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Author(s)	王, 堃垒
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Titania photocatalysis:

New insights in the photocatalytic mechanism, and exemplary applications

（酸化チタン系光触媒反応：光触媒反応機構における新しい視点と典型的応用）

Kunlei WANG

Although studies on titania photocatalysis were started more than a century ago and have been intensified during last four decades (after discovery of “Honda-Fujishima effect”), there are still many non-answered questions concerning the reason of high-low activity of titania photocatalysts and the clarification of key-factors of high activity. It is known that similar to catalytic reactions, small crystallite sizes and large specific surface area are responsible for high photocatalytic activity. However, in the case of photocatalysis, photoabsorption properties and intrinsic properties of distribution of electron traps are very crucial. Moreover, interactions between various phases in particular titania samples are also possible and could not be neglected. In the case of heterogeneous photocatalysis, the “photocatalyst” is semiconductor, in which electron is excited from the conduction band (CB) to valence band (VB) under irradiation with energy equal or larger than its bandgap. The excited electron and positive hole (formed in VB) initiate reactions that cannot carry out spontaneously without photocatalyst, and, at the same time, photocatalyst is not changed. When the position of VB is more positive the ability of oxidation is higher; whereas when the position of CB is more negative the ability of reduction is higher. Therefore, the wide bandgap of semiconductor results in the efficient redox properties, (e.g., simultaneous reduction and oxidation of water), but also at the same, wide bandgap means inactivity under visible light. In the case of titania, which is the best and the sole material, there are quite large variations in the photocatalytic activity of titania photocatalysts even if they are composed of same chemical composition. The merits of titania as photocatalyst are its photostability, sufficient redox ability, non-toxicity, and availability, as well as that their thin films are colorless and transparent to give no change in appearance of substrate materials.

Degussa (Evonik) P25 (P25), is a commercial titania photocatalyst, used widely because of its exceptionally high level of photocatalytic activity in many photocatalytic reaction systems. Actually, it is not easy to find a photocatalyst showing activity higher than that of P25. Therefore, P25 has been used as standard titania photocatalyst. P25 is white powder with fine particles (ca. 25 nm) and hydrophilic character meaning it interacts well with water because the titania surface is coated with hydroxyl groups that can form hydrogen bonds with water molecules. In P25 powder fine particles join and form aggregates (where many primary particles are loosely bound together). The density of P25 is ca. 3.9 g cm^{-3} and the specific surface area (SSA) is ca. 50 m^2 g^{-1}. The P25 powder contains a mixture of anatase and rutile

in an approximately 5.6:1 proportion. It has been proposed that the mixture of anatase and rutile in this proportion is important to ensure the best photocatalytic properties of titania. Although, there are thousands of reports on P25, they differ significantly, even on the properties of P25. The most often reported ratio of anatase to rutile in P25 was 70:30 or 80:20, without an exact determination of crystalline composition. Anatase, the main composite of P25 is usually the most photocatalytically active polymorph of titania, as shown in many reports. It was suggested that in P25, small crystals of anatase surround the large crystals of rutile. In many reports, rutile is described as low active phase of titania. In P25, its content does not extend ca. 30 %. It should be mentioned that P25 consists also amorphous titania. However, in many reports, amorphous phase has not been even considered in P25. Recently, some reports have discussed the photocatalytic activity of amorphous titania. Exceptionally high photocatalytic activity of P25 (mixed-phase titania) could not be simply explained by its properties (good, but not the best properties, such as crystallite size, specific surface area, crystallinity). Therefore, various reasons of its activity have been presented, and mainly the "synergy" between anatase and rutile has been postulated. To confirm "synergistic effect" (or/and IPCT), usually physical methods have been used, such as mixing and thermal treatment. Phase mixing can be performed either in the aqueous suspension of two or three kinds of titania particles or by grinding. Higher activity of the mixed-phase sample than that of sole anatase or rutile was explained as a proof for "synergistic effect". For example, Ohno et al. in 2003 reported "synergism" between rutile and anatase in photocatalytic oxidation of naphthalene for titania samples prepared by two methods: mixing of anatase and rutile and thermal treatment of anatase. The synergetic effect was found in both kinds of samples (activity higher than the simple sum of its parts), and it was proposed that IPCT was responsible for this synergy. Moreover, the activity of the most active mixed-phase titania was similar to that of P25. Based on these data, similar "synergy" was proposed for P25, i.e., electron transfer between anatase and rutile, resulting in its high photocatalytic activity. Investigation on "synergy" by thermal treatment method uses the intrinsic properties of titania, i.e., the stability. It is known that metastable anatase and brookite phase convert irreversibly to rutile upon heating. Therefore, during thermal treatment the mixture of anatase and rutile can be easily obtained, e.g., anatase particle can be loaded with rutile particle. For example, Jing et al. reported that anatase-rutile mixed sample were prepared by calcination of titania, prepared by precipitation method. However, in that study, the La_2O_3 was additionally loaded on the surface of titania samples, and thus, possible synergy between anatase and rutile could not be directly confirmed. Moreover, it should be pointed that thermal treatment can change not only the composition of samples (anatase/rutile ratio), but also all other properties, such as particle size, specific surface area, morphology, electron traps (ET) content, etc. In some studies, "synergy" in P25 was suggested in comparison to anatase and rutile that did not originated from P25, and thus with quite different properties than that in P25. Additionally,

