Photocatalysis

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Enhancement of the Photoinduced Oxidation Activity of a Ruthenium(II) Complex Anchored on Silica-Coated Silver Nanoparticles by Localized Surface Plasmon Resonance**

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Photocatalysts responsive to visible light that enable selective oxidation with molecular oxygen (O_2) are potential alternatives to conventional thermal catalysis. Photochemical excitation can be performed under mild conditions and avoids the use of noxious reagents, which minimizes undesirable side reactions. However, photocatalysis to date has predominantly focused on the degradation of organic pollutants with TiO_2-based materials under UV irradiation;[1] practical examples of photocatalysis being applied to the synthesis of specialty chemicals under visible-light irradiation are sparse due to the lack of satisfactory activity in many cases.[2]

The phenomenon of localized surface plasmon resonance (LSPR) induced by Ag and Au nanoparticles (NPs) has attracted considerable attention because of its great potential for developing sensors for molecular recognition and nano-optical devices.[3] In the vicinity of the metal surface, the local electromagnetic field is dramatically enhanced, as are Raman scattering and fluorescence processes of surface-anchored dye molecules.[4] This fascinating phenomenon has also made it possible to enhance photocurrent generation on polymer nanosheets incorporating dyes and to increase the absorption coefficient in dye-sensitized solar cells.[5] The primary importance of these achievements lies in the precise architecture and tailor-made fabrication of assemblies of metal nanostructures and photoresponsive sites.

Here we demonstrate for the first time a new phenomenon in which the photoinduced oxidation activity of a dye in a selective liquid-phase reaction is efficiently enhanced by the LSPR of Ag NPs.[6] The dye $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) was anchored on the surface of Ag NPs coated with a sufficiently thin SiO_2 layer. Absorption of visible light by this dye leads to an excited singlet metal-to-ligand charge-transfer state (^{1}MLCT), which then undergoes intersystem crossing with unit efficiency to a triplet MLCT state (^{3}MLCT).[7] In the absence of O_2, the excited ^{3}MLCT state exhibits phosphorescent emission, while potentially active oxygen species such as singlet oxygen ($^1O_2$) and superoxide anion (O_2^-) are generated by energy- and/or electron-transfer reactions from the excited ^{3}MLCT state to O_2.[8] It is theoretically expected and herein verified that the enhanced local electromagnetic field near the Ag NPs could boost the excitation rate and quantum efficiency of $[Ru(bpy)_3]^{2+}$, and thus increase the energy and/or electron transfer to O_2, which ultimately enhances the photooxidation activity.

A colloidal dispersion of Ag NPs was prepared from $AgNO_3$ in the presence of sodium citrate. To make the silver vitreophilic, a bifunctional ligand, namely, aminopropyltrimethoxysilane, was bound to the surface of the Ag NPs. Further protection with a passive SiO_2 thin layer was performed with sodium silicate to give Ag@SiO_2. Next, Ag@SiO_2 was modified with 3-(triethoxysilyl)propylsuccinic acid (TESP-SA) anhydride as a spacer molecule which bears a reactive anhydride group and subsequently forms two carboxyl groups after hydrolysis. Finally, $[Ru(bpy)_3]^{2+}$ can be successfully attached by electrostatic interaction with the two COO^- groups, affording $[Ru(bpy)_3]^{2+}$/Ag@SiO_2 (0.05 wt% Ru) (Figure 1 a). Formation of Ag metal as a single phase was confirmed by XRD and X-ray absorption fine structure (XAFS) at the Ag K-edge.[9] The TEM images of the NPs showed a spherical form with an average particle size of 58 nm (Figure 1 b and c). The thickness of the SiO_2 layer was determined to be about 2–3 nm from HRTEM images (Figure 1 d). The Ru K-edge X-ray absorption near-edge structure (XANES) spectrum was quite similar to that observed for free $[Ru(bpy)_3]^{2+}$. Fourier transform extended XAFS (EXAFS) showed a strong peak around 1.5 Å attributable to an Ru–N bond and a small second shell at about 2.5 Å assigned to neighboring carbon atoms, which together confirm a bidentate binding structure in the Ru^{II} oxidation state.[9]

We obtained $[Ru(bpy)_3]^{2+}$/Au@SiO_2 by the same method using colloidal Au NPs. The average diameter and thickness of the SiO_2 layer were determined by TEM analysis to be 61 and 3 nm, respectively.[9] To elucidate the benefit of the metal core in enhancing photoinduced oxidation by LSPR, colloidal SiO_2 NPs without metal (average diameter: 55 nm) were prepared by the Stöber method,[10] followed by the same

