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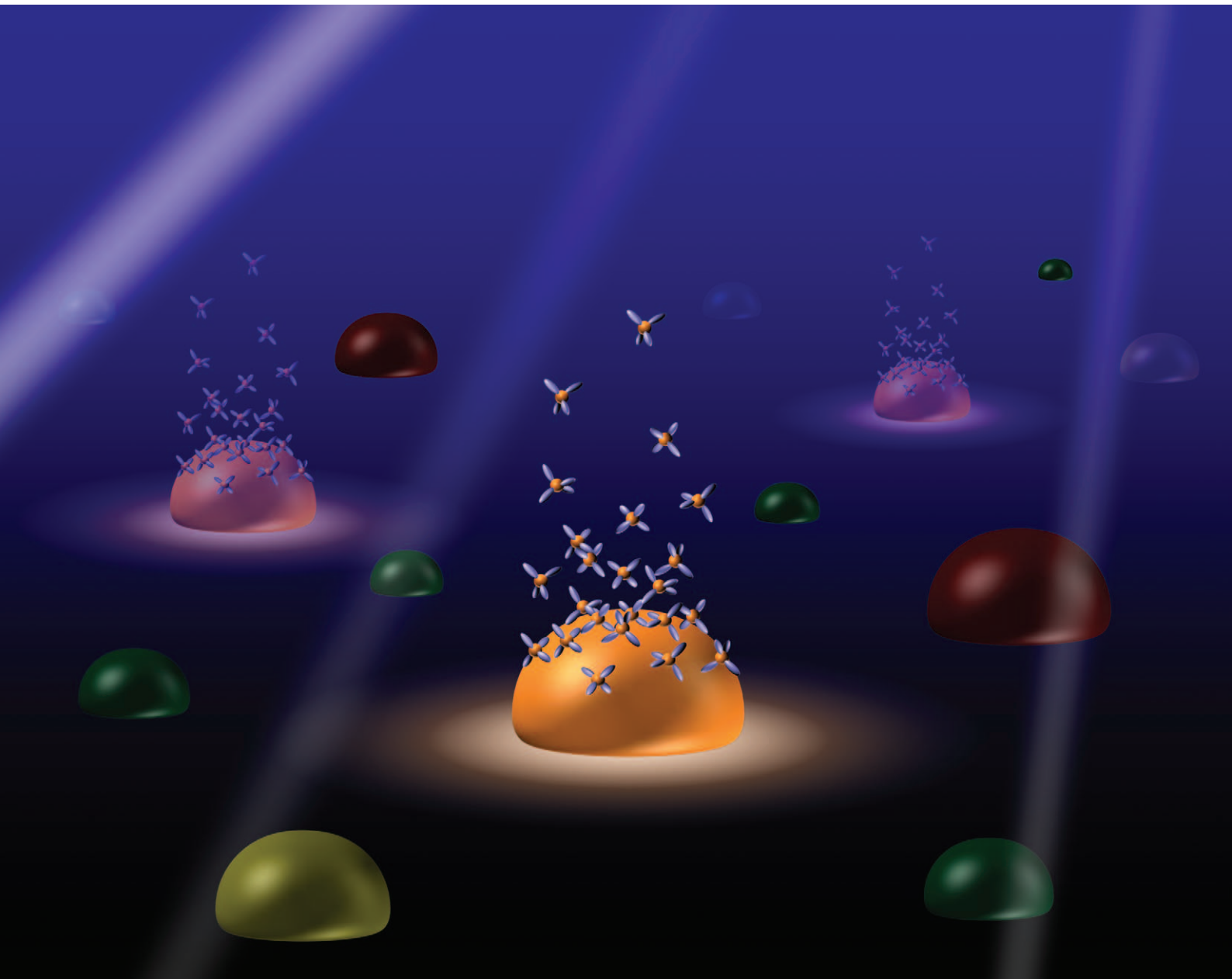

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Plasmon-induced oxidation of gold nanoparticles on TiO_2 in the presence of ligands

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The mechanism of plasmon-induced charge separation of gold nanoparticles (Au NPs) on TiO_2 was investigated with the help of anionic ligands. Au NPs are oxidized in the presence of KX (X = SCN, Br or Cl), chiefly *via* direct oxidation to $[AuX_4]^-$. The reactivity of Au NPs depends on the solution pH, the type of anion ligands and the excitation wavelength, suggesting that the photopotential of Au NPs during plasmon-induced charge separation depends on both the flatband potential of TiO_2 and the energy of irradiated photons. The results indicate that the reactivity and efficiency of the plasmon-induced charge separation and accompanying reactions can be tuned and optimized by changing those factors.