some photocatalytic activity tests were carried out in the presence of loaded co-catalyst and thus properties of co-catalyst could be more decisive for overall activity than that of titania components.

In the previous studies performed in Ohtani laboratory (Fig. 1), anatase and rutile particles were successfully isolated from P25 by chemical method, and photocatalytic activity of isolated titania particles and re-built P25 (R-P25, same anatase/rutile ratio as in original P25 titania) was tested in four kinds of photocatalytic reactions, e.g., (a) oxidative decomposition of acetic acid under aerobic conditions, (b) oxidative decomposition of acetaldehyde in air, (c) dehydrogenation of methanol in a deaerated aqueous solution and (d) oxygen liberation from a deaerated aqueous silver sulfate solution. It was confirmed that amorphous titania was almost inactive in all tested reactions (Unfortunately, amorphous titania was not isolated from P25 since it is impossible by chemical dissolution method. Therefore, other methods, e.g., vibration, have been tried to isolate amorphous titania from P25 in my study. Anyhow, it is not expected that the influence of amorphous phase on overall activity could be significant, due to its low content and negligible activity independently on preparation procedure (large content of defects as charge carriers' recombination sites)). Anatase showed highest activity for oxidative decomposition of acetic acid (a) and acetaldehyde (b), probably due to its larger bandgap than that of rutile (more negative CB allowing one-electron reduction of oxygen). In contrast, rutile showed the highest activity for oxygen evolution, which could be caused by co-presence of silver sulfate as electron acceptor and narrower bandgap (UV/vis light harvesting). It should be pointed that in three reaction systems (a, b and d) P25 and re-build P25 did not show the highest activity, and thus high activity of P25 could not be explained due to "synergy" or any IPCT between anatase and rutile, but by intrinsic high activities of it components (anatase and rutile) in different reaction systems. However, in the case of methanol dehydrogenation, P25 and R-P25 samples showed higher activity than that of anatase and rutile suggesting some interaction (e.g., IPCT) between two phases or between crystalline phases and amorphous titania. It should be mentioned that in this reaction, Pt NPs have been used as co-catalyst.

