TiO_2 photocatalytic reduction of bis(2-dipyridyl)disulfide to 2-mercaptopyridine by H_2O: incorporation effect of nanometer-sized Ag particles

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A highly endothermic reduction of bis(2-dipyridyl)disulfide to 2-mercaptopyridine by H_2O selectively proceeds using TiO_2 as a photocatalyst, being significantly enhanced upon incorporation of nanometer-sized Ag particles on TiO_2.

Thiols are the most important of the sulfur containing molecules, owing to their usefulness as starting materials for the syntheses of agrochemicals, pharmaceutical products, petrochemicals, *etc.* Several methods for reducing disulfides to the corresponding thiols use reducing agents, including lithium aluminium hydride, sodium hydride, chromium(II), and triphenylphosphine–H_2O.[1] On the other hand, sulfur compounds frequently have a poisoning effect on transition metal catalysts, which was also observed in the reduction of disulfides to thiols by Pd/charcoal catalyst.[2] Poisoning is generally caused by the high adsorption strength of sulfur compounds for the surface active sites of transition metals. This is the first report on TiO_2 photocatalytic reduction of bis(2-dipyridyl)disulfide (RSSR) to 2-mercaptopyridine (RSH) by H_2O. Particular emphasis was placed on the promoting effect with loading of nanometer-sized Ag particles on TiO_2 (Ag/TiO_2).

TiO_2 and Ag/TiO_2[3] absorb light intensely below 385 nm due to the band gap transition. Nanometer-sized Ag particles have a surface plasmon absorption in the wavelength range $300 < \lambda < 500$ nm.[4] In the spectrum of RSSR, there are two absorption bands above 220 nm, at 233 and 281 nm. Light with $\lambda < 300$ nm was cut off by a Pyrex glass filter and both TiO_2 and Ag were excited by irradiation. When the TiO_2 or Ag/TiO_2 suspension containing RSSR [solvent : H_2O–acetonitrile (99 : 1 v/v)] is irradiated under deaerated conditions, the peak intensities of RSSR weaken concurrently with the appearance of new two bands at 272 and 342 nm, which are in complete agreement with the peak positions of authentic RSH. The production of RSH was also confirmed by HPLC and negligible amounts of by-products were detected. A stoichiometric relation with a ratio of [RSH]/[RSSR] of *ca.* 2 was obtained in the conversion of RSSR to RSH, indicating the selective reduction of RSSR to RSH.

Photoillumination of either Ag/TiO_2 or TiO_2 was required to reduce RSSR. This reaction is thus induced not by Ag photoexcitation but by the band gap transition of TiO_2. During the reaction, a gradual decrease in pH of the solution from 5.8 to 4.8 was observed. A small amount of O_2 was detected in a closed reaction system by gas chromatography. This is probably due to its consumption through the successive reduction by the excited electron and/or the reaction with RSSR. The possibility of the oxidation of acetonitrile, which was added to H_2O in order to dissolve RSSR, was excluded, since no reduction occurred upon using dehydrated acetonitrile as the solvent. From these results above, the overall reaction can be written as eqn. (1).

$$\mathrm{RSSR} + \mathrm{H_2O} \xrightarrow[\mathrm{TiO_2\ \ or\ Ag/TiO_2}]{h\nu(\lambda > 300\ \mathrm{nm})} 2\mathrm{RSH} + 1/2\mathrm{O_2} \quad \Delta H = +207.9\ \mathrm{kJ\,mol^{-1}} \qquad (1)$$

This highly endothermic reaction may also be attractive from the viewpoint of converting light energy to chemical energy.

Fig. 1 shows time course of the RSH production in the presence of TiO_2 (a) and Ag/TiO_2 (b). The rate of the reaction calculated from the concentration of RSH formed after 100 min illumination (v) is increased by a factor of 5.2 with Ag loading. The continuous formation of RSH for more than 150 min suggests high chemical stability of the Ag deposits under the present conditions. The dependence of v on the amount of Ag loaded ($0 < x < 1$ wt.%) was examined. It was shown that v goes through a maximum near $x = 0.24$ wt.%. A possible explanation for the decrease in v at $x > 0.24$ wt.% is light shielding by Ag. This fact again precludes the possibility of Ag photoinduced reduction of RSSR.

