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Nanoparticle Photocatalysts

Viable Photocatalysts under Solar-Spectrum Irradiation: Nonplasmonic Metal Nanoparticles**

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Abstract: *Supported nanoparticles (NPs) of nonplasmonic transition metals (Pd, Pt, Rh, and Ir) are widely used as thermally activated catalysts for the synthesis of important organic compounds, but little is known about their photocatalytic capabilities. We discovered that irradiation with light can significantly enhance the intrinsic catalytic performance of these metal NPs at ambient temperatures for several types of reactions. These metal NPs strongly absorb the light mainly through interband electronic transitions. The excited electrons interact with the reactant molecules on the particles to accelerate these reactions. The rate of the catalyzed reaction depends on the concentration and energy of the excited electrons, which can be increased by increasing the light intensity or by reducing the irradiation wavelength. The metal NPs can also effectively couple thermal and light energy sources to more efficiently drive chemical transformations.*

Photocatalysis utilizing the localized surface plasmon resonance (LSPR) of plasmonic-metal (gold, silver, and copper) nanoparticles (NPs) has attracted significant interest recently.[1–8] Reactions catalyzed by plasmonic metal NPs were found to occur at lower temperatures when the NPs were irradiated with light than without light.[1–3,8] Lower operating temperatures not only significantly reduce equipment and operation costs but also decrease the formation of unwanted side products, thus making it possible to simultaneously achieve higher product selectivity and high conversion rates for some organic synthetic reactions. Although these advantages are highly desirable, organic reactions that can be catalyzed by the three plasmonic metals are relatively few when compared to the range and number catalyzed by nonplasmonic transition metals. Nanoparticles of nonplasmonic transition metals, such as palladium (Pd), platinum (Pt), rhodium (Rh), and iridium (Ir), supported by oxide solids are widely used as catalysts for the synthesis of important organic compounds.[9] The enhancement of the efficiency of these synthetic reactions through light irradiation, in particular with sunlight—the reliable, abundant, and "green" energy source—at ambient or moderate temperatures would be an immense achievement. However, until now, the use of light irradiation to enhance the efficiency of organic reactions with nonplasmonic metal NPs has been largely overlooked.

The light absorption of metal NPs is determined by a combination of the optical properties of the free electrons (conduction electrons) and the bound electrons (in filled energy bands lower than the conduction band).[10] Light absorption through the LSPR effect results in a collective oscillation of the free electrons, whereas absorption by the bound electrons excites individual electrons to high energy levels through interband transitions.[10,11] The contributions from the LSPR effect and interband transitions vary from metal to metal. Even in the absence of strong plasmonic resonance, nonplasmonic metal NPs do exhibit significant absorption of visible and UV irradiation,[12] which are major components of sunlight, whereby absorption through the bound electrons plays an important role.[13,14] The light-absorption spectra of Pd, Pt, Rh, and Ir NPs used in the present study are shown in Figure S1 in the Supporting Information. For these metal NPs, the absorption in the visible and UV range is dominated by the interband contribution (as discussed in the Supporting Information), which results in excited NP conduction electrons. In plasmonic metals, it is known that the LSPR effect produces excited electrons that can react with molecules adsorbed on the NP surface.[15,16] This behavior raises the interesting possibility that light-excited electrons in nonplasmonic transition-metal NPs could similarly facilitate reactions of molecules on the NPs. Therefore, it is of great interest to investigate the impact of light irradiation on the catalytic performance of nonplasmonic transition-metal NPs for various chemical reactions, since these metal NPs are widely used to thermally catalyze various organic synthetic reactions,[9] and significant benefits would arise if it were possible to drive these processes at lower temperatures by irradiation with visible light.

To enable the recovery and recycling of the catalysts, we loaded the metal NPs onto ZrO_2 powder by reducing the corresponding metal salt with $NaBH_4$ in the presence of ZrO_2 powder (details of the synthesis and characterization of the photocatalysts are given in the Supporting Information). Noble metals were selected because they are stable under the

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conditions required for oxidation reactions. ZrO_2 was selected as the support because it exhibits no light absorption at wavelengths longer than 370 nm. The metal NPs disperse on ZrO_2 powder (abbreviated as M@ZrO_2), thus adequately exposing the NP surface to the reactant. Transmission electron microscopy (TEM) images of these samples showed that the metals formed NPs with mean diameters of about 6 nm on ZrO_2 (see Figure S2 in the Supporting Information). X-ray photoelectron spectra of the samples (see Figure S3) suggested that the metal existed in a metallic state when formed on the ZrO_2 support. The performance of these samples as catalysts in chemical reactions under the illumination of incandescent light (mainly composed of visible light; see Figure S4), UV irradiation, and light-emitting-diode (LED) irradiation (at wavelengths in the visible range) are summarized in Figure 1.