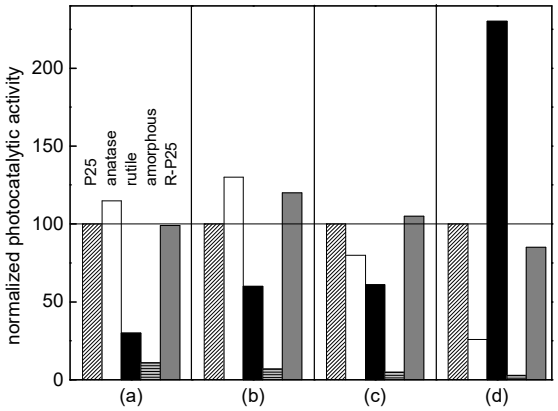


Fig. 1 The photocatalytic activity of P25, isolated-phases and re-constructed samples in four kinds of reaction. P25 was used as reference calculated the photocatalytic activity as 100%; (a) oxidative decomposition of acetic acid; (b) oxidative decomposition of acetaldehyde in air; (c) dehydrogenation of methanol in a deaerated aqueous solution; (d) oxygen liberation from a deaerated aqueous silver sulfate solution [B. Ohtani et al., *J. Photochem. Photobiol. A*, 216 (2010) 179].

Therefore, not only the properties of titania, but also the properties of Pt deposits should be considered for explanation of photocatalytic performance (both the efficiency and the mechanism). Accordingly, the first aim of my thesis was to explain the reason of high activity of P25 for methanol dehydrogenation, considering the properties of both titania and platinum.

During my study, P25 was homogenized first, and then crystalline phases (anatase and rutile) were isolated from it by chemical dissolution methods followed by samples' purification by washing and annealing (for rutile). It was found that purification resulted in efficient removal of adsorption species, such as ammonia/peroxy species and hydrofluoric acid from anatase and rutile surface, respectively. Unfortunately, it was impossible to remove all non-crystalline phase (mainly amorphous titania) since during chemical isolation, strong chemical etching could dissolve not only crystalline titania, but also initiate formation of amorphous titania (It is possible that amorphous titania layer could partly surround anatase and rutile crystals.). In addition, it was found that for dehydrogenation of methanol (test-c in previous studies; Fig. 1), rutile was responsible for high activity of P25, possibly due to ability of photoabsorption of more photons (narrow bandgap). It should be pointed that despite many reports on the migration of charge carries in titania particles have already been published, most of them only proposed that electrons are transferred to metal NPs changing the Fermi level, but difference in titania crystalline phase (anatase/rutile) are usually not even mentioned. Polymorphic forms of titania are different, i.e., they have different structure, different bandgap, and even in some mixed-phase titania (such as P25) anatase and rutile crystallites differ significantly, e.g., crystalline size, surface charge (zeta potential). Therefore, it must be expected that these differences should result in different migration of charge carries for anatase and rutile. Moreover, it is also clear that properties of deposited metal, as well as charge carriers' migration from titania to deposited metal could depend on titania kind. Of course, there are some reports on the influence of Pt properties and amount on the photocatalytic activity, but these reports are mainly for narrow range of platinum loading (0.5 wt% - 2.0 wt%) and not for different titania samples. To the best of my knowledge, there is no detailed study on the influence of platinum loading on the photocatalytic activity of P25 and isolated phases from P25. Moreover, my study on methanol dehydrogenation clearly indicates that rutile is more active than anatase (Chapter II). There are two main possible reasons of higher activity of rutile than anatase for methanol dehydrogenation: (1) better photoabsorption properties (narrower bandgap), (2) better distribution/deposition of Pt NPs (with double functions: inhibition of charge carriers' recombination and hydrogen evolution site). Therefore, platinum-deposited titania (both mixed-phase—P25 and single phase—anatase and rutile) have been investigated in detail (loading amount and action spectra). It was found that platinized rutile was more active than platinized anatase and platinized P25. Therefore, proposed in literature an electron transfer between two polymorphic forms of titania as the main reason of high photocatalytic activity of P25 has been discarded. It was found that with

