Journal Pre-proof

Spectrophotometric analysis: Challenge for a reliable evaluation of photocatalytic activity under visible light irradiation

Fitri Rizki Amalia, Bunsho Ohtani, Ewa Kowalska



PII: S1389-5567(25)00013-9

DOI: https://doi.org/10.1016/j.jphotochemrev.2025.100701

Reference: JPR100701

To appear in: Journal of Photochemistry & Photobiology, C: Photochemistry Reviews

date:

Please cite this article as: Fitri Rizki Amalia, Bunsho Ohtani and Ewa Kowalska, Spectrophotometric analysis: Challenge for a reliable evaluation of photocatalytic activity under visible light irradiation, *Journal of Photochemistry & Photobiology, C: Photochemistry Reviews,* (2025) doi:https://doi.org/10.1016/j.jphotochemrev.2025.100701

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2025 Published by Elsevier B.V.

Spectrophotometric analysis: Challenge for a reliable evaluation of photocatalytic activity under visible light irradiation

Fitri Rizki Amalia,^{1,*} Bunsho Ohtani² and Ewa Kowalska^{1,*}

¹ Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland

² Nonprofitable Organization Touche NPO, N4, W14, 060-0004 Sapporo, Japan

* Correspondence: fitri.rizki.amalia@uj.edu.pl; ewa.k.kowalska@uj.edu.pl

Abstract:

Even though dyes have often been used as a model pollutant in photocatalytic degradation tests, their utilization as a substrate might cause unreliable results. Under visible-light (vis) irradiation, dye absorbs light and might sensitize wide-bandgap photocatalyst, which usually is only active under UV. Consequently, dye-decoloration analysis should not be used in the evaluation of photocatalytic activity under vis. To obtain reliable data, colorless compounds are commonly considered as much better substrates for photocatalytic activity testing since they do not absorb vis. However, more expensive analytic methods (e.g., gas and liquid chromatography) than simple UV/vis spectrophotometry (or even spectrometry) must be used for estimation of their concentration. Moreover, colorless compounds might also interact with UV-active photocatalyst, e.g., via molecule to band charge transfer (MBCT), causing photoinduced activity under vis irradiation. Accordingly, this review presents possible prospective methods for reliable but also interpensive testing of photocatalytic activity under vis irradiation.

Keywords: photocatalytic activity; visible light; colorimetric analysis; dye decolorization; activity evaluation; colorless compound

1. Introduction

Water contamination as a result of improper disposal of wastes originating from various human activities, such as industry, medical facilities and agriculture, has been one of the major environmental problems [1,2]. Carcinogenic dyes, antibiotics and heavy metal ions are probably the most dangerous contaminants since they might cause fatal problems for human and aquatic life in the long term. There are many different methods of both pollution prevention and waste treatment. Considering the latter, heterogenous photocatalysis, belonging to advanced oxidation processes (AOPs), is one of the most preferable methods because high efficiency of pollutant mineralization could be achieved under mild conditions with negligible secondary pollution [3-6]. Photocatalysis as a method for pollutant mineralization can proceed simply with the use of only photocatalyst and light, and in the presence of air (Additional bubbling of air/oxygen is usually not necessary, though in some cases it might accelerate the purification process) [7-9]. Commonly, UV lamps are used as the light source due to the abundant availability of UV-active photocatalysts, e.g., the most famous – titania (titanium(IV) oxide). However, the use of UV lamps results in creation of additional costs (both investment and operation) for photocatalytic processes.

Therefore, many attempts have been made on the possibility of application of natural solar radiation as the light source for photocatalytic reactions. For example, the research on vis-active photocatalysts has attracted extensive attention as solar radiation consists of ca. 46% visible light, and thus many studies on preparation and characterization of vis-active materials have been carried out [10-13]. It should be pointed out that though vis-active photocatalysts could be successfully prepared, their activity under vis is usually much lower than that of titania under UV, and thus checking of their activity is not so simple. Accordingly, it must be underlined that a reliable method to evaluate the photocatalytic activity under vis is highly needed [15].