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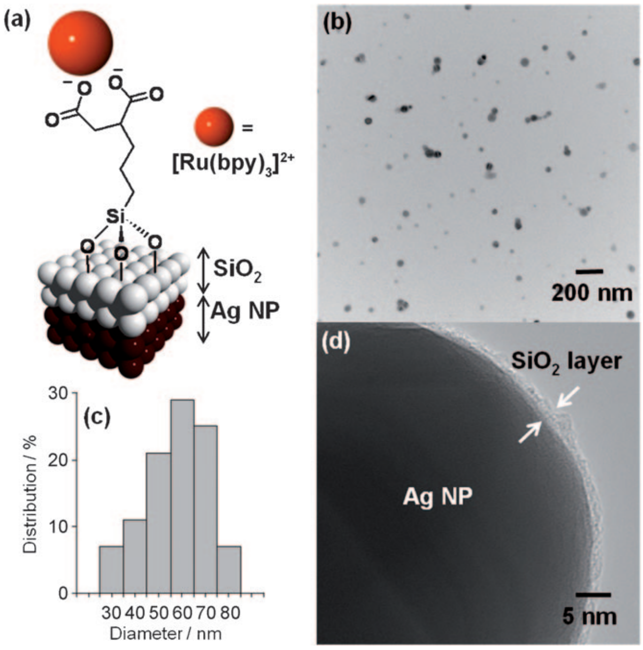

Figure 1. a) Illustration of surface structure, b) TEM image, c) size-distribution diagrams, and d) HRTEM image of [Ru(bpy)$_3$]$^{2+}$/Ag@SiO$_2$.

surface modification process with TESP-SA anhydride. Colloidal Ag NPs without the thin SiO$_2$ layer (average diameter: 51 nm) were also synthesized in the presence of 3-mercaptopropionic acid (HSC$_2$H$_4$COOH; 3-MPA) as stabilizing ligand.[11] [Ru(bpy)$_3$]$^{2+}$ can be easily attached to these reference materials to the same degree of loading to give [Ru(bpy)$_3$]$^{2+}$/SiO$_2$ and [Ru(bpy)$_3$]$^{2+}$/Ag, respectively. Analysis by XAFS revealed that [Ru(bpy)$_3$]$^{2+}$ kept its original structure, as in the case of [Ru(bpy)$_3$]$^{2+}$/Ag@SiO$_2$.[9]

As shown in Figure 2a, UV/Vis spectra of [Ru(bpy)$_3$]$^{2+}$/Ag@SiO$_2$ and [Ru(bpy)$_3$]$^{2+}$/Ag samples exhibit an MLCT band at 450 nm and a π–π* transition for the bpy ligand at about 290 nm as well as a peak due to the surface plasmon absorption of Ag NPs centered around 400 nm. In the case of [Ru(bpy)$_3$]$^{2+}$/Au@SiO$_2$, an additional surface plasmon absorption of Au NPs is observed at about 550 nm. As expected, the phosphorescence emission intensity of the [Ru(bpy)$_3$]$^{2+}$ dye associated with Ag@SiO$_2$ is enhanced under degassing conditions at room temperature,[12] and is twice as large as that of the sample without Ag NPs (Figure 2b). The Ag core NPs are more advantageous than Au core NPs in enhancing the phosphorescence emission intensity, while the Ag NPs without a SiO$_2$ layer exhibit marked quenching of the excited [Ru(bpy)$_3$]$^{2+}$ dye.[13]

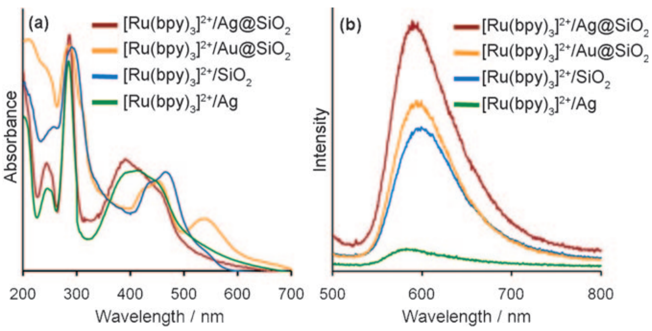

Figure 2. a) UV/Vis spectra and b) photoluminescence spectra (λ_{ex} = 450 nm) at room temperature.