an increase in Pt-loading amount, the photocatalytic activities increased for all tested samples, confirming that Pt NPs were necessary for efficient hydrogen evolution (Fig. 2 (left)). Although, the lower level of conduction band (CB) of rutile has been reported as the main reason of its lower photocatalytic activity than that of anatase (poor reduction ability of photogenerated electrons), the presence of Pt NPs (as a co-catalyst and an electron pool) compensates it, and probably the broader photoabsorption results in enhanced overall photocatalytic activity. For larger amount of loaded-platinum (2 wt%), the activities of all samples seemed to saturate (were almost the same), and slight decrease at the higher loadings are attributable to the shielding of light by Pt deposits. The saturation can be interpreted by the expectation that at least one Pt NP was deposited on each titania particle (all titania particles were modified), on the basis of assumption that only Pt-deposited particles were active for photocatalytic hydrogen evolution and the activity did not depend on the number of Pt NPs if at least one Pt NP was deposited, as was suggested previously. In the lower Pt content range (0.005–0.2 wt%), the photocatalytic activities of rutile and anatase were significantly (few times) larger than that of P25. It should be reminded that isolated samples were annealed at 473 K (for sample purification). Although this relatively low temperature

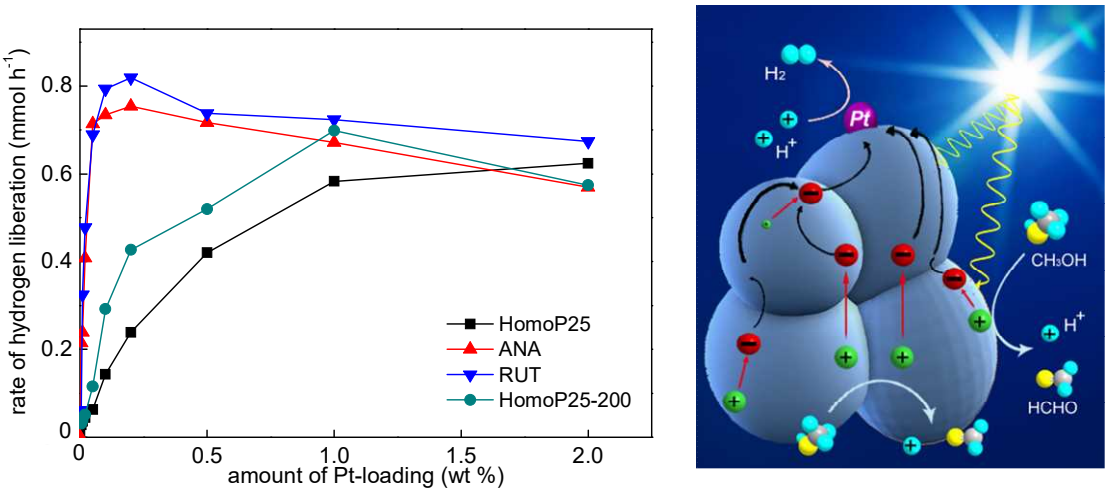


Fig. 2 The influence of platinum loading on efficiency of methanol dehydrogenation on P25 (HomoP25), anatase (ANA), rutile (RUT) and annealed P25 (HomoP25-200) (left), Schematic drawing of IPET for Pt-modified aggregated titania particles (right) [K. Wang et al., *Catal. Today,* 303 (2018) 327].

should not cause NPs sintering (that was confirmed by STEM observations since only a few larger rutile NPs could be noticed), it is proposed that the interface between NPs was increased allowing enhanced electron transfer between two (or more) titania NPs. In this regard, much lower amount of Pt could be sufficient for high photocatalytic activity, i.e., one Pt NP on one titania aggregate (as shown in Fig. 2 (right)). In other words, interparticle electron transfer (IPET) must occur within those aggregates/agglomerates formed by relatively low-temperature heating. Slight decrease in photocatalytic activity for larger than 0.2 wt% content of Pt for anatase and rutile is possibly caused by Pt aggregation (increase in Pt size with loading amount was observed) or “shielding effect” (as Pt NPs are dark limiting