1. Introduction

Noble metal nanoparticles (NPs) absorb and scatter light at specific wavelengths due to localized surface plasmon resonance (LSPR). As their resonance wavelength and intensity depend largely on the particle size, shape, interparticle distance and dielectric environment, they exhibit a variety of colours.[1,2] In our past research, we found that Au,[3,4] Ag[4,5] and Cu[6] NPs on TiO_2 or ZnO exhibit plasmon-induced charge separation, which is caused by light irradiation at LSPR wavelengths. Stable Au NPs have been applied to plasmon-based photocatalysis[3,7,8] and photovoltaic cells.[3,4,9–11] On the other hand, less stable Ag NPs undergo photo-oxidation and dissolution,[12] which have been applied to multicolour,[5,13] infrared[14] and high speed[15] photochromism, as well as photoinduced multicolour control of single NP[16] and photomorphing gels.[17] However, the mechanisms of the plasmon-induced charge separation have not yet been elucidated completely, and learning the details of the phenomenon may lead to an improvement of the reaction efficiency and the development of other applications.

We have reported that TiO_2 electrodes modified with Au[3,4] or Ag[4,18] NPs exhibit negative potential shifts and anodic currents under illumination. In contrast, Au[9,19] or Ag[9,20] NPs coated with TiO_2 exhibit positive potential shifts and cathodic currents. On the basis of these results, we concluded that the charge separation is caused by electron transfer from metal NPs to TiO_2, which is also supported in related studies by other groups.[7,8,10,11,21–23]

As mentioned above, Au NPs are generally so stable that the plasmon-induced charge separation does not cause their oxidative dissolution.[3] In our previous research, however, we have achieved the plasmon-induced oxidative dissolution of Au NPs with the aid of I^- (KI aqueous solution) and developed a multicolour change material, which is more resistive to white light than a Ag-based material.[24] However, it is yet to be elucidated whether the Au dissolution is predominantly due to direct oxidation ($Au + 4I^- \rightarrow [AuI_4]^- + 3e^-$, $E^\circ = +0.56$ V *vs.* NHE) or indirect oxidation *via* I_3^- ($3I^- \rightarrow I_3^- + 2e^-$, $E^\circ = +0.55$ V, then $2Au + 3I_3^- \rightarrow 2[AuI_4]^- + I^-$), because the potential of the former reaction is close to that of the latter (Fig. 1a). To obtain further information about this, here we used other ligands, *i.e.* Br^-, Cl^- and SCN^-. In the case of Br^- and Cl^-, the potentials of the direct oxidation are far more negative than the oxidation potentials of the halide ion to tri-halide ion. Also, in a solution of SCN^-, the indirect mechanism would not hold as SCN_3^- is known to be unstable in aqueous media.[25] In addition, examination of the reactions in the presence of different ligands and at different pH values sheds light on the photopotentials of Au NPs during the plasmon-induced charge separation.

2. Experimental

Preparation of a TiO_2 film and Au NPs

A TiO_2 film loaded with Au NPs was prepared as previously reported.[24] A TiO_2 film was prepared on a Pyrex glass substrate from a commercial anatase sol (STS-21, Ishihara, 75% aq.) by a spin-coating method (at 1500 rpm for 10 s) and calcined at 723 K for 1 h. Au NPs were deposited photocatalytically on the TiO_2 film as follows. A mixture of 10 mM aqueous solution of $HAuCl_4$ and ethanol (1 : 9 by volume, 32 mL cm^{-2}) was cast on the TiO_2 film and left for 15 min, followed by rinsing with water. The mixture was cast again and the film was irradiated