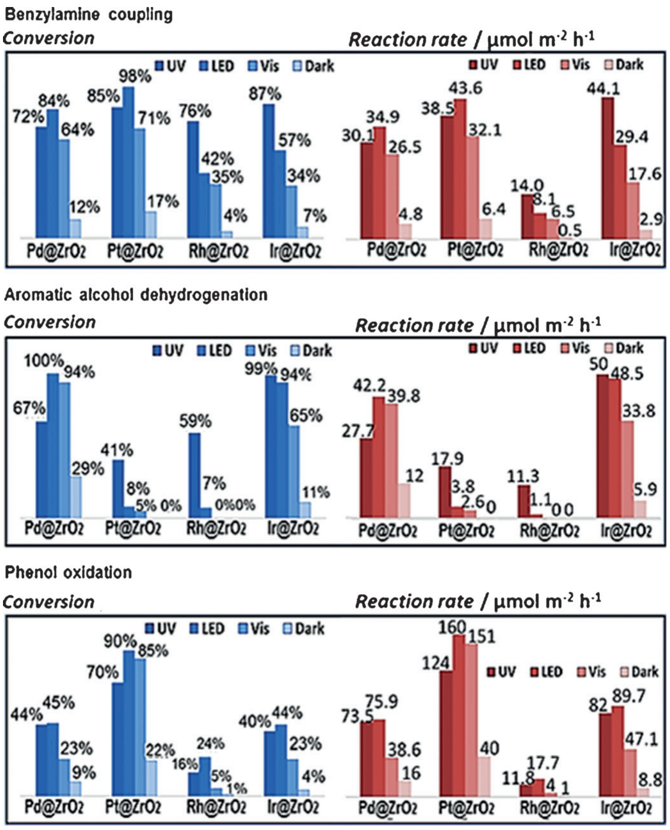

Figure 1. Enhanced catalytic performance of metal NPs on ZrO_2 support as a result of irradiation with UV light and with visible light from an incandescent lamp and an LED lamp for three reactions.

The results in Figure 1 show clearly that light irradiation enhanced the catalytic performance of all the metal NPs for all three reactions. No reaction was observed in a control experiment conducted in the absence of the NPs under otherwise identical conditions with ZrO_2 powder. The enhancement in many cases is significant. The calculated reaction rates of the photocatalytic reactions (all light sources) are around 6–13 times higher than those of reactions carried out in the dark at identical temperatures.

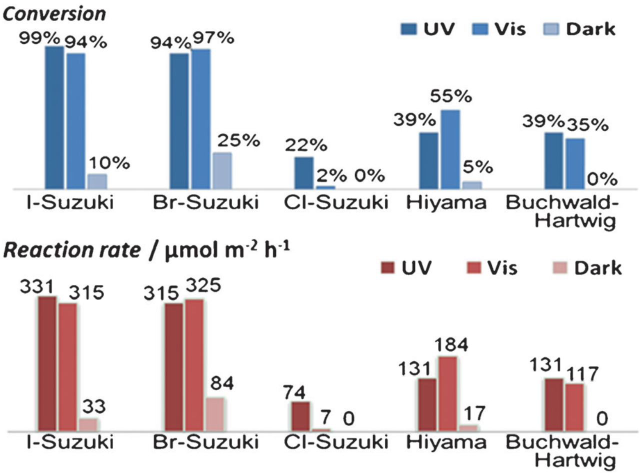

Figure 2. Enhancement of the catalytic performance of PdNPs on ZrO_2 through irradiation with light for the Suzuki–Miyaura, Hiyama, and Buchwald–Hartwig cross-coupling reactions. The results of control experiments in the dark at the same temperature are also provided for comparison.