The most common method for activity testing is dye-decoloration analysis, because it is simple, fast and cheap - the necessary instrument, i.e., spectrophotometer, is easily available in most laboratories. However, for evaluation of photocatalytic activity under vis irradiation, the utilization of dye as a substrate might cause unreliability due to photocatalyst sensitization (commonly used effect in dye-sensitized solar cells) [16-18]. On the other hand, the utilization of colorless compounds has been considered as a reliable method since they do not absorb visible light. However, chromatographic analysis is usually used for quantitative measurements of these compounds (and their degradation products), which is much more expensive than spectrophotometric analysis (or even spectrometric one) and not often available in some laboratories, especially in developing countries. Accordingly, the analysis of colorless compounds by spectroscopic methods is the most wanted. Indeed, there are some reports showing that it is possible. However, even though photocatalyst sensitization can be avoided, it has been found that colorless compound might interact with photocatalyst, inducing an enhancement of photoabsorption in vis region.

This review presents the problems and challenges of using dyes and colorless compounds as model compounds in photocatalytic-activity evaluation, and proposes the possible colorimetric method for a reliable evaluation of photocatalytic activity of vis-active materials.

2. Photocatalytic activity

2.1. Definition and Principles of Photocatalytic Activity

Photocatalytic activity/reaction or photocatalysis is often defined as a change of reaction rate caused by light absorption by photocatalyst [19]. Semiconductor photocatalysis occurs when semiconductor is excited (under irradiation) with light of energy same (or larger) than its band-gap energy [20]. As a result of light absorption, electrons (e⁻) are excited from the valence band (VB) to the conduction band (CB), thus forming charge carriers, i.e., electrons in CB and positive holes (h⁺) in VB, which then migrate to the conduction band bottom (CBB) and valence band top (VBT), respectively. The photogenerated e⁻ and h⁺ might either recombine (activity loss) or react with other compounds to initiate various redox reactions [21,22]. The respective reduction and oxidation reactions by photogenerated e⁻ and h⁺ are determined by the energy levels of CBB and VBT, respectively. More negative energy (more cathodic) of CBB and more positive energy (more anodic) of VBT than that of respective reduction and oxidation reactions, respectively, are necessary to initiate those reactions [23].

Therefore, based on the definition, it is necessary to confirm that the observed reaction (evaluated either via the formation of products or the consumption of reagents) originates from the photogenerated charge-carriers of photocatalyst. Action-spectrum analysis, i.e., wavelength dependence of apparent quantum efficiency (AQE), could be a possible method to confirm the origin of photocatalytic activity [24]. To calculate AQE, two rates must be estimated first, i.e., the reaction rate (multiplied by the number of necessity electrons/holes to drive this reaction) and the rate of incident photons (entering the reaction systems; thus "apparent" efficiency term is used

since it is hardly possible to estimate how many photons are really absorbed by photocatalyst), as shown below (eq. 1) [12,25,26].

$$AQE = n \times r / \Phi$$
 eq. 1

where:

n - number of participated e^- or h^+ in the reaction

r – photocatalytic reaction rate (mol s^{-1})

 Φ – rate of incident photon (mol s⁻¹).

It should be pointed out that photocatalysis might involve a complex reaction, e.g., radical chain mechanism, e.g., initiated by generation of reactive oxygen species (ROS), such as hydroxyl radical ('OH), superoxide anion radical (' O_2^-), hydrogen peroxide (H₂O₂), and singlet oxygen (1O_2), which is accelerated under aerated condition [27,28]. However, for convenience, the effect of possible radical chain mechanism is usually neglected, and the consumption of charge carriers (e⁻/h⁺) is assumed considering the stoichiometry of studied reaction.

2.2. Semiconductor photocatalysts

A semiconductor photocatalyst is usually defined as a material that can form charge carriers through excitation by light irradiation, and then utilize those photogenerated electrons and holes for chemical reactions. It means that photocatalyst is directly involved in the reaction, but these reactions could not change its properties (the photocatalyst must be stable) [29,30]. Inorganic materials, such as metal oxides (titanium(IV) oxide (TiO₂), zinc oxide (ZnO), and tungsten oxide (WO₃)) [22,31], metal sulphides (cadmium(II) sulfide (CdS) and zinc(II) sulfide (ZnS)) [21], and metal (oxy)nitrides (e.g., tantalum nitride (Ta₃N₅) and tantalum oxynitride (TaON)) [32,33], have been widely used as photocatalysts. However, for past few decades, the interest in organic-origin materials, e.g., polymeric carbon nitride (C₃N₄, formed from melamine, cyanamide or dicyandiamide during polymerization) and conductive polymers as a photocatalyst has also been increasing [34-37].