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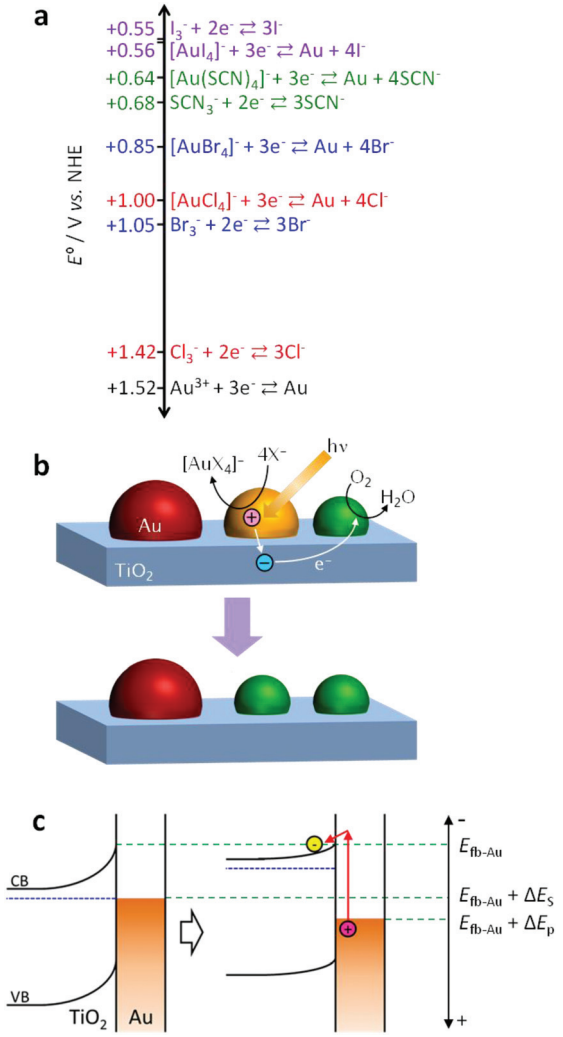

Fig. 1 (a) Values of the standard electrode potential E° for oxidative coordination of Au with anionic ligands (X^-) and oxidation of the anions to X_3^-. (b) Mechanism of spectral dip formation for the Au NP–TiO_2 system. (c) Potential shifts of Au NPs and TiO_2 due to the plasmon-induced charge separation in an open circuit system.

with UV light (260–370 nm, 25 mW cm^{-2}) for 10 s. Electrons in the TiO_2 valence band (VB) are excited to the conduction band (CB), and used for the reduction of $[AuCl_4]^-$ to Au NPs. The corresponding generated holes in the VB are consumed by oxidation of ethanol.

Photoinduced reactions

Extinction (= absorption + scattering) spectra were collected using a V-670 spectrophotometer (Jasco). The as-prepared Au NP–TiO_2 sample was soaked in 0.5 M KSCN, KBr or KCl aqueous solution until the spectrum was stabilized. Then, the sample in the solution was irradiated with 600–700, 700–800 or 800–1000 nm light (10 mW cm^{-2}) for 30 min. The light source was a Xe lamp (Luminar Ace LA-410UV, Hayashi Watch Works) (600–700 nm) or a halogen lamp (HA-150UX, Myutron) (700–800 and 800–1000 nm) equipped with a long-pass filter (SCF-50S-60R, SCF-50S-70R or CLDM-50S, Sigma Koki) and a short-pass or band-pass filter (FSWP-800-25.0M or SPF-1000-1.00, CVI Melles Griot; ITF-50S-83RT, Sigma Koki).

For monochromatic light irradiation (4 mW cm^{-2}) in 0.5 M KCl at pH 7, 8 or 9 (adjusted with KOH), a band-pass filter (full width at half maximum = 10 nm) for 700 nm (Asahi Spectra) or 800 or 900 nm (CVI Melles Griot) was used with the Xe lamp (700 nm) or the halogen lamp (800 and 900 nm).

3. Results and discussion

Spectral dip formation

The deposited Au NPs show an extinction peak at 545 nm and a tail extending to the near infrared region (~1000 nm) (Fig. 2a) as a result of the formation of NPs with various size and anisotropy on the contact area with TiO_2 which exhibit different LSPR wavelengths.[24]

The Au NP-modified TiO_2 sample was irradiated with 600–700, 700–800 or 800–1000 nm light (10 mW cm^{-2}) in 0.5 M KSCN, KBr or KCl aqueous solution for 30 min. Normalized difference extinction spectra after the light irradiations are shown in Fig. 2b–d. In all these cases, extinction decreased preferentially at around the irradiation wavelengths and wavelength-selective extinction dips were formed. These spectral changes are explained in terms of selective oxidation and dissolution of resonant Au NPs to $[AuX_4]^-$ (X: halogen or SCN) (Fig. 1b).[24] The peaks at ~540 nm in the difference spectra are attributed to smaller NPs formed eventually by the dissolution, which exhibit LSPR at ~540 nm.[24] Small Au NPs deposited by recombination of the $[AuX_4]^-$ ions and electrons transferred to TiO_2 may also be responsible for the peaks.[24,26]

