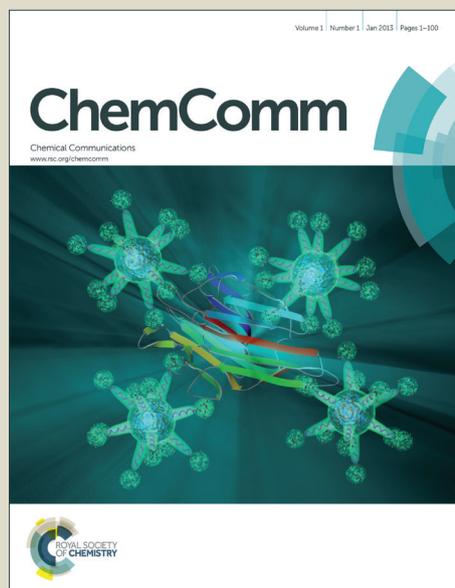


ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Titania photocatalysis through two-photon band-gap excitation with built-in rhodium redox mediator

Joanna Kuncewicz^{*a} and Bunsho Ohtani^b

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Titania particles modified with extremely small amount (< 0.01mol%) of rhodium species exhibited photocatalytic activity for oxidative decomposition of acetaldehyde in air under visible-light irradiation through two-photon band-gap excitation mechanism, resembling so-called Z-scheme with an external redox couple, using a built-in Rh(III)/Rh(IV) redox couple.

It has been often stated in papers of studies on visible light-active photocatalysts that titanium(IV) oxide (titania) has many advantages as a photocatalyst, e.g., chemical stability both in the dark and under photoirradiation, sufficient redox ability in the excited state even inducing water splitting, non-toxicity, and high availability, though titania can be excited only by ultraviolet light (UV).¹ To overcome this sole disadvantage of titania, there are two strategies. One is to find a photocatalyst absorbing visible light keeping the advantages of titania, but such a "superman" metal-oxide photocatalyst has not yet been discovered in spite of at least 40-years attempts by many researchers. The other strategy is to modify titania to give visible-light absorption, by e.g., doping with nitrogen,² sulfur³ or carbon⁴ or loading metal oxide clusters⁵ to put filled and vacant electronic states, respectively, in the band gap of titania. However, one of the titania advantages, sufficient redox ability, may be lost, since, in the former and the latter cases, positive holes in the valence band (VB) and photoexcited electrons in the conduction band (CB) of titania, which induce redox reactions when titania is excited by ultraviolet light, cannot be used, respectively. Therefore, a remaining strategy to develop visible light-active titania is to introduce a mechanism of two-photon band-gap excitation.

Rhodium (Rh)-doping, modifying with small amount of Rh species without changing the original crystal structure, has been already employed to develop visible light-active titania⁶⁻⁹ or

strontium titanate (SrTiO₃).¹⁰⁻¹⁴ It has been claimed that photoexcitation from Rh(III) to the CB of titania or SrTiO₃ leaves Rh(IV) which oxidizes compounds adsorbed on the surface. Thus, though the CB electrons can be used in a reduction step same as that in the case of UV band-gap excitation, oxidation is induced by localized species, Rh(IV), but not by VB positive holes. Here we report the visible light-induced photocatalysis by titania modified with extremely small amount of Rh, in which VB positive holes, as well as CB electrons, participate through two-photon band-gap excitation.

In present work, Rh-modified titania (Rh-TiO₂) samples were prepared by impregnation of commercial titania (Showa Denko Ceramics FP6, anatase) with rhodium(III) chloride (RhCl₃; Wako Pure Chemical; 0.001–0.1mol%) followed by calcination in air at 923 K for 3 h to result in rutile-based materials as confirmed by X-ray diffractometry (SI). A reference sample (0% Rh-TiO₂; rutile) was prepared by the similar calcination process without adding RhCl₃. Representative photoabsorption spectra are shown in Fig. 1. In addition to the absorption at < 420 nm by rutile titania, two shoulders at around 450 nm and 620 nm attributable to Rh(III) and Rh(IV), respectively,^{7, 15} appeared by Rh-modification. The latter was evident for the sample with relatively large amount of Rh (> 0.01%), i.e., loaded Rh was predominantly in the valency of Rh(III).