Adsorption isotherms of RSSR on TiO_2 (a) and Ag/TiO_2 (b) were measured at 28.5 ± 0.5 °C. From the analyses of the Langmuir plots, the saturated adsorption amount (Γ_s) and the constant indicative of adsorption strength (β) were calculated to be 1.07×10^{-6} mol g^{-1} and 1.27×10^5 dm^3 mol^{-1} for TiO_2, and 1.92×10^{-5} mol g^{-1} and 1.56×10^6 dm^3 mol^{-1} for Ag/TiO_2. Various self-assembled monolayers (SAMs) of surface active organosulfur compounds such as thiols (R′SH), sulfides (R′SR′) and disulfides (R′SSR′) that adsorb on Ag or Au, owing to the specific interaction of R′S–Ag or R′S–Au, have been a topic in the field of surface science.[5] It has been revealed that R′SSR′ chemisorbs on the surface of Ag(111) or Au(111) *via* S–S bond cleavage.[5] The RS group was previously confirmed by other workers to adsorb on Ag stably without S–C bond fission.[6] The areas occupied by one RS group in the Ag/TiO_2 were calculated to be 6.4 nm^2 group^{-1} for TiO_2 and 0.1 nm^2 group^{-1} for Ag. The corresponding areas for the RS group adsorbed in

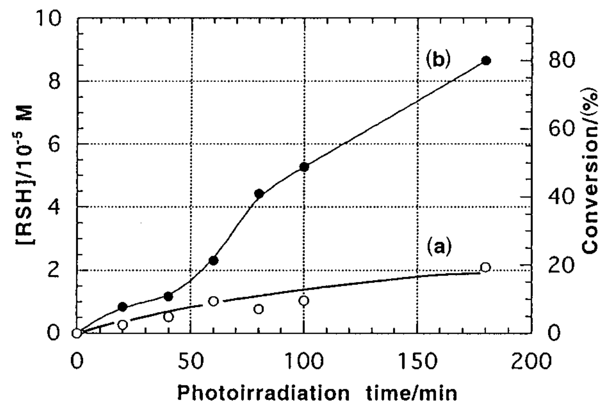

Fig. 1 Time courses of the RSH production in the presence of TiO_2 (a) and Ag/TiO_2 (b). A 5.41×10^{-5} M RSSR solution (50 ml of H_2O–acetonitrile (99 : 1 v/v) was irradiated in the presence of 50 mg TiO_2 or Ag/TiO_2 at 22 ± 1 °C. The light intensity integrated from 320 to 400 nm was 4.62 mW cm^{-2}. Irradiation was commenced after removal of dissolved O_2 by 15 min N_2 bubbling and attainment of adsorption equilibrium by stirring for 1 h in the dark; N_2 bubbling was continued throughout the reaction.

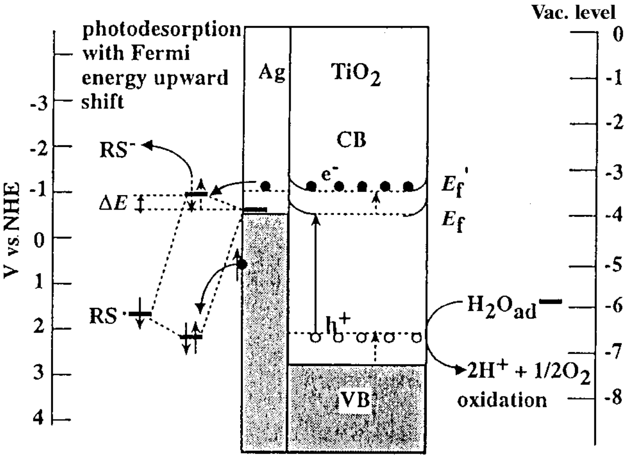

Fig. 2 Energy diagram of the reaction system. The following values were used for its construction: work function of Ag = 4.0 eV;[8] electron energy for the standard hydrogen electrode (SHE) = −4.5 eV *vs.* SHE;[9] flat band potential of TiO_2 at pH 5.5 = −0.45 V from the vacuum level;[10] band gap energy of TiO_2 = 3.2 eV;[10] oxidation potential of H_2O at pH 0 = 1.23 V *vs.* SHE;[10] HOMO of $RS\cdot$ radical = −6.4 eV (this value was obtained from PM3 MO calculations).

the closest packing states were estimated to be *ca.* 0.16 nm^2 $group^{-1}$ for the flat lying orientation and 0.1 nm^2 $group^{-1}$ for the vertical orientation using the PM3 optimized molecular structure. Clearly, the RS groups adsorb on the surface of nanometer-sized Ag particles in a close packed state analogous to those in SAMs, while most of the TiO_2 surface is directly in contact with H_2O.