The [Ru(bpy)$_3$]$^{2+}$/Ag@SiO$_2$ system was found to be an effective photocatalyst for the selective oxidation of styrene derivatives to oxygenated products under visible-light irradiation ($\lambda > 400$ nm) in the presence of O$_2$ at room temperature (Figure 3).[14] No reaction was observed either under dark conditions in the presence of O$_2$ or under visible-light irradiation without O$_2$. Furthermore, photooxidation did not occur in the presence of Ag@SiO$_2$ without anchoring of the [Ru(bpy)$_3$]$^{2+}$ dye under identical conditions. The material balance between the substrates and products after the reaction was in reasonable agreement, which indicated that undesirable mineralization was negligible. The turnover numbers (TON) based on Ru content approached 860 in the oxidation of α-methylstyrene with [Ru(bpy)$_3$]$^{2+}$/Ag@SiO$_2$, which is larger than that of the [Ru(bpy)$_3$]$^{2+}$/SiO$_2$ system by a factor of about two. More significantly, the catalyst could be completely recovered without leaching of active components. In the oxidation of α-methylstyrene, the recovered [Ru(bpy)$_3$]$^{2+}$/Ag@SiO$_2$ retained 90 % of its original photocatalytic activity, which suggests that photooxidation proceeded on the [Ru(bpy)$_3$]$^{2+}$ attached to the Ag@SiO$_2$ surface, but not with detached Ru species. [Ru(bpy)$_3$]$^{2+}$/Au@SiO$_2$ showed a slight enhancement of photocatalytic activity, but the Ag core NPs also proved to be more advantageous than Au core NPs.

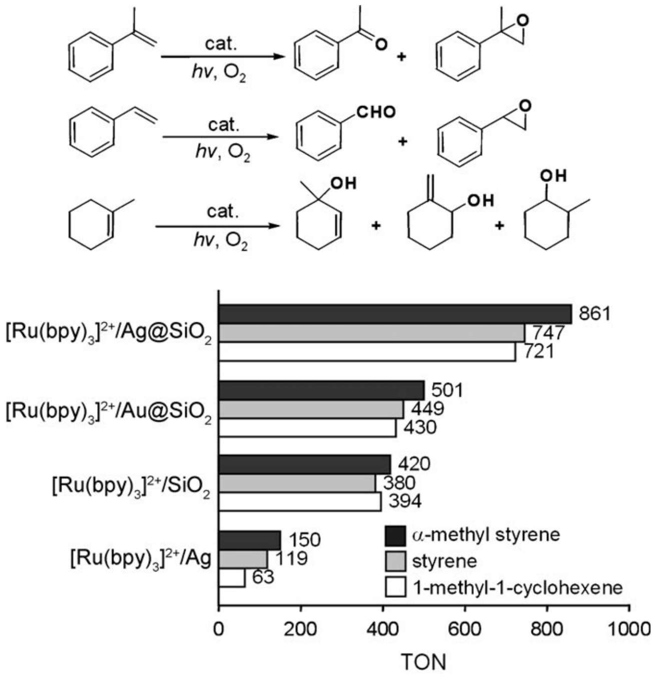

Figure 3. TON for the photocatalytic oxidation of styrene derivatives and 1-methyl-1-cyclohexene with O$_2$. Reaction conditions: Ru cat. (0.02 g), solvent (15 mL), substrate (10 mmol), O$_2$ (1 atm), photoirradiation (24 h, > 400 nm). TON = products [mol]/Ru atoms on catalyst [mol].

Again, the use of the Ag NPs without the SiO_2 layer deactivated the photoinduced oxidation ability to a significant extent. Similar phenomena were observed in the oxidation of 1-methyl-1-cyclohexene.[14] This tendency is consistent with increased phosphorescent emission from the lowest ^{3}MLCT state. The efficient quenching of the emission on addition of O_2 indicates that $[Ru(bpy)_3]^{2+}$ efficiently interacts with O_2 in the ^{3}MLCT state. The Stern–Volmer equation ($I_0/I = 1 + k_{sv}[Q]$) can be used to represent quenching of the emission by O_2, where I_0 and I are the intensities of emission in the absence and presence of O_2, respectively, and k_{sv} and [Q] are the quenching rate constant and the concentration of O_2, respectively. As expected, $[Ru(bpy)_3]^{2+}$/Ag@SiO_2 gave a k_{sv} value of 4.8, which is much larger than that of 1.3 observed for $[Ru(bpy)_3]^{2+}$/SiO_2. This result clearly indicates smooth interaction of the ^{3}MLCT state with O_2 in the presence of Ag NPs, and corresponds well to the observed increase in phosphorescence emission intensity as well as the photoinduced oxidation ability. Thus, the present study has unambiguously demonstrated that interaction with the LSPR of Ag NPs can enhance the photocatalytic activity of a dye complex anchored to the surface. The importance of the thin SiO_2 layer is also confirmed. It is known that the electromagnetic field enhanced by LSPR excitation is localized to the surface between the metal and the dielectric with a roughly exponentially decaying strength in space.[15] However, some studies proved that the specific distance between metal and dye play a crucial role for attaining maximum effect of LSPR.[16] The SiO_2 layer therefore not only offers chemical inertness, transparency, and versatility for conjugation of dye molecules, but also provides a spacer to limit quenching via energy transfer with the core Ag NPs, and thus optimizes the LSPR effect. We also note the importance of using Ag cores. Some reports have proved that Ag NPs gave much higher LSPR enhancement effects than Au NPs.[17] One possible explanation is that the surface plasmon from Au NPs does not couple to the excitation wavelength of the Ru complex dye, while the plasmon resonance frequency generated on Ag NPs may closely match the excitation frequency of the dye to offer reasonable enhancement.