photon absorption by titania). To confirm that enhanced photocatalytic activity could be obtained by titania NPs aggregation by annealing, P25 was also annealed at the same temperature as anatase and rutile (473 K), and obtained data for this sample (HomoP25-200) are shown also in Fig. 2 (left). It was found, that lower amount of Pt was sufficient to cause the same photocatalytic activity for HomoP25-200, e.g., the same photocatalytic activities for both samples were obtained for 0.2 wt% (HomoP25-200) and 0.5 wt% (HomoP25) of Pt loading. By the annealing at 473 K in air, the activity of HomoP25-200 at the lower region of Pt-loading amount was slightly improved compared with that of P25, i.e., the amount of Pt deposits required for activation of titania particles was reduced by annealing, but was lower than those of anatase and rutile. This may be also explained by the aggregation/agglomeration of titania particles by the relatively low-temperature heating to enable photoexcited electrons transfer within aggregates/agglomerates (IPET), and the effective size of HomoP25-200 aggregates/agglomerates for IPET is smaller than those of ANA (anatase) and RUT (rutile).

Action spectra of methanol dehydrogenation on bare and platinized-samples (for 0.2 wt% of Pt) were investigated, and obtained data are shown in Fig. 3. The necessity of Pt NPs' presence was confirmed since bare samples were practically inactive in this reaction system. At short UV range (350–365 nm), the apparent quantum efficiency (Φ_{app}) of platinized

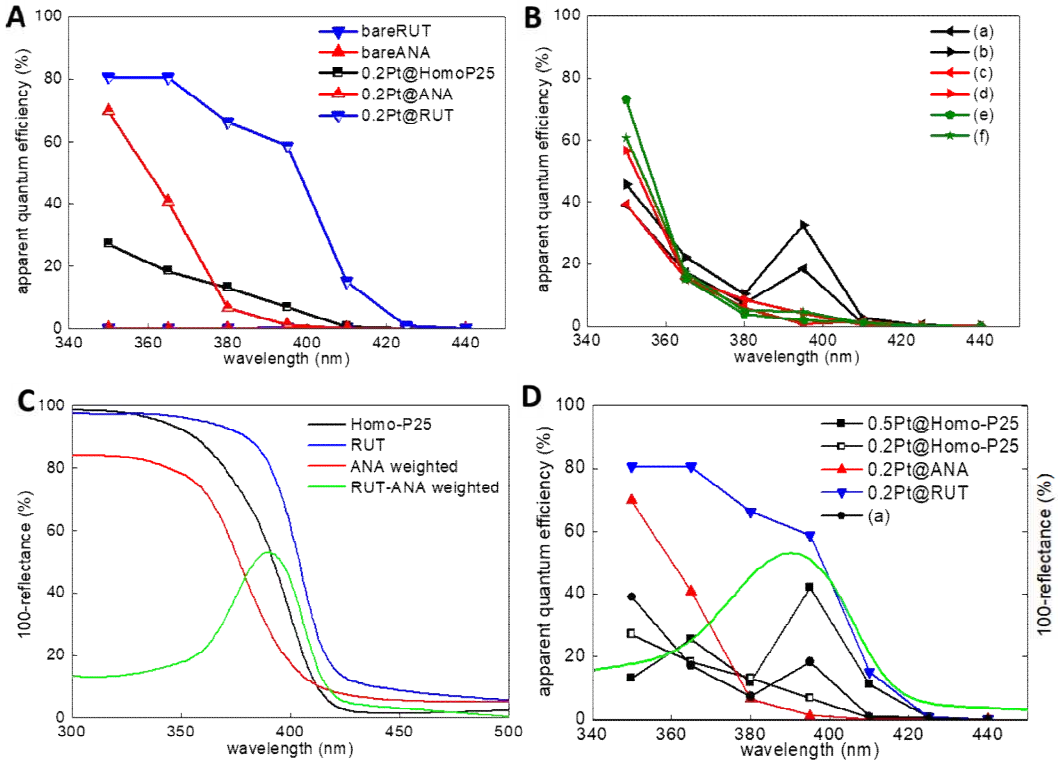


Fig.3. Action spectra (A, B, D) and absorption spectra (C, D) of samples. (a) 15% Pt(0.2 wt%)/RUT and 85% ANA; (b) 50% Pt(0.2 wt%)/RUT and 50% ANA; (c) 15% RUT and 85% Pt(0.2 wt%)/ANA; (d) 15% RUT and 85% Pt(0.1 wt%)/ANA; (e) 15% Pt(0.2 wt%)/RUT and 85% Pt(0.2 wt%)/ANA; (f) 15% Pt(0.1 wt%)/RUT and 85% Pt(0.1 wt%)/ANA [K. Wang et al., *Catal. Today,* 303 (2018) 327].