Light irradiation was also able to significantly promote the catalytic ability of palladium NPs (PdNPs) at ambient temperature for three cross-coupling reactions: Suzuki–Miyaura, Hiyama, and Buchwald–Hartwig cross-coupling (Figure 2). These cross-coupling reactions are widely used to synthesize complex molecules,[17,18] but they often require elevated temperatures to occur at reasonable reaction rates. Buchwald–Hartwig coupling cannot proceed in the dark unless the temperature is 45 °C or greater, but it can be initiated by irradiation with light to enable 35–39 % conversion. Cross-coupling with chlorobenzene as a reactant is considered a challenging process owing to the high bond energy of C−Cl bonds; however, it was found that the reaction could be initiated by irradiation with light, especially with UV light.

Light absorption by the metal NPs also promoted the catalytic activity of numerous reduction reactions. For example, the conversion of the selective hydrogenation of acetophenone to the corresponding alcohol with Rh NPs on ZrO_2 increased to 20 % upon irradiation with incandescent light (0.4 W cm^{-2}) from 6 % in the dark at the same temperature (40 °C).

The impact of the irradiance (light intensity) on the catalytic reaction rate was investigated by varying the irradiance while maintaining other experimental conditions unchanged. The results are shown in Figure 3 for the dehydrogenation of benzyl alcohol with Pd@ZrO_2, the degradation of phenol with Pt@ZrO_2, and the oxidative coupling of benzylamine with Rh@ZrO_2 as representative examples. These results clearly show that at higher irradiance, the contribution of light irradiation to the reaction rate is larger. At a controlled reaction temperature, an increase in the irradiance resulted in a linear/superlinear increase in the reaction rate for both reactions up to an irradiance of 1.2 W cm^{-2}. The increase in the reaction rate may be due to an increase in the number of energetic conduction electrons at

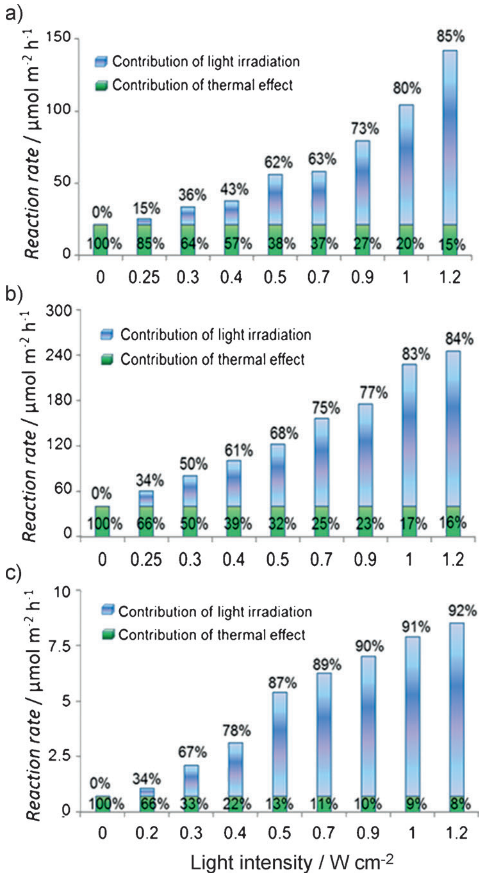

Figure 3. Dependence of the contributions from light irradiation and the thermal effect on the light intensity: a) dehdrogenation of benzyl alcohol to benzyldehyde on Pd@ZrO$_2$ at 45°C; b) degradation of phenol with Pt@ZrO$_2$ at 30°C; c) oxidation coupling of benzylamine on Rh@ZrO$_2$ at 50°C. The temperature of the reaction was maintained at the designated temperature when the irradiance was changed. The contribution due to light irradiation to the reaction rate was calculated by subtracting the rate of the reaction in the dark (performed at the same temperature) from the rate under light irradiation. The relative contributions of light irradiation and thermal catalysis to the reaction rate could then be determined.

higher irradiance and the ability of these electrons to enhance the reaction rate.

The impact of the irradiation wavelength on the catalytic reaction rate is illustrated by the action spectrum, in which the photocatalytic reaction rate of the reaction under investigation is plotted against the wavelength of light irradiation (Figure 4). The action spectra show that the dependence of the apparent quantum efficiency (AQE %) of the reactions catalyzed by the supported photocatalysts on the wavelength of irradiation is remarkably similar to the light-absorption spectra displayed by the unsupported metal NP colloid. The highest activity is observed at wavelengths at which the NPs strongly absorb light. Clearly, the light absorbed by the metal NPs is the driving force of the photocatalytic reactions.