As already mentioned, the energy of CBB and VBT determines the possibility of photocatalytic reaction to proceed. On the other hand, also properties of photocatalysts, e.g., crystalline phase, specific surface area and crystal/particle size, might affect the performance of photocatalysts. For example, in aerobic decomposition of organic compounds, high content of anatase phase (one of the crystalline forms of titania) often corresponds to high photocatalytic activity. There are two contrary reasons proposed in the literature (depending also on CBB/VBT): (i) the more negative position of anatase CBB than that of rutile (another form of titania), enabling the formation of O_2^{-} from O_2 [38-40], and more positive VBT of anatase than that of rutile, resulting in higher oxidation power of formed holes [41,42]. Additionally, high content of defects and high specific surface area are also desirable for photocatalytic decomposition of organic compounds[38,43-45]. However, anatase does not always have superior photocatalytic activity, especially in reduction reactions. Moreover, crystalline phase often correlates with particle size, and hence, it is not easy to predict photocatalytic activity just from the crystalline form [38]. For example, in the photocatalytic evolution of hydrogen (H₂) on Au- or Pt-modified titania, rutile and anatase with large and fine particles, respectively, show high photocatalytic activity. It should be pointed out that not only photocatalyst properties, but also external factors, such as pH value, also affect the photocatalytic activity [46]. All these aspects on property/condition-governed activity (though very important also for this manuscript) are not discussed here in details since many valuable papers, including also reviews, have already been published in this topic [38,43,47].

3. Dye-Decoloration Analysis for Pollutant Degradation Purpose

At the beginning, photocatalytic decoloration of dyes was widely investigated due to urgent need to solve the problem of water contamination with dyes. Therefore, initially, dye decoloration was not used to evaluate the level of photocatalytic activity of various photocatalysts, but it was merely intended to decompose dye pollutants in water [48]. Accordingly, many reports on dye decoloration by different AOPs (processes based on generation of hydroxyl radicals as oxidation species), have been published, including also photocatalytic degradation. The effect of photocatalytic degradation has been tested for different types of dyes, as shown in Table 1. The research has focused mainly on the optimization of experimental conditions of dye degradation (pH values, concentration of dyes, content of photocatalyst, co-existence of other artificial and natural compounds in (waste)water, intensity and duration of irradiation and aspects connected with photoreactor design, operation conditions and energy cost, as well as combination of photocatalysis with other treatment methods) [49-65]. The analysis of the level of dye decoloration has usually been performed, based on the change in dye concentration, tested (after photocatalyst separation) by a spectrophotometer (or spectrometer), using the Lambert-Beer's law (eq. 2).

$$A = \log (I_0/I) = -\log T = \varepsilon \times c \times d$$

where:

A – absorbance

 I_0 – initial intensity of the light beam before passing through the sample solution

- I light-beam intensity after passing through the sample solution
- T transmittance
- ε molar absorptivity
- c concentration of chemical compound
- d thickness of the sample cuvette-cell.

It should be mentioned that most of these tests have been performed under UV or UV/vis irradiation (usually with the use of mercury or xenon lamps), and thus at the parameters correlating well with the optimal conditions of reaction for the most active wide-bandgap semiconductors, such as titania. Of course, there are also many reports (especially nowadays) showing degradation of dyes under natural or simulated solar radiation, which are performed to prove that dye decoloration could be successfully achieve in nature, and thus with almost no costs [66-71]. However, it must be stressed that in such case, the mechanism of dye decoloration might not be clearly explained as the direct effect of photocatalyst activation, as discussed further.