Photocatalytic activity of samples was evaluated by the rate of carbon dioxide (CO₂) liberation by visible-light photoirradiation (> 440 nm) of a sample (50 mg; spread in a 1 cm²-area sample holder) in a reaction chamber (357 mL) containing air and 224 ppm of acetaldehyde (ACh). As Fig. 2 shows, the activity higher than that of TiO₂ was observed for the sample modified with

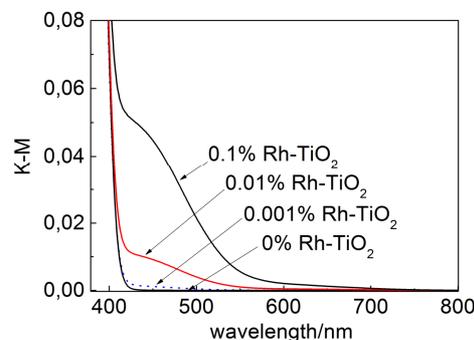


Fig. 1. Diffuse reflectance spectra of Rh-TiO₂ and a reference sample without rhodium species.

^aFaculty of Chemistry, Jagiellonian University, ul. R. Ingardena 3, 30-011 Kraków, Poland, Fax: +48 126340515; Tel: +48 126632005; E-mail: kuncewicz@chemia.uj.edu.pl

^bCatalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan, Fax: +81 11 706 9133; Tel: +81 11 706 9132; E-mail: ohtani@cat.hokudai.ac.jp

†Electronic Supplementary Information (ESI) available: Preparation procedure and experimental details, example of the time-course curve of photocatalytic test reaction, dependency of photocatalytic reaction rate on Rh-concentration determined for the materials calcined at 973 K. See DOI: 10.1039/b000000x/

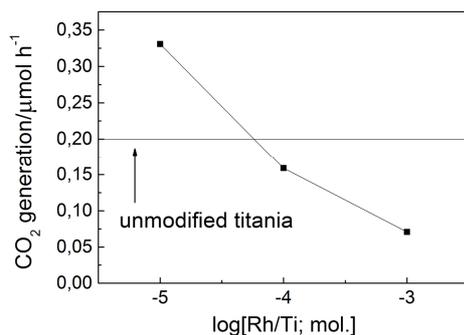


Fig. 2 Rates of CO₂ liberation in first two hours of the process of acetaldehyde oxidative decomposition in the presence of materials with various Rh concentration (black line – CO₂ generation rate in the presence of bare titania).

extremely small amount of Rh (<0.01%). Although the origin of visible-light activity of TiO₂ (non-modified) may be very small undetectable absorption due to surface states and is still ambiguous, the loading-amount depending activity suggests that the TiO₂-originated activity might be diminished by overlaying of Rh species of relatively high content hindering intrinsic photoabsorption of titania. A possible reason for lower photocatalytic activity of samples with relatively large amount of Rh might be also higher content of Rh(IV), which was negligible for extremely low Rh-loaded samples as seen in Fig. 1, which may act as an electron trap to enhance electron-hole recombination.^{7, 12} Thus, extremely small amount of Rh gives titania visible-light activity. The optimal Rh concentration should be around 0.0005–0.001%, what was confirmed also by studies on photocatalytic activity of less active samples calcined at slightly higher temperature (973 K) (SI). Characterization of the sample with Rh in such low concentration was rather difficult due to small intensity of photoabsorption of Rh species, therefore, a 0.01% sample was used for the following experiments. It is suggested that active Rh species were small and attached on the surface because repeated rinsing of the samples with water caused appreciable, not complete, decrease in the photoabsorption but almost complete loss of photocatalytic activity under visible-light irradiation. Considering extremely small amount, i.e., ~0.008–0.08 Rh atoms per 1 nm² of titania of specific surface area 10 m² g⁻¹, isolated Rh ions might be dispersed on the titania surface in the form of oxide clusters or even be embedded in titania crystal lattice near to the surface, which is supported by the observed strong interaction of these species with titania.