Since the irradiance and reaction temperature were held constant at each wavelength (Figure 4), the total input energy gained by the metal NPs under irradiation at different wavelengths was identical in a given reaction period. The

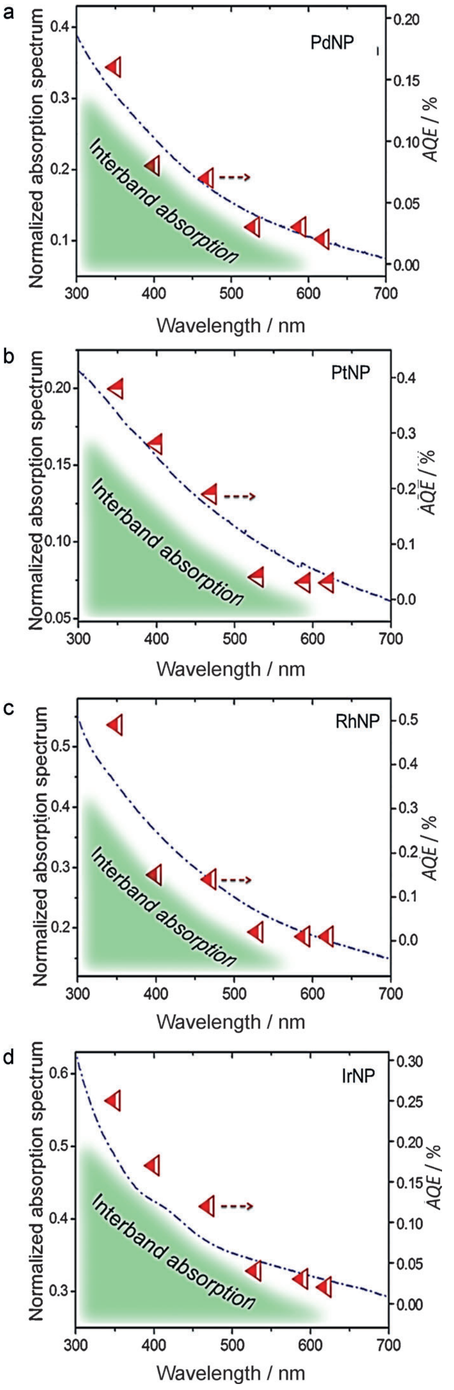

Figure 4. Action spectra of four photocatalytic reactions. The apparent quantum efficiency (AQE) of the metal NPs on ZrO$_2$ for a specified reaction is plotted against the wavelength of irradiation. LED lamps with wavelengths of (350 ± 5), (400 ± 5), (470 ± 5), (530 ± 5), (590 ± 5), and (620 ± 5) nm were used. The irradiation intensity was held constant at each wavelength by adjustment of the power input. The AQE was calculated as: AQE (%) = $[(Y_{\text{light}} - Y_{\text{dark}})/(\text{number of incident photons})] \times 100$, in which Y_{light} and Y_{dark} are the number of product molecules formed under light irradiation and in the dark, respectively. a) PdNP-catalyzed dehydrogenation of benzyl alcohol; b) PtNP-catalyzed oxidative coupling of benzyl amine; c) RhNP-catalyzed oxidative coupling of benzyl amine; d) IrNP-catalyzed dehydrogenation of benzyl alcohol.

impact of external heating has been excluded from AQE values, as the number of product molecules formed in the dark was deducted. Assuming that the input photon energy is totally converted into a thermal effect, the catalytic activity caused by this photothermal effect should be similar. However, the AQE at the wavelength (400 ± 5) nm is much higher than that at the wavelength (620 ± 5) nm. For example, for phenol degradation (Figure 4b), the AQE at (400 ± 5) nm was 9.3 times the AQE at (620 ± 5) nm, whereas the photon energy of the 400 nm light is only 1.55 times the energy of the photons of the 620 nm light. For other reactions catalyzed by different metal NPs, a similar situation was observed (see Table S1 in the Supporting Information). The extraordinary high enhancement in activity with shorter-wavelength photons indicates that photoenhancement at 400 nm is not only due to a simple photothermal effect. The photons with a shorter wavelength are able to excite metal electrons to higher energy levels, and these electrons are thus more effective at inducing reactions than those excited by photons with a longer wavelength of 620 nm (Figure 4). The detailed mechanism is discussed below (Figure 6). Therefore, the contribution from photoexcitation increases significantly as the wavelength decreases. With this relationship in mind, the AQE at the longest wavelength ((620 ± 5) nm) in this study is more likely the result of a photothermal contribution, as the AQE values at long wavelengths are low, and they show limited variation when compared with the AQE values at short wavelengths (< 500 nm). Therefore, by comparing the AQE observed at short wavelengths with that observed at long wavelengths, we can estimate the contribution from the photoexcitation. For example, the AQE due to photoexcitation is about 7.75 (9.3–1.55) times that resulting from the photothermal effect for benzylamine oxidative coupling catalyzed by Pt NPs.

