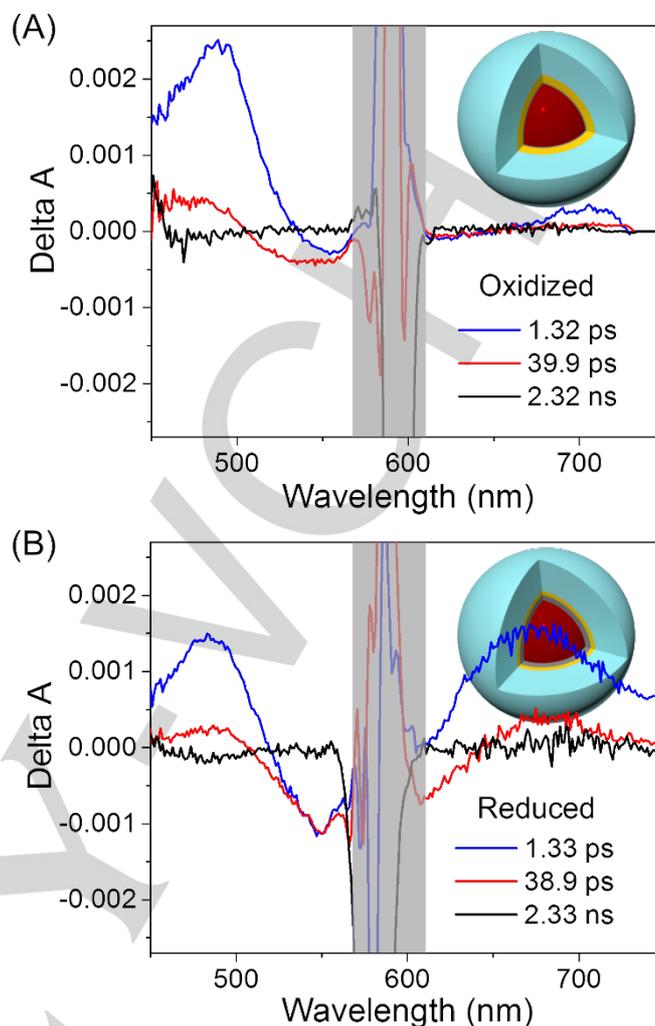


**Figure 4.** UV-Vis absorption spectra of Au@FeO<sub>x</sub> core-shell nanoparticles (A) after shining with white light in the FPT cell for varied times, and (B) followed by exposing to ambient oxidation for different times. The y-axes of the spectra are aligned against the peak absorbance of the Au SPR. The full range UV-Vis spectra can be found in Figure S6A and S6B (SI). Evolution of (C) Peak height and (D) peak position of the Au SPR during 2 cycles of alternating light illumination and ambient oxidation. The corresponding UV-vis spectra recorded in the 2<sup>nd</sup> cycle are presented in Figure S6C and S6D (SI). The peak heights are defined by subtracting the Au SPR peak absorbance with the absorbance value at the left valley position. The red curves are for guidance only.

left valley of the Au SPR peak gradually shifts to lower absorbance when the exposure time to ambient oxidation increases. The reversible damping/recovery of the Au SPR strength can be repeated by alternatively exposing the core-shell nanoparticles to white light under inert atmosphere, and subsequently, to ambient oxidation (Figure 4C, Figure S6 & S9). The SPR peak position is also reversibly shifted during cycles between light illumination and ambient oxidation. As shown in Figure 4D, the Au SPR peak progressively blue-shifts with light illumination time, and subsequent ambient oxidation progressively shifts the SPR peak to the red. The "fatigue", *i.e.*, the variation of peak height and intensities during cycles, could be due to the subtle morphological variation of the Fe/FeO<sub>x</sub> shells, which can influence the optical properties of the core-shell nanostructure.

To further correlate the iron composition with optical properties, the oxidation states of the iron-containing shells are monitored with XANES spectroscopy of representative samples in Kapton tubes (SI, Figure S7) during the cycle of light illumination/ambient oxidation. As shown in Figure S8 (SI and analysis in caption), light illumination induces reduction of FeO<sub>x</sub> to form Fe, and exposure to ambient oxidation initiates the oxidation of metallic Fe back to FeO<sub>x</sub>. Besides, theoretical calculation in Figure S9 unambiguously shows the continuous blue-shifting and dampening of Au SPR with the increase of Fe composition in the shell. Accordingly, the blue-shift and intensity decrease of the Au SPR peak during light illumination under inert atmosphere can be attributed to the formation of metallic Fe around the Au cores, and oxidation of Fe induces the red-shift and intensity increase of the Au SPR peak during ambient oxidation.

