

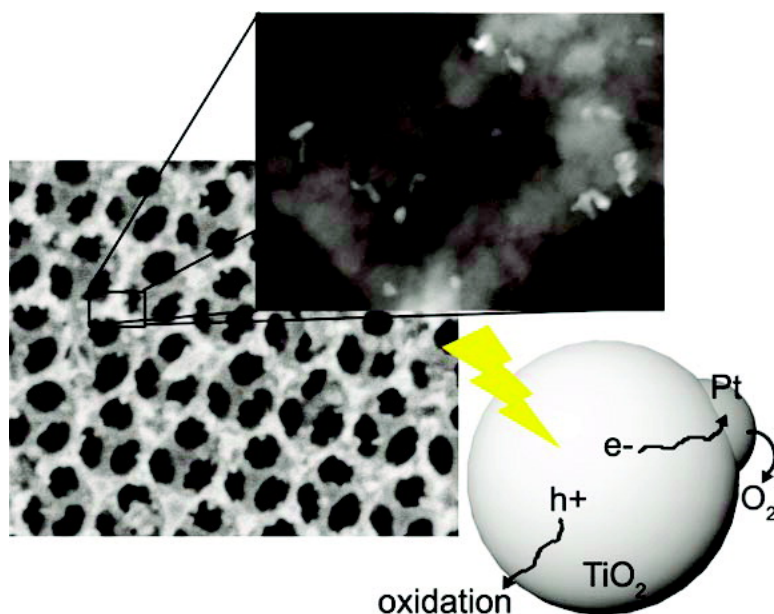
Communication

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Synergy of Slow Photon and Chemically Amplified Photochemistry in Platinum Nanocluster-Loaded Inverse Titania Opals

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While the feat of utilizing solar energy efficiently has been realized by mother nature, it remains as one of the major challenges in making solar applications practical. Enhancing the light energy conversion efficiency should therefore prove valuable in the fields of photovoltaic cells,¹ hydrogen fuel generation from water,² and photocatalysis for environmental remediation.³ In our previous work, we showed that slow photons in photonic crystal can significantly increase the interaction of light with TiO₂.^{4–6} By reducing the group velocity of light at energies near the edge of the photonic stop-band, a higher probability of absorption was achieved and the photodegradation efficiency of TiO₂ doubled. Such optical amplification has also been accomplished in other structural configurations utilizing the surface resonant modes in planar defects,⁷ multiple path lengths from a Bragg back-reflector,⁸ and random light scattering in structures like the photonic sponge.⁹ While these different architectures enthralled the idea of increasing the path length of light for optical amplification, there exists a wealth of chemical modifications that can independently improve the efficiency of the photoactive material.¹⁰ For TiO₂, they generally entail doping with other elements to increase the visible-light absorption¹¹ or incorporating noble metals like Au or Pt to enhance the separation of the UV-excited electrons and holes.¹² We hypothesized that the enhancements arising from two fundamentally different origins can be united to give a cooperative effect. Herein we demonstrate for the first time the synergy of slow photon optical amplification with chemical enhancement in inverse TiO₂ opals loaded with Pt nanoclusters (i-Pt-TiO₂-o). By incorporating Pt nanoparticles on the surface of inverse TiO₂ opals, more light is absorbed and the lifetimes of the UV-excited electron and holes are extended. A 4-fold increase in the photodegradation efficiency was achieved.

The photodegradation efficiency of i-Pt-TiO₂-o was investigated using adsorbed acid orange as probe molecules. The amount of dye adsorbed was controlled to be monolayer coverage so that all samples were standardized with respect to their surface area.¹³ To test our hypothesis of cooperative amplification, we studied the kinetics of photodegradation of acid orange on various samples: (i) nanocrystalline TiO₂ (nc-TiO₂) which serves as the reference sample; (ii) inverse TiO₂ opal (i-TiO₂-o) with slow photon enhancement according to our previous work,⁴ and (iii) i-Pt-TiO₂-o of different Pt loadings derived from sample ii. Figure 1a shows the logarithmic plot of relative extinction of acid orange on these samples as a function of irradiation time. First-order decay is observed and the decay rate constants are extrapolated and plotted in Figure 1b. The relative efficiency with respect to nc-TiO₂ is shown on the right axis of Figure 1b as the enhancement factor (EF),