In all reactions, the reaction rate increased as the reaction temperature was raised (Figure 5). This behavior is linked to the continuous electronic energy structure of metals[16] and has been observed in reactions catalyzed by heating thermal metal NP catalysts[9] but not in those catalyzed by semiconductor photocatalysts.[19,20] Upon further analysis (see Figure S5), the linear dependence of photoenhancement on the irradiance for all three reactions demonstrated that the photoexcitation of the metal electrons is the primary factor responsible for the light-enhanced activity.[8] It has also been reported that the photothermal heating effect is negligible in plasmonic photocatalysts at around room temperature,[21] and that at low irradiance the photothermal effect dominates, whereas at high irradiance, photoexcitation becomes more important.[21]

An increase in the temperature leads to redistribution of the NP electrons into higher energy levels, which are additionally raised in energy through light absorption once irradiated.[4,5] This increase in energy further increases the probability that the energetic electrons can activate the reactant molecules adsorbed on the NP surface to overcome the activation barrier and thus induce the reaction. Furthermore, higher temperatures lead to an increase in the relative population of adsorbed reactant molecules in excited states as dictated by the Bose–Einstein distribution,[5] which means that the reactant molecules require less energy to overcome the activation barrier. The ability to use thermal energy also leads to the possibility of utilizing infrared radiation, a major component of sunlight, to facilitate chemical reactions. Therefore, the ability to effectively couple thermal and light energy sources to more efficiently drive chemical transformations makes the metal NPs superior to both conventional semiconductor photocatalysts and conventional thermal catalysts.

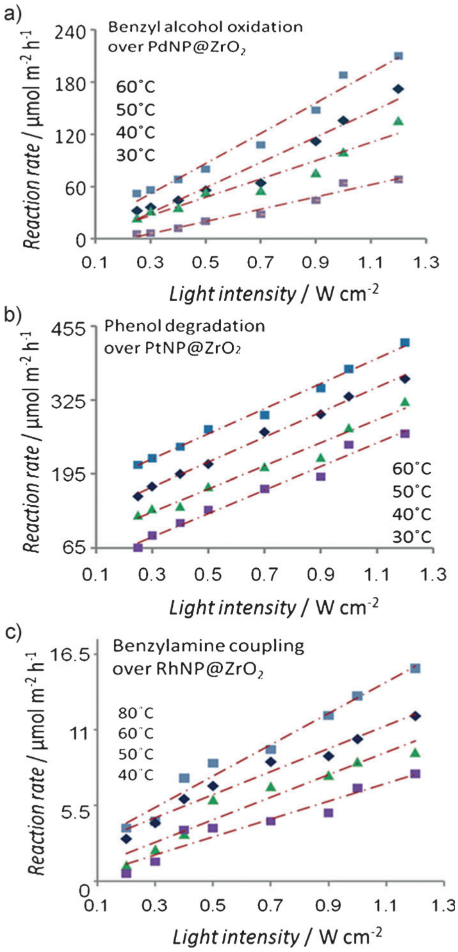

Figure 5. Photocatalytic rate of three reactions as a function of irradiance for various temperatures. The dotted lines show the linear trend observed with respect to the source intensity.

The oxidant-free dehydrogenation of benzyl alcohol has a sole reactant, benzyl alcohol. Insight into the enhancement in catalytic activity produced by light irradiation is obtained from the results of this reaction. It is known that light-excited metal-NP electrons can populate unoccupied orbitals of the molecules adsorbed on the NPs to yield a transient anion species.[15,16,22] Results of a density functional theory (DFT) simulation (the detailed calculation method is given in the Supporting Information) show that in a benzyl alcohol molecule, the distances between the α-C and the two H atoms are 1.098 and 1.100 Å, respectively, whereas in the transient benzyl alcohol anion species, one C−H distance remains at 1.100 Å, whereas the other is elongated to 1.104 Å. The energy required to break one of the C−H bonds at the α-