It should be noted that photoabsorption of the active samples changed during the photoirradiation and the behavior depended on the photoirradiation-wavelength range. Upon irradiation with light of the wavelength range 440–550 nm, overlapping the absorption band assigned to Rh(III), decrease in the band intensity along with the increase in the intensity of band assigned to Rh(IV) could be observed, while subsequent irradiation with full wavelength range light (440–730 nm) caused slight increase and decrease in the intensity of the 450-nm band and the 620-nm band, respectively, i.e., the longer wavelength part of the irradiation (550–730 nm) recovered Rh(III) from once produced Rh(IV) (Fig. 3, upper). Irradiation with light of the longer wavelength ranges (590–730 nm) recovered Rh(III) to the

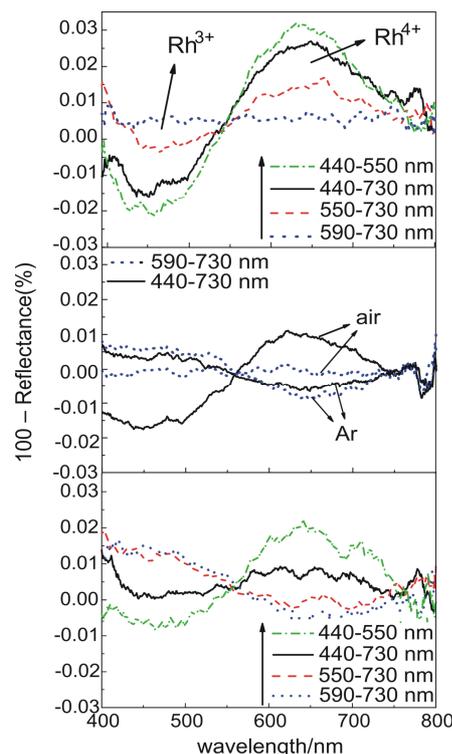


Fig. 3 Differential absorption spectra of 0.01% Rh-TiO₂ (with reference to the spectrum of the sample kept in a dark) under photoirradiation with light of various wavelength ranges (upper) in air, (middle) in air or under argon, and (lower) in the presence of AcH in air.

original concentration, since transition of Rh(III) to Rh(IV) cannot be induced by this longer-wavelength irradiation. Photoinduced regeneration of Rh(III) under the irradiation with light from the range 590–730 nm, seems to be slower than the reversed process. In-situ photoabsorption measurements shown in Fig. 3 (lower) confirmed light wavelength-controlled reversibility of this redox processes during the photocatalytic reactions.

The photoinduced absorption changes depended strongly on the presence/absence of electron acceptors and donors in the system (Fig. 3). In the absence of oxygen, photoinduced generation of Rh(IV) was not observed or even original Rh(IV)-concentration decreased upon irradiation, indicating that the shorter-wavelength light does not work, i.e. electrons excited from Rh(III) to the titania CB must be consumed by oxygen adsorbed on the surface. On the other hand, the presence of AcH enhanced photoinduced regeneration of Rh(III); higher and lower concentration of Rh(III) and Rh(IV), respectively, were observed in all the cases of wavelength ranges. These facts suggested that efficiency of photoinduced reduction of Rh(IV) may be improved by enhancement of consumption of the VB positive holes by AcH. It was also observed that the Rh(IV)/Rh(III) ratio was decreased slowly in the dark in the presence of AcH, indicating that AcH reduces Rh(IV) slowly.