samples correlated with the overall photocatalytic activity of those samples (Fig. 3A), i.e., Pt@RUT > Pt@ANA > Pt@HomoP25. Much lower photocatalytic activity of Pt@HomoP25 was caused by insufficient amount of Pt in that sample (non-aggregated titania NPs), as has been discussed above (Fig. 2 (left)). The shape of action spectra of Pt@ANA and Pt@RUT resembled respective absorption spectra. Interestingly, the photocatalytic activity of Pt@HomoP25 was higher than that of Pt@ANA at UV range of 380-395 nm. It should be reminded that at this UV range mainly rutile absorbs light (especially at 395 nm). Therefore, higher photocatalytic activity of Pt@HomoP25 than that of Pt@ANA indicates that rutile was platinized first, especially taking into consideration much lower content of rutile than anatase in HomoP25 (14% vs. 78%). To confirm this assumption, various composition of samples (physical mixtures) were prepared and tested, i.e., (a) 15% Pt(0.2 wt%)/RUT and 85% ANA; (b) 50% Pt(0.2 wt%)/RUT and 50% ANA; (c) 15% RUT and 85% Pt(0.2 wt%)/ANA; (d) 15% RUT and 85% Pt(0.1 wt%)/ANA; (e) 15% Pt(0.2 wt%)/RUT and 85% Pt(0.2 wt%)/ANA; (f) 15% Pt(0.1 wt%)/RUT and 85% Pt(0.1 wt%)/ANA. Firstly, larger content of platinized sample in the mixture resulted in enhanced photocatalytic activity, i.e., (b) > (a), (c) > (d), and (e) > (f). At short wavelengths, the mixtures of both platinized phases ((e) and (f)) showed higher photocatalytic activities than that of mixtures composed of one bare and one modified phase, which is not surprising since both platinized phases showed high photocatalytic activities (as shown in Fig. 3A). It should be pointed that all those mixtures had lower activity than that of Pt@RUT. However, the Φ_{app} of (e) sample (Φ_{app}=73%, containing platinized anatase and rutile) was higher than that of Pt@ANA (Φ_{app}=69%) confirming that rutile was more active phase in this system. The most interesting is the shape of action spectra of (a) and (b) samples containing only platinized rutile with the sharp peak at 395 nm. The explanation is similar to that used for explanation of higher photocatalytic activity of Pt@HomoP25 than Pt@ANA (Fig. 3A), i.e., at this wavelength only rutile can absorb light, whereas at shorter wavelength (380 nm) both phases absorb light. Therefore, a decrease in Φ_{app} (at 380 nm) was caused by the competition between two phases: active (Pt@RUT) and inactive (ANA), about photon absorption. Interestingly, re-estimated absorption spectrum (from the DRS measurements of ANA and RUT) clearly shows characteristic peak (Fig. 3C) observed at action spectrum. The characteristic peak in the spectrum is clearly caused by the difference in photoabsorption properties between anatase and rutile, due to the difference in the bandgap of rutile (3.0 eV) and anatase (3.2 eV), i.e., i) at the wavelengths shorter than ca. 390 nm both anatase and rutile can absorb photons; ii) at 390–400 nm the absorption properties of anatase are decreasing, and iii) at the wavelength longer than ca. 400 nm only rutile can absorb photons. In addition, HomoP25 with larger content of platinum (0.5 wt%) was also tested and characteristic peak at 395 nm was obtained (Fig. 3D; the same as for (a) and (b) samples), confirming that rutile phase was platinized first. Therefore, it was shown that rutile is more active form of titania for methanol dehydrogenation in the presence of

platinum as a co-catalyst. Moreover, at first rutile was platinized, despite larger content of anatase in P25. One of the possible reasons is preferable adsorption of Pt precursor (hexachloroplatinum(IV) ions) on rutile particles in P25. As a general trend, it has been often reported that rutile particles tend to exhibit higher photocatalytic activity for deposition of metal such as silver than anatase particles. Another possible reason is preferable electron transfer from anatase particles, as a major component absorbing light, to rutile particles, which has often been claimed in the literature, since the conduction-bottom position of rutile is reported to be slightly lower than that of anatase.