C atom in the molecule is 371 $kJ\,mol^{-1}$, but only 242 $kJ\,mol^{-1}$ is required to break the longer C–H bond at the α-C atom in the transient anion species. Hence, the reaction under light irradiation can facilitate hydrogen abstraction from the α-C atom through the excitation of NP electrons to the benzyl alcohol molecules adsorbed on them. Once this abstraction is completed, the subsequent abstraction of the hydrogen atom from the hydroxy group of the transient anion species proceeds readily to produce the aldehyde as the final product.[23,24]

PdNPs exhibited substantial benzyl alcohol conversion in the dark (29%, see Figure 1b) due to a strong chemical adsorption of benzyl alcohol on PdNPs. This was confirmed by infrared spectroscopy (see Figure S6). The light-excited electrons from metal NPs can be injected directly into the antibonding orbital of the chemically adsorbed molecules[15,16] to induce the reactions. This mechanism is consistent with the results of DFT simulations performed on a system of benzyl alcohol adsorbed on the Pd cluster (see the Supporting Information). Such a direct electron transfer (as shown in Figure 6b) does not require excited electrons with high energy, thus explaining the high reaction rate of benzyl alcohol on PdNPs when irradiated by either visible or LED light. The adsorption of benzyl alcohol on other metals is weaker than that on Pd, and as a result, electron transfer to the antibonding orbital can take place only with light-excited electrons with sufficiently high energy (Figure 6a). Therefore, for these metals, higher-energy UV photons are more effective than visible light in driving this reaction.

The catalytic behavior of Rh NPs is particularly interesting, since they exhibited no activity in the dark or under illumination by visible incandescent light, thus suggesting that excited electrons with high energy are necessary to induce the reaction. Indeed, good catalytic activity (a conversion rate of 59%) was observed when these particles were irradiated with UV light. However, clear activity was also observed upon irradiation with LED light. Although the wavelength of the LED source was in the visible range, it had a much higher irradiance (6.0 $W\,cm^{-2}$) than the other two light sources (0.4 $W\,cm^{-2}$). This result suggests that the high-energy electrons generated by LED irradiation may be excited by two-photon processes that act on the same electron. The numerous continuous electron energy levels of the metal NPs[16] permit such upconversion processes.

In the cross-coupling reactions, electron transfer from the Pd atoms to the halogen atoms, so-called oxidative addition, is regarded as the rate-determining step, which facilitates the carbon–halogen bond cleavage.[17,18,22] DFT calculations on the transfer of one electron from the NP surface to the reactant iodobenzene molecule (the detailed calculation methods are provided in the Supporting Information) suggest that when one electron enters an unoccupied orbital, the C–I