Table 1. Examp	ples of dyes	s used as mod	el substrates	for testing of	photocatal	ytic degradation
----------------	--------------	---------------	---------------	----------------	------------	------------------

Name	Molecular structure	Tested parameters	λ_{max}/nm	Ref.
congo red		pressure of membrane, initial dye concentration	498	49

eq. 2

patent blue			639	
maxilon red			530	
methyl violet		рН	587	_ 50
cibacron blue			609	
reactive yellow 17		initial dye concentration; amount of photocatalyst; pH, amount of hydrogen peroxide, potassium persulphate, sodium carbonate and sodium chloride	596	51
red-3BA		рН	519	54
acid orange 7		pH, initial dye concentration, photocatalyst concentration, incident photon energy	485	55
reactive black 5		photocatalyst	597	
reactive orange	Na* Na* Na* $a^{\circ} \xrightarrow{0} \xrightarrow{0} \xrightarrow{0} \xrightarrow{1} \xrightarrow{1} \xrightarrow{1} \xrightarrow{1} \xrightarrow{1} \xrightarrow{1} \xrightarrow{1} 1$	concentration, initial dye concentration, pH	490	56
reactive brilliant red X- 3B (reactive red 2)		photocatalyst concentration, initial dye concentration	540	57
remazol red 133	-	initial dye concentration and pH	518	59

acid blue (AB- 113)		pH, initial dye concentration, photocatalyst concentration	600	60
acid blue 40		pH, argon purging, initial dye concentration	610	62
acid red 14		pH, photocatalyst concentration	515	63
C.I. direct 80 (3BL)		2.4	530	
C.I. direct blue 160 (RL)	H,N OH H,N OH NaOOC N N N N N N N N N N N N N N N N N N	oxygen, temperature, photocatalyst concentration, pH, and inorganic ions.	570	64
C.I. reactive yellow 2 (X6G)	NaO ₃ S- NH-NH-NH-NH-NH-N-N-N-N-N- CI NBO ₃ Na Me	· –	400	_
reactive red 198	HN HO ₃ SCH ₂ CH ₂ O ₂ S HO ₃ SCH ₂ CH ₂ O		518	
acid black		pH	619	65
acid blue 7	NaO38		638	-
direct green 99		-	625	_
methylene blue		photocatalyst	664	- 72
methyl orange		concentration, pH	470	12
orange II		support material	484	73

4. Dye Decoloration Analysis for Evaluation of Photocatalytic Activity

As already mentioned, dyes besides their role as a target pollutant (environmental hazard) have been used as a model compound to evaluate the photocatalytic activity of many new photocatalysts. Organic dyes decoloration, i.e., a decrease in dye concentration (measured as a decrease in photoabsorption) during photocatalytic activity test, is a well-known and commonly used method for evaluation of photocatalytic activity because of its simplicity and low cost [74]. Regardless the convenience of this method, several problems have been reported considering the reliability. The further details of these problems are described below.

4.1 Photolysis

Photolysis, known also as photodecomposition, photodissociation and photofragmentation, is a chemical reaction in which chemical compounds are broken down under irradiation, i.e., the interaction of one or more photons with one target molecule results in molecule decomposition into two parts. In the case of dyes, four types of mechanism could be considered under irradiation. First, as typical for all organic compounds, UV irradiation causes direct photolysis of various bonds, including also benzene ring cleavage, and thus decomposing dyes. Second, dye might be excited under vis irradiation with an electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Then, the excited state of dye might inject electron to an electron acceptor, and thus oxidation of dye starts. Third, in the case of aerobic conditions, molecular oxygen (O_2) might work as an electron acceptor (electrons from excited state of dye (ii case)), and thus superoxide radical anions are formed, which further oxide dye molecules [75]. Fourth, the formation of other reactive oxygen species (ROS) should also be considered in the presence of oxygen, water and UV, and thus oxidative decomposition of dyes by ROS could happen. Therefore, dye degradation might also proceed in the absence of photocatalyst - not caused by the activity of photocatalyst. Methylene blue (MB) is a good example of dye with ability to be decomposed by simple vis irradiation [76]. However, there are also several dyes with high stability under vis irradiation and even near-UV, e.g., methyl orange (MO, from aromatic azo dyes), due to rapid trans-cis photoisomerization. During photoirradiation, the dye molecules are excited and transform from the low-energy isomer to high-energy one. However, the excited state releases the energy rapidly, and hence, returns to the ground state. Since the lifetime of the excited state is very short, the aromatic azo dyes are considered to be stable even under photoirradiation [77-80].