Although, there are many reports claiming interparticle electron transfer (IPET) in heterogeneous photocatalytic systems, especially preferable transfer from anatase to rutile particles in P25, within my knowledge, there seemed to be no direct evidence for IPET. Therefore, in this thesis it is proposed that for P25 photocatalysis, no synergetic effect due to IPET between anatase and rutile is required for interpretation of high photocatalytic activity of P25. It is suggested that IPET may occur not only between anatase and rutile (hetero-IPET), but also between single anatase particles and single rutile particles when isolated ANA and RUT are heated at relatively low temperature to form aggregates/agglomerates (homo-IPET). This may be the first evidence for IPET of titania particles (Fig. 2 (right)).

Although, during my investigations new findings on titania photocatalysis have been discovered, such as interparticle electron transfer (IPET) and preferential platinization of rutile, some problems have been also observed, such as aggregation of Pt NPs. Therefore, second aim of my study was to inhibit this aggregation. I have found new method of metal photodeposition on titania, which allows to control the properties of platinum (and other noble metals), and thus resultant photocatalytic activities. The final aim of this research was to propose/obtain the photoactive materials with ability to work under solar radiation (both UV and vis range of solar spectrum) for environmental applications, such as decomposition of organic compounds, evolution of hydrogen and inactivation of microorganisms (bacteria and fungi).

Surface modification of titania with noble metal is one of the most efficient methods for improving the photocatalytic activity of titania photocatalysts. When metal NPs are deposited on the surface of titania, not only the surface properties of titania are changed, but also (photo)catalytic performance, by e.g., 1) improvement of activity by retardation of charge carriers' recombination (noble metal as an electron pool), 2) increasing the wavelength response range (light harvesting, e.g., due to surface plasmon resonance), and, 3) changing the selectivity and yield of products. Noble metals (NM: Pt, Au, Ag, Ir, Pd) in the form of either adsorbed complexes or metallic deposits have been used for improvement of photocatalytic activity of semiconductors. Surface modification of titania with NMNPs results in electrons transfer from titania to the modifiers forming the Schottky barrier. Moreover, there are plenty

of examples indirectly proving an electron transfer from titania to NM by enhancement of photocatalytic activity after semiconductor modification in both oxidation and reduction pathways. However, scavenging of electrons by NMNPs could also result in a decrease in photocatalytic activity, especially for reduction reactions occurring on titania surface (not on NM), because of decrease in number of available electrons, due to their transfer from titania to deposited NMNPs. The properties of both semiconductor and noble metal nanoparticles (NMNPs) strongly influence the resultant properties of NMNPs, such as specific surface area, crystallinity, crystalline size, photoabsorption properties, morphology, and thus resultant photocatalytic activities. Although, photodeposition method results in formation of large and non-uniform NPs, it is one of the best methods for preparation of NM-modified titania for few reasons: (1) fast and simple, (2) no need to use any organic solvents and stabilizing/capping agents, which are difficult to be removed from photocatalysts surface (influencing an overall activity), (3) polydispersity of formed NMNPs could be also advantageous. Therefore, photodeposition method has been used in this study. However, since NMNPs aggregate during fast photodeposition process, the interface between NM and titania is not large. To inhibit aggregation of NMNPs (to enhance NM-titania interface), and thus overall activity, NMNPs have been deposited on titania by modified photodeposition method (to slow down photodeposition speed). Modified photodeposition method allows to prepare photocatalysts with different properties, i.e., sizes and distribution of NMNPs, and thus different photocatalytic activity. In the case of methanol dehydrogenation, platinum (or other NM) is usually used as co-catalyst. However, aggregation of Pt NPs during fast photodeposition (anaerobic conditions and in the presence of methanol as hole scavenger) could result in low photocatalytic activity for hydrogen evolution since deposition of large aggregates of Pt NPs on titania (or in some cases these aggregates are surrounded by fine titania NPs) results in co-presence of many un-modified titania particles (with negligible activity), which compete with Pt-modified titania for photon absorption Therefore, preparation of NM-modified titania by novel photodeposition method, allowing to slow down photodeposition speed (e.g., in the initial presence of oxygen as electron scavenger), enables to obtained photocatalysts with more-uniform NM NPs, and thus well distributed on titania support.