The dynamics during plasmon-mediated reduction of FeO<sub>x</sub> are further studied by transient absorption (TA) spectroscopy. Two representative samples, *i.e.*, Au@FeO<sub>x</sub> nanoparticles oxidized in ambient oxidation and the same sample after photo-reduction, are presented as oxidized and reduced core-shell nanoparticles for simplicity. After the excitation pulse near the SPR peak position (*i.e.*, 582 ± 6 nm), the oxidized core-shell nanoparticles in Figure 5A



**Figure 5.** Transient absorption (TA) spectra of (A) oxidized and (B) reduced core-shell nanoparticles excited with a laser of 588 nm. The insets schematically illustrate the corresponding compositional constructions of the core-shell nanoparticles using the same color scheme as Figure 1.

exhibit asymmetric photo-induced absorption (PA) spectra with strong signals at the blue side of the SPR peak position and negligible signal at the red side of the SPR peak position. This corresponds to a blue shift of the SPR peak position after resonant excitation, brought about by the reduction of FeO<sub>x</sub>. In contrast, for the reduced core-shell nanoparticles, the PA spectra are more symmetric as shown in Figure 5B. Especially at a delay time of 1.33 ps, the features for this sample are almost the same as pure Au nanoparticles, with a bleach at the resonance position and similar PA intensity at both sides of the SPR peak position.<sup>[16]</sup> The divergent TA features from oxidized and reduced core-shell nanoparticles suggest that hot electrons are likely injected into the shells of the oxidized core-shell nanoparticles to reduce FeO<sub>x</sub> into Fe, leading to a dramatic change of the relaxation dynamics of the excited Au SPs. Hence, we conclude that the Au SPR is the actual source of hot electrons for the reduction of FeO<sub>x</sub> layer during light illumination.

In summary, we have demonstrated a reversible self-modulation of optical properties of Au@FeO<sub>x</sub> core-shell nanoparticles by alternating cycles of plasmon-mediated reduction of FeO<sub>x</sub> into Fe and ambient oxidation of Fe back into FeO<sub>x</sub>. Combining the investigations from UV-Vis absorption spectroscopy, XANES spectroscopy, transient absorption kinetics, and theoretical calculations, we reveal that reducing FeO<sub>x</sub> into Fe around the Au nanoparticle in

Au@FeO<sub>x</sub> core-shell nanoparticles is responsible for the damping of the Au SPR peak intensity and the blue-shift of the SPR peak position, and that the backward oxidation of Fe into FeO<sub>x</sub> conversely recover the intensity and position of the Au SPR peak. Optimization of the sample composition and operational environment should increase the extent of reversible modulation of the metal SPR, given the current limitation on penetration depth of hot electrons and air-tight nature of the cell. For example, stronger plasmonic materials, such as silver, may be more efficacious in altering the oxidation state of shell layers under illumination conditions. Correspondingly, stronger SPR modulation should be observed in this system, as theoretically predicted for the Ag@Fe@FeO<sub>x</sub> core-shell nanostructure (see Figure S10). To conclude, our results pave the way for convenient and reversible control of the surface plasmon properties in metal nanoparticles by making use of surface redox chemistry.

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**Keywords:** surface plasmon resonance • gold nanocrystals • materials science • reversible self-modulation • surface redox chemistry

- [1] P. W. Atkins, J. De Paula, *Atkins' Physical chemistry*, Oxford University Press, Oxford; New York, **2014**, pp. 944-945  
 [2] a) K. A. Willets, R. P. Van Duyne, *Annu. Rev. Phys. Chem.* **2007**, *58*, 267; b) J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J.