A plausible reaction mechanism is summarized as follows. In the initial stage of the reaction, selective RSSR adsorption on the surface of Ag accompanied by S–S bond cleavage takes place. Electron–hole pairs are generated by the band gap excitation of TiO_2. Most of the pairs are lost by recombination but a portion of the electrons excited to the conduction band (CB) flow into Ag, while the holes are left in the valence band (VB) of TiO_2. The Schottky barrier at the Ag/TiO_2 interface would assist the charge separation. The hole has enough potential to oxidize H_2O to yield H^+ and O_2. The coupling of H^+ and RS^-, driven to desorb reductively by the excited electron, forms RSH. A similar reductive desorption of *n*-alkanethiols from an Au electrode has been reported by Widrig *et al.*[7] In the TiO_2 system, the reduction of RSSR is thought to proceed in a similar manner as in the Ag/TiO_2 system; however, the alternative reduction site would be surface Ti^{3+} ions. Three factors for reaction enhancement effect of the Ag loading can be proposed. The first is enhanced adsorption of RSSR, the second is the separation of reduction (Ag) and oxidation sites (TiO_2) and the third is that the oxidant (RSSR) and the reductant (H_2O) selectively adsorb on the reduction and oxidation sites, respectively, resulting in a highly selective reaction.

Since the turnover number is calculated to be *ca.* 6.7×10^{14} molecules cm^{-2}, this reaction is qualified to be catalytic. The strangest and most intriguing question raised by this reaction is why RS adsorbed on Ag desorbs from the surface upon irradiation despite its strong adsorption strength as evidenced by the large β value of 1.56×10^6 dm^3 mol^{-1} for Ag/TiO_2. Fig. 2 depicts the energy diagram of the reaction system. A couple of bonding and antibonding orbitals are formed as the result of the interaction between the highest occupied molecular orbital (HOMO) of $RS\cdot$[11] and an unoccupied molecular orbital (UMO) above the Fermi energy (E_f) of Ag.[12] In the ground state, the bonding orbital is occupied by two electrons, each of which originally belongs to $RS\cdot$ and Ag, respectively, leading to a strong interfacial RS–Ag bond. The contribution of the HOMO of $RS\cdot$ to the bonding orbital is much greater than that of the UMO of Ag. Thus the interfacial bond can approximately be described as RS^-–Ag^+, which is confirmed by XPS measurements of SAMs.[13] On the other hand, in the photoexcitation state, E_f is raised by several hundreds of meV (E_f'),[14] which corresponds to the bonding energy of R′SSR′ on Au (*ca.* 0.5 eV per R′S group).[15] If E_f' exceeds the energy of the interfacial antibonding orbital, it would be occupied by the two electrons from Ag. The destabilizing energy will enable the desorption of RS^- upon illumination, and further the photocatalytic cycle in this reaction. We refer to this as photodesorption with an upward shift of the Fermi energy. Essentially, the electrochemical reductive desorption of *n*-alkanethiol monolayers from Ag and Au electrodes can be interpreted as desorption with an upward shift of the Fermi energy induced by the application of external electric voltage. Widrig *et al.* explained the fact that the reductive desorption from Ag as compared to Au occurs at 0.30 V more negative potential due to the differences in the point of zero charge for the two metals.[7] According to our theory, this can alternatively be attributed to the differences in the work function (Ag = 4.0 ± 0.15 eV, Au = 5.1 ± 0.1 eV),[8] assuming comparable interaction energy (ΔE in Fig. 2).

In conclusion, it has been demonstrated that a highly endothermic reduction of RSSR to RSH by H_2O proceeds selectively and efficiently using Ag/TiO_2 as a photocatalyst. The essential reaction mechanism is presented on the basis of the adsorption and kinetic data. Photodesorption with an upward shift of the Fermi energy is proposed as a key process in the catalytic cycle. This action of Ag/TiO_2 may open up a new field of photocatalytic reactions of heterocompounds, whose thermal catalytic reactions using transition metal catalysts are usually not straightforward due to their poisoning effect.

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$$R'SH + M^0 \rightarrow R'S^-{-}M^I + 1/2\ H_2 \qquad (2)$$

$$R'SH + M^I \rightarrow R'S^-{-}M^I + H^+ \qquad (3)$$

In the case of RSSR, homolytic dissociated adosrption appears to be plausible [eqn. (4)].

$$RSSR + 2M^0 \rightarrow 2R'S^-{-}M^I \qquad (4)$$

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