Thus, it was clarified that the photocatalysis by Rh-TiO₂ contains at least two independent photoexcitation processes; excitations from Rh(III) to the titania CB by 440–550-nm light and from the titania VB to Rh(IV) by irradiation of wavelengths

from 590 to ca. 730 nm. In order to confirm the synergy of these two photoreactions, the following experiments were performed (SI), as shown in Fig. 4, in which full output (440–730 nm) of a xenon arc was divided by wavelength ranges into two parts, 440–550 nm and 590–730 nm (provided by two light sources assuring similar intensities of both radiations (SI)), corresponding to photoabsorption by Rh(III) and Rh(IV), respectively. Negligible photocatalytic activity under the irradiation of only the longer-wavelength region was attributed to lower concentration of Rh(IV) to be excited, which could not be generated under such irradiation conditions, and/or accumulation of electron in Rh(III) without transferring to oxygen. However, the rate of CO₂ liberation when irradiated in both wavelength ranges was higher than that under irradiation with light of the shorter-wavelengths, i.e., synergetic effect was observed for 0.01% Rh-TiO₂, while no such synergetic effect of full range irradiation was seen for 0% Rh-TiO₂. Analysis of the absorption spectra of 0.01% Rh-TiO₂ recorded during the full-range irradiation in the presence of AcH showed negligible detectable change in the Rh(III)/Rh(IV) ratio, while shorter-wavelength irradiation caused accumulation of Rh(IV) due to slow reduction by AcH without photoinduced reduction, which might induce the slow deactivation of the sample in such conditions (Fig. 3, lower). Slightly higher enhancement of the reaction upon full-range irradiation observed at the beginning of the reaction, might be explained by the recapturing of active Rh(III) through reduction of Rh(IV) intrinsically present in the sample.

On the basis of above-mentioned results and discussion, mechanism of the present photocatalytic reaction system with Rh-TiO₂ can be schematically shown in Fig. 5. Photons of relatively higher energy (440–590 nm) excite electrons in Rh(III) into the titania CB to leave Rh(IV) while photons of lower energy (590–730 nm) excite electrons in the titania VB to Rh(IV) to leave positive holes in the VB and to recover Rh(III). As a result, CB electrons and VB positive holes are generated by two visible-light photons, i.e., two-photon band-gap excitation proceeds using Rh species, a built-in redox mediator. Such mechanism is supported by theoretical calculations which showed that Rh-doping of rutile titania should induce intermediate bands within titania band gap.^{15–17} This photocatalysis has, at least, three advantages. First, the two different excitation processes occur in each titania particle because of the built-in redox mediator, which is contrastive to so-called Z-scheme photocatalysis using two kinds of photocatalyst particles.^{18–21} Second, the sufficient redox ability of titania is kept by the ensuant band-gap excitation. Third, two excitations require different range of light wavelength which are not overlapped with each other. Since the ordinary light sources, e.g., solar radiation, contains light of wide range of wavelengths covering both excitation processes in the present photocatalyst, the overall efficiency is not lowered even if two photons are required to make band-gap excitation.

At present, the overall efficiency is quite low to be competitive with rutile titania under visible-light irradiation. This must be improved by increase in concentration of "active" Rh species avoiding formation of large aggregates of Rh oxide. One possible strategy to realize this is "true doping" of Rh(IV) ion in the titania lattice, since the ionic radius of Rh(IV) is almost same as that of Ti(IV) and valency and coordination are the same for

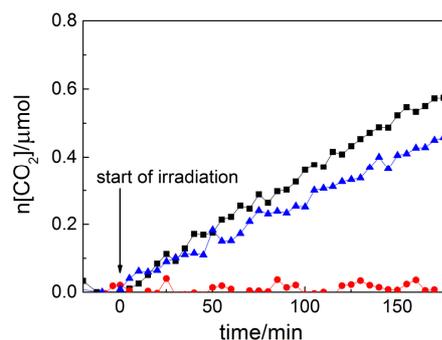


Fig. 4 Amounts of CO₂ generated in the process of AcH oxidative decomposition in the presence of 0.01% Rh-TiO₂ under irradiation with various light ranges ([440–550 nm and 590–730 nm] - black squares, [440–550 nm] - blue triangles, [590–730 nm] - red circles).