Titania is probably the most widely studied and commonly applied heterogenous photocatalyst for both environmental purification (water/wastewater treatment, air purification, surface cleaning) and solar energy conversion. Exemplary applications, presented in this study, are focused on the most urgent problems focusing humanity, i.e., microbiological pollution and low quantum yield of heterogeneous photocatalysis under solar radiation. Therefore, titania photocatalysts, prepared during this research, have been applied for inactivation of microorganisms (bacteria and fungi) and decomposition of organic pollutants under visible light (vis) irradiation. It was found that titania photocatalysts could be efficiently used as antifungal agent for various strains of fungi. Its activity was confirmed

under irradiation and in the dark. It was shown that properties of titania were crucial for antifungal action. Though polymorphic forms of titania (anatase and rutile), isolated from commercial P25 photocatalyst, had similar surface properties (crystalline size), their activity highly differed, possibly due to slight difference in band-gap energy and thus ability of photoabsorption of more photons by rutile phase. In addition, it was shown that purification of isolated phases could result in slight change of their surface properties, i.e., particle aggregation, removal and/or adsorption of chemical species, which resulted in significant change in their antifungal properties. It is important to remind that different fungi had different demand for water and nutrient, and thus adsorbed water and some impurities (e.g., F^-, Na^+, HOO^-) on titania surface could either inhibit or stimulate their growth. Another important finding is that even when mycelium growth was similar, the sporulation and mycotoxin generation was highly inhibited by light and titania presence.

Modification of titania with noble metals (Pt, Au, Ag and Cu) resulted in high enhancement of photocatalytic and antimicrobial activities. It was found that kind of metal and preparation method significantly influenced resultant properties and thus activities of photocatalysts. All modified photocatalysts showed activity under visible light irradiation and inactivity in the dark except for Pt-modified titania (mainly, due to its "dark" catalytic activity). The visible activity of titania modified with Au and Ag (due to activation of their plasmon resonance (LSPR)) is well known and at present under extensive study. It was proposed that light absorption at broader wavelengths (wide LSPR) resulted in enhanced photocatalytic activity since more photons (of different energy) could be absorbed, and then efficiently participated in overall photocatalytic activity. Therefore, change of deposition conditions (from anaerobic to aerobic) correlates well with photoabsorption properties, i.e., broader LSPR results in higher activity. The visible activity of Cu-modified titania should result from excitation of Cu oxides possessing much narrower band-gap than titania (2.0-2.2 eV for Cu_2O and 1.3-1.6 eV of CuO). Details of this research (and other studies presented in my thesis) have already been published in the following papers:

[1] E. Kowalska et al., *Adv. Sci. Technol*., 93 (2014) 174;
[2] A. Markowsa-Szczupak et al., *Cent. Eur. J. Publ. Health*, 23 (2015) 267;
[3] A. Markowska-Szczupak et al., *J. Photochem. Photobiol. B*, 151 (2015);
[4] Z. Wei et al., *Catal. Today*, 280 (2017) 29;
[5] Z. Wei et al., *Chem. Eng. J*., 318 (2017) 121;
[6] Z. Wei et al., *Appl. Catal. B*, 206 (2017) 393;
[7] K. Wang et al., *Catal. Today*, 303 (2018) 327.

Other results from this thesis (after completion) will be published soon.