In the case of X = SCN, the dip formation must be caused by the direct oxidation ($Au + 4SCN^- \rightarrow [Au(SCN)_4]^- + 3e^-$),

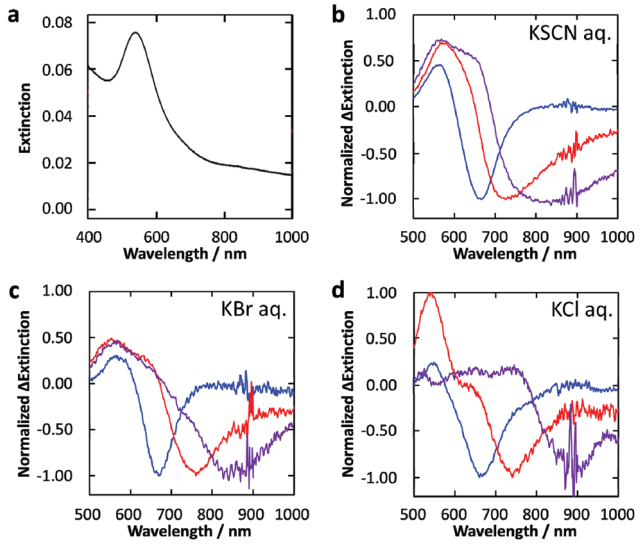

Fig. 2 (a) Extinction spectrum of Au NPs deposited photocatalytically on the TiO_2 film. (b–d) Normalized difference extinction spectra of Au NPs on TiO_2 after 600–700 (blue), 700–800 (red) and 800–1000 (purple) nm light irradiation (10 mW cm^{-2}, 30 min) in 0.5 M aqueous solution of (b) KSCN, (c) KBr and (d) KCl.

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because SCN_3^- is unstable in aqueous media,[25] as described above. The direct oxidation should also be the major pathway in the case of X = Br and Cl, because the potentials for the direct oxidation are more negative than those for the X_3^- generation (Fig. 1a). In particular, the potential for Cl_3^- generation is even more positive than that of water oxidation.

Photoreactivity at different pH

Next we examined the dependence of the photoreactivity on the solution pH, which affects the flatband potential of TiO_2 at the TiO_2–solution interface E_{fb-sol}. Actually, the flatband potential of TiO_2 is known to shift by −0.06 V per pH unit due to deprotonation of surface hydroxyl groups.[27] We irradiated the Au NP-modified TiO_2 sample with monochromatic light at 700, 800 and 900 nm (4 mW cm^{-2}, fwhm = 10 nm) in 0.5 M aqueous KCl at pH 7, 8 or 9 (adjusted with KOH; the film was damaged at pH 10). As a result, dip formation was observed at all the wavelengths at pH 7 (Fig. 3a), whereas it was not observed at 900 nm at pH 8 and 9 (Fig. 3b, c). The E_{fb-sol} values were estimated for the TiO_2 film without Au NPs by voltammetry to be −0.14, −0.20 and −0.25 V *vs.* NHE at pH 7, 8 and 9, respectively. On the other hand, the potential for the Au/$[AuCl_4]^-$ redox couple E_{Au-Cl}, which does not involve H^+ or OH^-, should not depend on pH.

There are two possible explanations for the suppression of the photoreactions at high pH. (I) If the TiO_2 CB level at the TiO_2–Au NP interface E_{fb-Au} is not affected by the CB level at the TiO_2–solution interface E_{fb-sol}, the rise of the latter could slow down electron transport from the TiO_2–Au NP interface to other parts of TiO_2 and thereby lower the charge separation efficiency. However, the dependence of the reactivity on the excitation wavelength only at higher pH is not explained by this hypothesis. (II) If E_{fb-Au} is affected by E_{fb-sol} because the area of the TiO_2–Au NP interface is so small, the photopotential at Au NPs may depend on pH. The photopotential may also depend on the excitation wavelength.