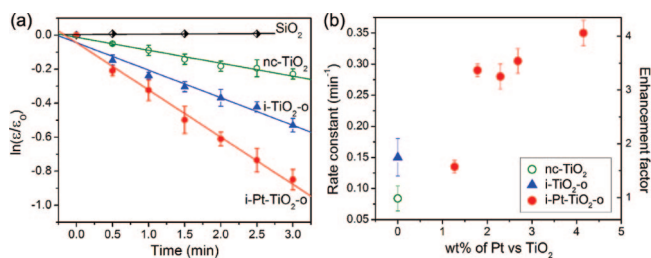


Figure 1. Photodegradation of acid orange under white-light irradiation: (a) logarithmic plot of dye extinction as a function of irradiation time for the blank (SiO₂), nc-TiO₂, i-TiO₂-o, and i-Pt-TiO₂-o with 2.3 wt % Pt; (b) first-order decay rate constant, also shown as the enhancement factor, of i-Pt-TiO₂-o with different Pt loadings in comparison to nc-TiO₂.

defined as the ratio of the decay rate constant of inverse opal to that of nc-TiO₂. The i-TiO₂-o alone gives an EF of ~1.7 due to the increased absorption arising from slow photons, whose energy was strategically chosen to overlap with the anatase absorption.⁴ The incorporation of Pt on i-TiO₂-o at 1.3 wt % initially did not yield any additional enhancement. However, a dramatic and abrupt increase in EF is observed when Pt loading reaches 2 wt %, and then the EF rises only slightly to 4 with additional incorporation of Pt (Figure 1b). A similar trend has been observed for the oxidation of CO by Pt, where it has been suggested that a critical cluster size must be reached for the Fermi level of Pt to align or be above the HOMO of O₂ for fast electron transfer.¹⁴ The process of separating the electrons and holes, whereby the excited electrons in the conduction band of the semiconductor travels to the metal centers and are subsequently scavenged rapidly by O₂ to form O₂⁻, is also highly sensitive to the nature of the metal centers, the oxidation state of Pt and the preparation methods.^{15,16} Therefore to better understand the effect of Pt on i-Pt-TiO₂-o, surface analysis by XPS and morphological studies by STEM were employed.

Figure 2 shows the binding energies (B.E.) of Pt 4f electrons in i-Pt-TiO₂-o at 1.3 wt % (a) and 2.7 wt % (c). At a loading of 1.3 wt %, Pt 4f_{7/2} peaks at 72.4 and 73.4 eV were fitted suggesting the formation of oxidized Pt²⁺ species like Pt(OH)₂ and PtO, whose reported B.E. are 72.6 and 73.8 eV, respectively.¹⁷ Since there are no ligand capping groups on the Pt clusters, it is plausible that hydroxides and oxides cover the surface and make up all of the composition of the extremely small clusters. Unlike Pt⁰, the higher oxidation states, Pt²⁺ and Pt⁴⁺, have been reported to adversely increase the recombination rate.¹⁶ Therefore the surface dominated Pt²⁺ species in i-Pt-TiO₂-o with 1.3 wt % loading does not provide any additional chemical enhancement in the photodegradation efficiency. On the other hand, the Pt 4f spectrum of i-Pt-TiO₂-o with 2.7 wt % Pt shows 4f_{7/2} B.E. of 71.2 and 73.0 eV,

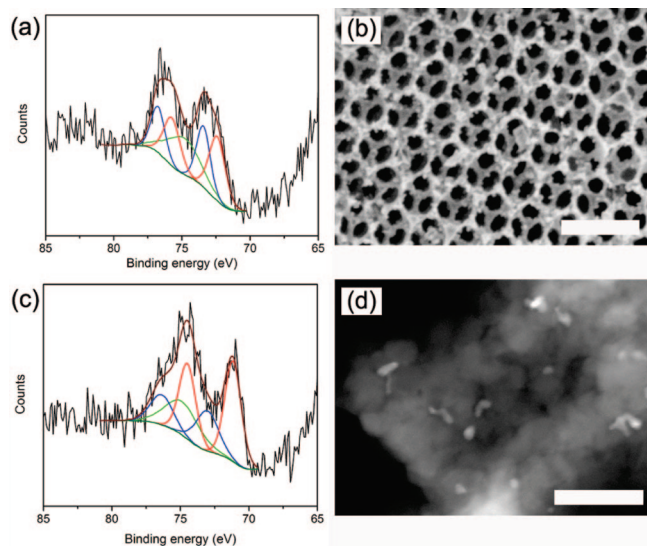


Figure 2. XPS spectra of Pt 4f and STEM images for i-Pt-TiO₂-o with 1.3 wt % Pt (a, b) and 2.7 wt % Pt (c, d). Each pair of the fitted 4f_{7/2} and 4f_{5/2} peaks is shown in the same color. A single peak at 74.87 eV accounts for the loss structure of Ti 3p.¹³ The scale bars are 300 and 30 nm for panels b and d, respectively.