In summary, we have prepared a new class of nanosized photocatalysts composed of core/shell Ag@SiO_2 NPs with an anchored $[Ru(bpy)_3]^{2+}$ dye. The enhanced electromagnetic field in the vicinity of the Ag NPs due to LSPR significantly enhances emission intensity of the dye, which ultimately results in the enhanced catalytic activity for photooxidation with O_2. This work provides a novel pathway to the design of new photocatalysts enabling selective organic transformation even under limited light exposure.

Experimental Section

Materials: $AgNO_3$ and sodium silicate were purchased from Wako Pure Chemical Ind., Ltd. Trisodium citrate dehydrate was obtained from Nakarai Tesque. Aminopropyltrimethoxysilane and $[Ru(bpy)_3]Cl_2$ were supplied by Sigma-Aldrich. 3-(Triethoxysilyl)propylsuccinic acid anhydride was purchased from Gelest Solvents and all commercially available organic compounds for catalytic reactions were purified by standard procedures.

Synthesis of Ag@SiO_2: A colloidal dispersion of Ag NPs was prepared by dropwise addition of a degassed solution of sodium citrate (0.54 mmol) in water (16 mL) to 400 mL of boiling aqueous solution containing $AgNO_3$ (0.82 mmol) under vigorous stirring. After heating to reflux for 1 h under an Ar atmosphere, the reaction solution was cooled to room temperature. The as-prepared solution of Ag NPs was centrifuged, and the solid washed with distilled water several times. Next, a solution of aminopropyltrimethoxysilane (0.042 mmol) in ethanol (6.0 mL) was added to an aqueous solution of as-synthesized Ag NPs (1.8 L, 0.46 mM). The mixture was stirred for 30 min at room temperature, and finally a solution of sodium silicate (0.07 g) in water (200 mL) was added to allow sol–gel condensation. After stirring for 24 h, the encapsulated particles were repeatedly centrifuged and washed with copious distilled water to give Ag@SiO_2.

Synthesis of $[Ru(bpy)_3]^{2+}$/Ag@SiO_2: First, Ag@SiO_2 was modified by treatment with 3-(triethoxysilyl)propylsuccinic acid anhydride (0.19 mmol) in solution in toluene (60 mL) for 24 h. The colloidal solution was centrifuged, and the solid washed with toluene several times and dried under vacuum overnight. Next, the obtained material was treated under aqueous conditions to allow hydrolysis of anhydride to carboxyl groups. After 3 h, the solution was centrifuged, and the solid washed with distillated water several times. Finally, the obtained material was treated with 15 mL of an aqueous solution of $[Ru(bpy)_3]Cl_2$ (0.87 μmol) at room temperature. After 24 h, the solution was centrifuged, and the solid washed with distilled water several times to afford $[Ru(bpy)_3]^{2+}$/Ag@SiO_2 (0.05 wt% Ru).

Liquid-phase photooxidation: The photocatalyst (0.02 g), α-methylstyrene (10.0 mmol), and acetonitrile (15 mL) were added to a quartz reaction vessel (30 mL), which was then sealed with a rubber septum. The resulting mixture was sonicated and bubbled with oxygen for 30 min in the dark. Subsequently the sample was irradiated from the side with an Xe lamp (500 W; SAN-EI ELECTRIC XEF-501S) through a glass filter ($\lambda > 400$ nm) for 24 h with magnetic stirring at ambient pressure and temperature. After the reaction, the resulting solution was centrifuged and the supernatant was analyzed by GC with an internal standard on a Shimadzu GC-14B with a flame ionization detector equipped with TC-1 columns. The turnover number (TON) was determined by the following equation: TON = (acetophenone [mol])/(Ru atoms on catalyst [mol]).

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