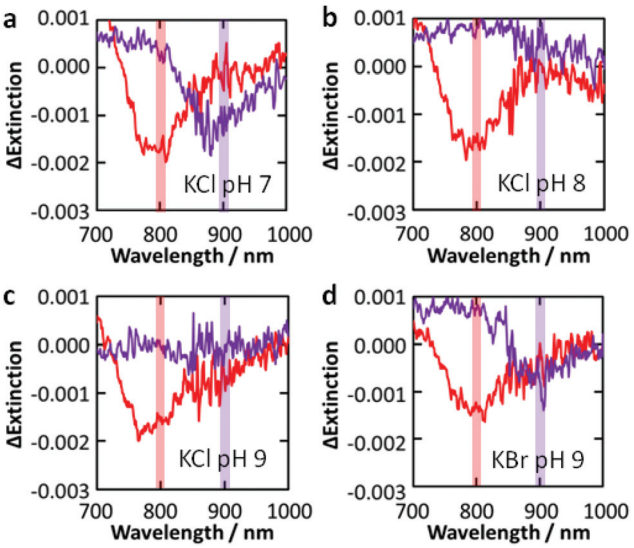

Fig. 3 Difference extinction spectra of Au NPs on TiO_2 after irradiation with 800 and 900 nm (4 mW cm^{-2}, 30 min) light in 0.5 M KCl ((a) pH 7, (b) 8 and (c) 9) and (d) KBr (pH 9) aqueous solutions.

In the plasmon-induced charge separation, some electrons in a resonant Au NP should be transferred to TiO_2 through the Schottky barrier at the TiO_2–Au NP interface.[3,19] The barrier height ΔE_S is estimated to be ~1.2 eV or higher, as the electron affinity of nanoparticulate anatase TiO_2 and the work function of Au are ~3.9 eV[28,29] and 5.1–5.47 eV,[30,31] respectively. Sönnichsen *et al.*[32] described that LSPR decays partially *via* inter- or intraband transition. However, it may not be reasonable to assume that those excited states are long-lived enough to be involved in the electron transfer from Au NPs to TiO_2, unless electrons pass through trap states, if any, at the TiO_2–Au interface. If not, it is likely that the electron transfer is due to hot electron injection or external photoelectric effect. Under irradiation of photons with an energy of ΔE_p eV that is higher than the Schottky barrier height ΔE_S (*i.e.* $\Delta E_p \geq \Delta E_S$), those types of electron transfer may shift the potential of Au NPs positively up to $E_{fb-Au} + \Delta E_p$ V (Fig. 1c). If this is the case, the spectral dip formation should be suppressed when the $E_{fb-Au} + \Delta E_p$ is more negative than $E_{Au-Cl} + \Delta E_{op}$, where ΔE_{op} is the overpotential needed for the redox reaction. That is, the photo-induced redox reaction could be suppressed at high pH and at a long wavelength even if $\Delta E_p \geq \Delta E_S$.

Actually, the reaction occurs under 700 and 800 nm light (ΔE_p = 1.77 and 1.55 eV, respectively) at pH 7–9, where $E_{fb-Au} + \Delta E_p$ = +1.30–+1.63 V *vs.* NHE on the assumption that $E_{fb-Au} = E_{fb-sol}$. Also, it occurs under 900 nm light (ΔE_p = 1.38 eV) at pH 7 ($E_{fb-Au} + \Delta E_p$ = +1.24) but not at pH 8 and 9 ($E_{fb-Au} + \Delta E_p$ = +1.13–+1.18). Therefore, the threshold exists at +1.18–+1.24 V. The difference between this threshold potential and the standard electrode potential for the formation of $[AuCl_4]^-$ (+1.00 V *vs.* NHE) may be explained in terms of the reaction overpotential and/or the difference between E_{fb-Au} and E_{fb-sol}.

Photoreactivity in the presence of different anions

Replacement of KCl with KBr resulted in dip formation in all the cases examined, even at pH 9 under 900 nm light (Fig. 3d), where the $E_{fb-Au} + \Delta E_p$ value is +1.13 V *vs.* NHE. This value is sufficiently positive compared with the standard potential for the formation of $[AuBr_4]^-$ (+0.85 V *vs.* NHE; Fig. 1a), even taking the possible overpotential of 0.18–0.24 V into account. It is thus suggested that the photopotential of Au NPs is dominated by E_{fb} and ΔE_p. Since E_{fb} is related not only to pH but also to the coexisting cations and semiconductor, these factors as well as the light wavelength would be optimized for intended reactions.

4. Conclusions

Wavelength-selective spectral dip formation was observed for the Au NP–TiO_2 system in the presence of KX (X = SCN, Br or Cl). These results suggest that the dip formation is caused by direct oxidation of Au NPs to $[AuX_4]^-$. The reactivity of Au NPs

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depends on both solution pH and excitation wavelength, suggesting that the photopotential of Au NPs depends on both the flatband potential of TiO_2 and the energy of irradiated photons. The results indicate that the reactivity and efficiency of the plasmon-induced charge separation can be tuned and optimized by changing those factors.