corresponding to Pt⁰ and Pt²⁺ species (Figure 2c). Since Pt⁰ has been demonstrated to facilitate the scavenging of the excited electron by O₂, the abrupt increase in EF of i-Pt-TiO₂-o when Pt loading reaches >2 wt % can be attributed to a more efficient electron-hole separation. As these clusters are high in surface area, some hydroxides and oxides are still present even at higher Pt loadings. Figure 2b shows the ordered macroporous structure of i-Pt-TiO₂-o. Interestingly, the STEM images reveal a significant difference in the size distribution of the particles for different Pt loading. At 1.3 wt %, high fractions of the clusters are subnanometer in size and exhibit platelet-like morphology.¹³ Increasing the loading from 1.3 wt % to 2 wt % saw the growth of Pt nanoparticles from an average size of 1.5 to 2.5 nm (Figure 2d). The particle size then remains constant up to 4 wt % loading.¹³ On the basis of the XPS and STEM studies, the concomitant growth of Pt particles beyond the critical size of ~2 nm and the incorporation of Pt⁰ lead to the dramatic increase in the photodegradation efficiency for i-Pt-TiO₂-o with >2 wt % Pt.

We have demonstrated that slow photon in i-TiO₂-o increases the photodegradation rate by a factor of 1.7 in comparison to nc-TiO₂ and that the incorporation of Pt⁰ brings an additional chemical enhancement of 2-fold, to give an overall EF of 4. Since there is negligible change in the optical spectra of the inverse opal film before and after Pt deposition,¹³ the photonic properties should remain the same suggesting slow photons in i-Pt-TiO₂-o. This hypothesis is further supported by scalar-wave approximation modeling that suggests a negligible change in the group velocity of light at <5 wt % of Pt. To better elucidate the effect of Pt in the absence of any photonic properties, we examined disordered i-Pt-TiO₂-o. The disordered i-TiO₂-o was obtained according to our previous work,⁶ with binary sphere composition chosen so that no slow photons were observed. Such a disordered porous structure provides similar surface area and porosity, so that a comparable loading of Pt as in an ordered inverse structure was achieved. The disordered i-TiO₂-o showed a comparable rate as nc-TiO₂ without any Pt (EF of 1.1), but with the incorporation of 2.5 wt % Pt we observed a maximum chemical enhancement by a factor of 1.8. This result suggests that Pt alone cannot bring about the 4-fold increase in the efficiency of the ordered i-Pt-TiO₂-o. Quantitatively, the overall enhancement does not appear to be a direct additive

effect of the two contributions, as the amount of the additional enhancement would be 150% (70% from slow photons and 80% from Pt), or an EF of ~2.5. Rather, the incorporation of Pt nearly doubles the rate of the initial TiO₂ photocatalyst, such that disordered i-TiO₂-o with original EF close to 1 became 1.8 times more efficient with the presence of Pt, while ordered i-TiO₂-o with initial EF of 1.7 became 3.5–4 times more efficient.¹³ It suggests that an increase in the population of electrons and holes does not diminish the rapid electron transfer from Pt clusters to O₂. The overall enhancement of 4-fold in i-Pt-TiO₂-o is then likely the cooperative effect of slow photon and extended electron-hole lifetime by the incorporation of Pt clusters.

We have shown that the inverse TiO₂ opal structure is versatile toward further chemical modifications like the incorporation of metal nanoparticles. By tuning photonic properties with respect to the anatase absorption and varying the amount of Pt loading on the surface of the anatase nanocrystals, we have realized a synergistic photochemical enhancement in TiO₂-based inverse opals. This proof of principle opens the door to the integration of different physical or chemical enhancements that may prove extremely valuable in photochemistry and photocatalysis.

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Supporting Information Available: Experimental procedure, adsorption isotherm, STEM images, size distribution, XPS data, rate constants, optical spectra, and SWA modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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