Even though dye photolysis could disturb in evaluation of photocatalytic activity of semiconductor photocatalysts, it has been believed that the blank test, i.e., dye decoloration experiment without photocatalyst, could solve this problem by subtraction of dye photolysis effect from photocatalytic efficiency. However, this might be incorrect considering a possible parallel reaction as described below.

4.2 Self-Sensitized Dye Decoloration (Photosensitization)

The mechanism of self-sensitized dye decoloration is similar to that described above for photolysis-based mechanism, i.e., caused by excitation of dye molecule from HOMO to LUMO under vis irradiation. However, in the case of self-sensitized dye decoloration, the presence of photocatalyst that adsorbs the dye is required. Generally, in the presence of photocatalyst, dye is decolorized through photocatalytic mechanism. The photocatalytic dye decoloration may occur through either direct redox reaction of dye with the photogenerated electrons and/or positive holes, or via indirect reaction of dye with ROS (formed due to the reaction of adsorbed O_2 with the photogenerated electrons from the CBB of photocatalyst). However, under vis irradiation, the adsorbed dye on the photocatalyst could be excited from HOMO to the LUMO, followed by the transfer of the excited electrons from LUMO of dyes to CBB of photocatalyst which further could

reduce the adsorbed O_2 to form ROS. Then, ROS are also playing a role in dye decoloration (see **Figure 1**) [81]. Thereby, dye decomposition in this process is also caused by photogenerated electrons from dye itself, i.e., not actual photocatalytic action of photocatalyst. Additionally, since the presence of photocatalyst is a prerequisite in self-sensitized dye decoloration, the photocatalyst sensitization by dye could not be excluded from photocatalyst-performance evaluation even by performing a blank test [47]. Unlike photolysis that occurs on dye molecules in solution, the adsorbed dye molecules on the photocatalyst surface are mainly responsible for this self-sensitized dye decoloration [82]. During UV irradiation, this self-sensitized dye decoloration might not occur. However, under vis irradiation, where titania and other wide band-gap photocatalysts are inactive (hence vis-absorbing photocatalysts are prepared), the utilization of dye as a substrate for photocatalysis could cause unreliability. Even though photocatalyst sensitization by dye is not recommended for photocatalytic activity testing, dyes are often used in other photocatalytic applications, e.g., in dye-sensitized solar cells (DSSCs) to enhance the light harvesting ability, as introduced by Oregan and Gratzel [16,31].



Figure 1. The possible mechanism of photocatalyst sensitization by dye as reported by Ohtani, B., with (a) photoirradiated light, (b) lowest unoccupied molecular orbital (LUMO) of dye, (c) semiconductor and (d) adsorbed molecular oxygen (O_2) on semiconductor [83]. Reprinted with permission of Royal Society of Chemistry through CCC, Inc. Copyright 2014 Royal Society of Chemistry.

To avoid photocatalyst sensitization by dye, the proper selection of photocatalyst and dye is one of possible solutions, i.e., the CBB of photocatalyst should be more negative than LUMO of dye. However, it is hardly possible to find such materials, as shown in **Figure 2** (though such band positions seem not to be fixed) [84], i.e., even if photocatalyst is resistant to dye sensitization, e.g., zinc sulfide (ZnS), its oxidation ability is very low (VBT level).



Figure 2. Energy band structure of photocatalysts, potential reduction of several reaction, and energy structure of several dyes (RhB – Rhodamine B, CV – crystal violet or gentian violet, MB – methylene blue, MO – methyl orange, EY – eosin Y). Reproduced from Chiu, Y., et al. [85]. Copyright under the terms of the Creative Commons Attribution License.