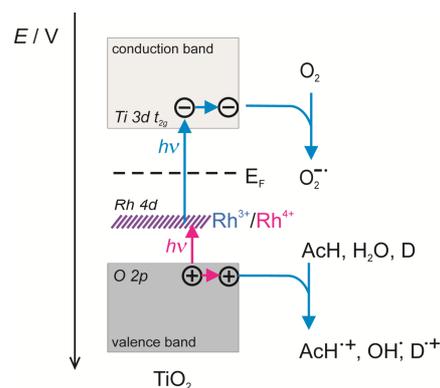


Fig. 5 Schematic representation of mechanism of photocatalytic reaction with Rh-TiO₂ (D - electron donor).

Rh(IV) and Ti(IV). Study on this line is now in progress.

The present mechanism of "two-photon band-gap excitation" of titania is, within the authors' knowledge, sole possible solution for overcoming the disadvantage of a titania photocatalyst, not excited by visible light, without losing the advantages and gives a new insight on visible light-induced photocatalysis by metal-oxide particles.

This work was supported by Ministry of Science and Higher Education in Poland within Iuventus Plus grant (No.:IP 2012030572).

References

1. A. Fujishima, X. Zhang and D. A. Tryk, *Surf. Sci. Rep.*, 2008, **63**, 515-582.
2. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269-271.
3. T. Umabayashi, T. Yamaki, H. Itoh and K. Asai, *Appl. Phys. Lett.*, 2002, **81**, 454-456.
4. H. Irie, Y. Watanabe and K. Hashimoto, *Chem. Lett.*, 2003, **32**, 772-773.
5. Y. Nosaka, S. Takahashi, H. Sakamoto and A. Y. Nosaka, *J. Phys. Chem. C*, 2011, **115**, 21283-21290.
6. W. Choi, A. Termin and M. R. Hoffmann, *J. Phys. Chem.*, 1994, **98**, 13669-13679.
7. R. Niishiro, R. Konta, H. Kato, W.-J. Chun, K. Asakura and A.

-
- Kudo, *J. Phys. Chem. C*, 2007, **111**, 17420-17426.
8. A. K. P. D. Savio, J. Fletcher and F. C. R. Hernandez, *Ceram. Int.*, 2013, **39**, 2753-2765.
9. Y. Matsumoto, T. Shimizu, A. Toyoda and E. Sato, *J. Phys. Chem.*,
5 1982, **86**, 3581.
10. R. Konta, T. Ishii, H. Kato and A. Kudo, *J. Phys. Chem. B*, 2004,
108, 8992-8995.
11. K. Iwashina and A. Kudo, *J. Am. Chem. Soc.*, 2011, **133**, 13272-
13275.
- 10 12. K. Furuhashi, Q. Jia, A. Kudo and H. Onishi, *J. Phys. Chem. C*, 2013,
117, 19101-19106.
13. H. W. Kang and S. B. Park, *Int. J. Hydrogen Energ.*, 2013, **38**, 823-
831.
14. P. Shen, J. C. Lofaro Jr., W. R. Woerner, M. G. White, D. Su and A.
15 Orlov, *Chem. Eng. J.*, 2013, **223**, 200-208.
15. F. E. Oropeza and R. G. Egdell, *Chem. Phys. Lett.*, 2011, **515**, 249-
253.
16. K. K. Ghuman and C. V. Singh, *J. Phys. Condens. Matter*, 2013, **25**.
17. K. Song, X. Han and G. Shao, *J. Alloys Compd.*, 2013, **551**, 118-124.
- 20 18. Y. Sasaki, H. Nemoto, K. Saito and A. Kudo, *J. Phys. Chem. C*,
2009, **113**, 17536-17542.
19. K. Sayama, K. Mukasa, R. Abe, Y. Abe and H. Arakawa, *J.*
Photoch. Photobio. A, 2002, **148**, 71-77.
20. Y. Sasaki, A. Iwase, H. Kato and A. Kudo, *J. Catal.*, 2008, **259**, 133-
25 137.
21. R. Abe, *J. Photoch. Photobio. C*, 2010, **11**, 179-209.