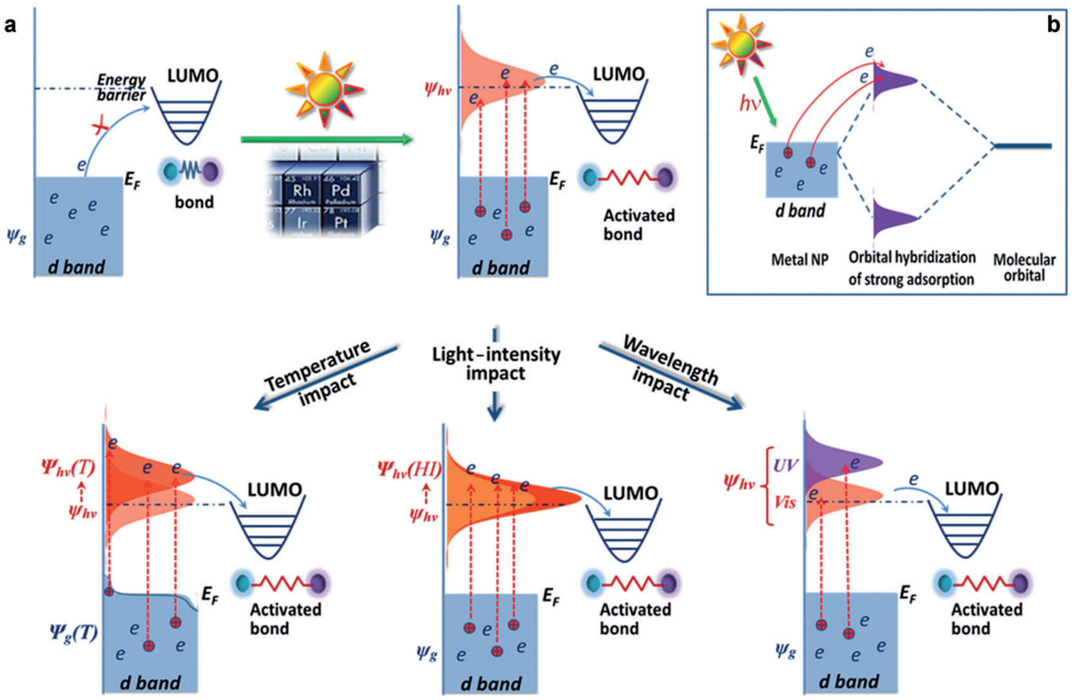

Figure 6. Proposed mechanisms of the photocatalytic reactions with nonplasmonic metal NP photocatalysts. a) Electron transfer cannot occur in the dark at low temperatures, as the energy barriers could be considerably high for physical adsorption or weak chemisorption of the reactant molecules on the NPs. b) In the case of strong chemisorption of reactant molecules on the NPs, the molecular orbitals of the adsorbed reactant interact with the electron states of the d electrons to result in bonding and antibonding orbitals of the adsorbed molecules.[22] Light-excited electrons can be directly injected into the antibonding orbitals to facilitate reactions of the adsorbed reactant molecules. Symbols: E_F, Fermi level; ψ_g, ground state; $\psi_{h\nu}$, light-excited energetic state; $\psi_g(T)$, ground state at elevated temperature; $\psi_{h\nu}(T)$, light-excited energetic state at elevated temperature; $\psi_{h\nu}(HI)$, light-excited energetic state at high irradiance. The impact of the wavelength is indicated by the position of excited states. A higher position means a higher energy level of excited states. The impact of the light intensity is indicated by the area of the excited state, whereby a larger area ($\psi_{h\nu}(HI)$) indicates a larger number of excited electrons.

bond elongates from 0.214 to 0.300 nm, thus making it easier to cleave the C–I bond. Evidently, irradiation plays an essential role in the catalytic mechanism of these reactions through the activation of the reactants.

An interesting trend was observed (see Figure S7): In general, the enhancement induced by visible-light irradiation is greater for systems that display a higher conversion rate in the dark. The rational explanation for this observation is that a high conversion in the dark indicates a strong adsorption of the reactant molecules on the NPs; thus, it is more probable that visible-light-excited electrons with moderate energy can result in the photoexcitation process (as in the case of the dehydrogenation of benzyl alcohol on PdNPs). UV-light irradiation of the NPs can initiate the photoexcitation of reactant molecules that are even weakly adsorbed on the metal NPs. Hence, there is no clear correlation between the conversion of a reaction under UV irradiation and that observed for the same reaction in the dark (see Figure S7 b).

On the basis of the aforementioned findings and previously reported information, we propose tentative mechanisms for the photocatalytic reactions with nonplasmonic metal NPs as catalysts in Figure 6. Light irradiation at shorter wavelengths excites the bound electrons to a high-energy band through interband transitions (from ψ_g to $\psi_{h\nu}$). An excited electron with sufficiently high energy to overcome the energy barrier can be injected into the lowest unoccupied molecular orbital of a reactant molecule adsorbed on a metal NP in a similar way to that observed for light-excited electrons of plasmonic metal NPs.[3,15,16] The contribution from such a photoexcitation process increases as the irradiation wavelength decreases. Electrons excited by light with long wavelengths do not have sufficient energy for photoexcitation, but can contribute to the reaction through the photothermal effect. Higher irradiance can yield more excited electrons for both the photoexcitation and photothermal processes.

Since the irradiation of the nonplasmonic metal NPs with light at ambient temperatures can yield energetic electrons that can be transferred to reactant molecules to catalyze many reactions through photoexcitation, high reaction temperatures are not required to drive the reactions. One can increase the irradiance or reduce the irradiation wavelength to optimize the catalytic reaction rate. Finally, the results obtained by irradiating the reaction systems with simulated sunlight (with an irradiance of 0.4 W cm^{-2}) indicate that one could use focused sunlight to enhance the catalytic activity of many metal NPs for organic synthesis (see Figure S8). Since NPs of nonplasmonic metals have been widely used for various applications, the reported discovery may significantly broaden the application of catalytic processes driven by light, and most importantly, our study indicated that plasmonic excitation is not the only mechanism involved when the irradiation of metal particles with light leads to enhanced catalytic activity.

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