Of course, it must be pointed out that in the case of UV/vis-activity testing for widebandgap semiconductors, the activity under UV (the classical photocatalysis mechanism) is much higher than that under vis (due to sensitization), and thus participation of sensitization in the overall activity (UV/vis) in many cases could be neglected. However, for novel materials with claimed vis response (e.g., modified/doped titania or complete new materials), the sensitization could be a large part (even the main) of the overall vis response, and thus in such cases, dyes could not be used for activity testing, as discussed below.

The first study to prove the dye decoloration by sensitization was shown by Yan et al. in 2006 with the use of action-spectrum analysis (see **Figure 3**) [86]. Two kinds of photocatalysts were used, i.e., UV-active photocatalyst (P25) and vis-active one (S-TiO₂), and MB dye for photocatalytic-activity testing. The action spectra of MB decomposition under aerobic condition were compared with the photoabsorption properties (diffuse reflectance (DR) spectra) of the respective photocatalysts. Region I, region II and region III, shown in **Figure 3**, correspond to UV region (290- 400 nm), vis region of 400-540 nm (strong photoabsorption by S-TiO₂), and vis of 540-700 nm (the peak of dye photoabsorption at vis).

Obviously, in region I, the action spectra resemble the respective DR spectra, confirming that observed effect in UV region is caused by semiconductor photoactivity. The most interesting data are observed in the region III, in which vis activities are observed for both photocatalysts, even for non-vis-absorbing P25. Moreover, the action spectra resemble dye spectrum instead of DR spectra of photocatalysts. Accordingly, it has been confirmed that dye sensitization is responsible for MB degradation under vis irradiation, Hence, in the region III, the utilization of MB could cause unreliability in the photocatalytic activity evaluation.



Figure 3. Action spectra of methylene blue (MB) decoloration on (A) S–TiO₂ and (A') P25 in (a) UV-vis region and (b) vis region, diffuse reflectance (DR) spectra of (B) S–TiO₂ and (B') P25; (C) DR spectrum of adsorbed MB. Reproduced with modification and permission from Yan, X., et al. [86]. Copyright 2006 Elsevier.

4.3 Apparent-Quantum-Efficiency Estimation

For evaluation of photocatalytic activity, AQE is often used, as already mentioned (see eq. 1 for calculation). Even though only the action of photogenerated charge carriers (e^- or h^+) in photocatalytic reaction is considered (since the effect of radical reaction(s) is omitted), the correct estimation of AQE in dye-decoloration analysis still faces some adversities. First, stoichiometry of photocatalytic reaction is required to estimate the overall reaction rate through the rate of product evolution or substrate consumption, but dye decoloration does not proceed according to a clear stoichiometry due to the complex radical chain reactions [87]. More importantly, dye decoloration is often caused by the transformation of dyes, e.g., blue-colored MB into colorless leuco form of MB, instead of complete mineralization of dye. Accordingly, this leads to some inaccuracy of photocatalytic-activity analysis [88].

4.4 Shifting of Wavelength at Absorption Maximum

It is important to mention that in the case of dyes, a hypsochromic shift of the main absorption peak at vis range has been observed for several dyes, e.g., MB [89], RhB [90], sulforhodamine B (SRB) [91,92], malachite green (MG) [93], and toluidine blue O [94], due to N-dealkylation [95-98]. In the case of RhB (N,N,N',N'-tetraethylrhodamine) degradation, the hypsochromic shift is caused by stepwise N-deethylation of RhB molecule to form N,N,N'-triethylrhodamine, N,N'-diethylrhodamine, N-ethylrhodamine and rhodamine (Rh-110) with different values of molar absorptivity (ϵ) and wavelengths at absorbance maximum (λ_{max}) [82,99].

Interestingly, different course of reaction has been observed during RhB degradation, depending on the irradiation wavelengths, i.e., UV or vis ranges [100]. In the case of vis irradiation, a hypsochromic shift (from 558 to 498 nm) indicates N-deethylation of RhB (Figure 4 (left)). In contrast, under UV irradiation, N-deethylation does not happen, while degradation proceeds much faster (efficient formation of ROS on UV-active photocatalyst) with additional decomposition of the aromatic ring (disappearance of peak at ca. 260 nm), as shown in Figure 4 (right). In the case of methylene blue, similar observation has also been noticed, i.e., a hypsochromic shift (from 664 to 610 nm) [101].