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Notes and references

1 S. Link and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 8410.
2 T. Jensen, L. Kelly, A. Lazarides and G. C. Schatz, *J. Cluster Sci.*, 1999, **10**, 295.
3 Y. Tian and T. Tatsuma, *J. Am. Chem. Soc.*, 2005, **127**, 7632.
4 Y. Tian and T. Tatsuma, *Chem. Commun.*, 2004, 1810.
5 Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota and A. Fujishima, *Nat. Mater.*, 2003, **2**, 29.
6 T. Yamaguchi, E. Kazuma, N. Sakai and T. Tatsuma, *Chem. Lett.*, 2012, **41**, 1340.
7 E. Kowalska, R. Abe and B. Ohtani, *Chem. Commun.*, 2009, 241.
8 H. Kominami, A. Tanaka and K. Hashimoto, *Chem. Commun.*, 2010, **46**, 1287.
9 Y. Takahashi and T. Tatsuma, *Appl. Phys. Lett.*, 2011, **99**, 182110.
10 Z. H. Chen, Y. B. Tang, C. P. Liu, Y. H. Leung, G. D. Yuan, L. M. Chen, Y. Q. Wang, I. Bello, J. A. Zapien, W. J. Zhang, C. S. Lee and S. T. Lee, *J. Phys. Chem. C*, 2009, **113**, 13433.
11 P. Reineck, G. P. Lee, D. Brick, M. Karg, P. Mulvaney and U. Bach, *Adv. Mater.*, 2012, **24**, 4750.
12 T. Tatsuma, *Bull. Chem. Soc. Jpn.*, 2013, **86**, 1.
13 K. Naoi, Y. Ohko and T. Tatsuma, *J. Am. Chem. Soc.*, 2004, **126**, 3664.
14 E. Kazuma and T. Tatsuma, *Chem. Commun.*, 2012, **48**, 1733.
15 N. Crespo-Monterio, N. Destouches, L. Bois, F. Chassagneux, S. Reynaud and T. Fournel, *Adv. Mater.*, 2010, **22**, 3166.
16 I. Tanabe and T. Tatsuma, *Nano Lett.*, 2012, **12**, 5418.
17 T. Tatsuma, K. Takada and T. Miyazaki, *Adv. Mater.*, 2007, **19**, 1249.
18 K. Kawahara, K. Suzuki, Y. Ohko and T. Tatsuma, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3851.
19 N. Sakai, Y. Fujiwara, Y. Takahashi and T. Tatsuma, *ChemPhysChem*, 2009, **10**, 766.
20 Y. Takahashi and T. Tatsuma, *Nanoscale*, 2010, **2**, 1494.
21 Y. Nishijima, K. Ueno, Y. Yokota, K. Murakoshi and H. Misawa, *J. Phys. Chem. Lett.*, 2010, **1**, 2031.
22 T. Tachikawa, T. Yonezawa and T. Majima, *ACS Nano*, 2013, **7**, 263.
23 A. Furube, L. Du, K. Hara, R. Katoh and M. Tachiya, *J. Am. Chem. Soc.*, 2007, **129**, 14852.
24 Y. Konishi, I. Tanabe and T. Tatsuma, *Chem. Commun.*, 2013, **49**, 606.
25 O. Barbosa-Filho and A. J. Monhemius, *Trans. Inst. Min. Metall. C*, 1994, **103**, C105.
26 K. Matsubara, K. L. Kelly, N. Sakai and T. Tatsuma, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2263.
27 A. Fujishima, A. Sakamoto and K. Honda, *Seisan Kenkyu*, 1969, **21**, 450.
28 R. Könenkamp, *Phys. Rev. B: Condens. Matter*, 2000, **61**, 11057.
29 F. Lenzmann, J. Krueger, S. Burnside, K. Brooks, M. Grätzel, D. Gal, S. Rühle and D. Cahen, *J. Phys. Chem. B*, 2001, **105**, 6347.
30 H. B. Michaelson, *J. Appl. Phys.*, 1977, **48**, 4729.
31 D. E. Eastman, *Phys. Rev. B: Solid State*, 1970, **2**, 1.
32 C. Sönnichsen, T. Franzl, T. Wilk, G. von Plessen, J. Feldmann, O. Wilson and P. Mulvaney, *Phys. Rev. Lett.*, 2002, **88**, 077402.

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