- Zhao, R. P. Van Duyne, *Nat. Mater.* **2008**, *7*, 442; c) P. K. Jain, X. Huang, I. H. El-Sayed, M. A. El-Sayed, *Acc. Chem. Res.* **2008**, *41*, 1578.  
 [3] S. Eustis, M. A. El-Sayed, *Chem. Soc. Rev.* **2006**, *35*, 209.  
 [4] a) S. Nie, S. R. Emory, *Science* **1997**, *275*, 1102; b) K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari, M. S. Feld, *Phys. Rev. Lett.* **1997**, *78*, 1667.  
 [5] a) P. Mulvaney, *Langmuir* **1996**, *12*, 788; b) K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B* **2003**, *107*, 668; c) G. V. Hartland, *Chem. Rev.* **2011**, *111*, 3858; d) Y. Sun, S. K. Gray, S. Peng, *Phys. Chem. Chem. Phys.* **2011**, *13*, 11814.  
 [6] a) X. Lu, M. Rycenga, S. E. Skrabalak, B. Wiley, Y. Xia, *Annu. Rev. Phys. Chem.* **2009**, *60*, 167; b) S. Peng, J. M. McMahon, G. C. Schatz, S. K. Gray, Y. Sun, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 14530; c) R. Jiang, H. Chen, L. Shao, Q. Li, J. Wang, *Adv. Mater.* **2012**, *24*, OP200; d) Y. Sun, J. J. I. Foley, S. Peng, Z. Li, S. K. Gray, *Nano Lett.* **2013**, *13*, 3958.  
 [7] a) V. V. Temnov, G. Armelles, U. Woggon, D. Guzатов, A. Cebollada, A. Garcia-Martin, J.-M. Garcia-Martin, T. Thomay, A. Leitenstorfer, R. Bratschitsch, *Nature Photon.* **2010**, *4*, 107; b) E. Ferreiro-Vila, M. Iglesias, E. Paz, F. J. Palomares, F. Cebollada, J. M. Gonzalez, G. Armelles, J. M. Garcia-Martin, A. Cebollada, *Phys. Rev. B* **2011**, *83*; c) H. Choi, W. T. Chen, P. V. Kamat, *ACS Nano* **2012**, *6*, 4418.  
 [8] C. Clavero, *Nature Photon.* **2014**, *8*, 95.  
 [9] A. Marimuthu, J. Zhang, S. Linic, *Science* **2013**, *339*, 1590.  
 [10] E. V. Shevchenko, M. I. Bodnarchuk, M. V. Kovalenko, D. V. Talapin, R. K. Smith, S. Aloni, W. Heiss, A. P. Alivisatos, *Adv. Mater.* **2008**, *20*, 4323.  
 [11] S. Peng, Y. Lee, C. Wang, H. Yin, S. Dai, S. Sun, *Nano Res.* **2008**, *1*, 229.  
 [12] a) T. Hyeon, S. S. Lee, J. Park, Y. Chung, H. Bin Na, *J. Am. Chem. Soc.* **2001**, *123*, 12798; b) S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, G. Li, *J. Am. Chem. Soc.* **2004**, *126*, 273; c) K. Woo, J. Hong, S. Choi, H. W. Lee, J. P. Ahn, C. S. Kim, S. W. Lee, *Chem. Mat.* **2004**, *16*, 2814; d) A. Cabot, V. F. Puentes, E. Shevchenko, Y. Yin, L. Balcells, M. A. Marcus, S. M. Hughes, A. P. Alivisatos, *J. Am. Chem. Soc.* **2007**, *129*, 10358; e) E. V. Shevchenko, J. B. Kortright, D. V. Talapin, S. Aloni, A. P. Alivisatos, *Adv. Mater.* **2007**, *19*, 4183.  
 [13] a) J. Park, E. Lee, N. M. Hwang, M. S. Kang, S. C. Kim, Y. Hwang, J. G. Park, H. J. Noh, J. Y. Kini, J. H. Park, T. Hyeon, *Angew. Chem.-Int. Edit.* **2005**, *44*, 2872; b) S. Peng, C. Wang, J. Xie, S. Sun, *J. Am. Chem. Soc.* **2006**, *128*, 10676; c) S. Peng, S. Sun, *Angew. Chem.-Int. Edit.* **2007**, *46*, 4155.  
 [14] S. K. Cushing, J. Li, F. Meng, T. R. Senty, S. Suri, M. Zhi, M. Li, A. D. Bristow, N. Wu, *J. Am. Chem. Soc.* **2012**, *134*, 15033.  
 [15] A. O. Govorov, H. Zhang, Y. K. Gun'ko, *J. Phys. Chem. C* **2013**, *117*, 16616.  
 [16] A. Comin, K. Korobchevskaya, C. George, A. Diaspro, L. Manna, *Nano Lett.* **2012**, *12*, 921.

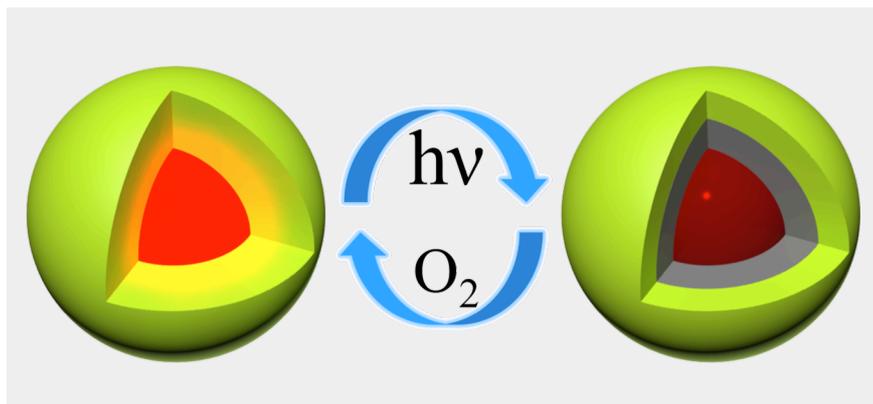
## Entry for the Table of Contents

## COMMUNICATION

Zheng Li,<sup>[a],‡</sup> Jonathan J. Foley, IV,<sup>[a],‡</sup>  
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