Therefore, it is proposed that such N-dealkylation under vis irradiation suggests that dye decomposes by its self-sensitization. Accordingly, when new photocatalysts are tested for vis response with dyes, and such hypsochromic shift is observed, it might be expected that the vis activity is not caused by the properties of new photocatalysts, but rather because of its sensitization by dyes.



Figure 4. Exemplary data of RhB degradation under vis (left) and UV (right) irradiation on titania modified with Pt clusters (drawn based on data presented in ref [100]).

Very interesting and detailed study on photocatalytic degradation of RhB was performed by Jakiminska et al. [102], who confirmed that N-deethylation was initiated by an electron transfer from dye to photocatalyst (**Figure 5**) under vis irradiation. Aside of the hypsochromic shift, it is worth mentioning that RhB and its N-deethylation products (see structures of 2(-Et), 2(-2Et), and the products after 3rd and 4th cycles in **Figure 5**) exist in the same solution after photoirradiation and the absorption of N-deethylation products might interfere with the absorption of RhB. Consequently, it is difficult to determine the concentration of RhB in solution correctly.



Figure 5. Mechanism of stepwise N-deethylation of RhB. Reprinted from Jakiminska et al. [102]. Copyright under the terms of the Creative Commons Attribution License.

4.5 Colour recovery

Although, usually dye degradation is performed in the presence of air/oxygen, dyes could also decompose via reductive pathway, i.e., by photogenerated electrons, especially under anaerobic condition. Under UV irradiation, both electrons and holes are simultaneously formed. In most cases, dye decoloration via oxidation pathway is reported. It is understandable as oxidation of dyes could happen not only via reaction of dyes with h⁺, but also by ROS. In the absence of air, ROS formation is significantly suppressed. For example, Yogi et al. have reported the photocatalytic decoloration of MB under UV irradiation under anaerobic condition [103]. After photoirradiation, a new peak was observed at 256 nm in the photoabsorption spectra of MB solution. This new peak was considered as a sign of leuco-methylene blue (LMB; the doubly reduced form of MB) presence. On the other hand, in the presence of water, photogenerated positive holes also played a role in the formation of LMB via formation H⁺ (see eqs. 5 and 6).

$MB + e^- \rightarrow MB^{}$	eq. 3
$2MB^{\bullet-} \rightarrow MB + LMB$	eq. 4
$H_2O + h^+ \rightarrow OH^{\bullet} + H^+$	eq. 5
$MB^{\bullet-} + 2e^- + H^+ \rightarrow LMB$	eq. 6

However, an ambient environment during the measurement of absorbance might also cause the color recovery of decolorized dye. In the case of MB, it has been found that LMB (colorless), formed during MB photoreduction, could recover the original blue color after a contact with oxygen (in air) during colorimetric analysis, and this could be accelerated by vis irradiation [104]. However, re-oxidation of LMB, which is probably the main reasons for the color recovery, might take few hours [89,105,106].

5. The Use of Colorless Substrate – the comparison with dye decoloration analysis

Due to unreliability of photocatalytic activity testing by dye bleaching, especially under vis irradiation, the photocatalytic activity should be tested for degradations of colorless compounds. Indeed, the utilization of colorless compounds for a reliable evaluation is more and more popular in the field of photocatalysis. There are several reports showing the evaluation of photocatalytic activity with the use of both dye and non-dye substrates, as shown in Table 2. It is not easy to compare the photocatalytic degradation of dye with photocatalytic activity tested for colorless compounds since the evaluation method to calculate the photocatalytic effect are usually different. However, generally, the photocatalytic activity is much higher in the case of degradation of dyes than other compounds (as presented in 3rd and 4th column), confirming that photocatalyst sensitization by dye happens, and do participate in the overall effect. Interestingly, in the case of vis irradiation, photocatalysis are practically inactive in these conditions (as sole dye decolorization could not be used for activity confirmation).

Dhotopotalyst	Testing	Photocat	alytic activity	Pof
Filotocataryst	conditions	D	ND	Kel.
BiOIO ₃		MO: 0.015 h ⁻¹		
20%Ag/AgBr/BiOIO3	C _i :	0.903 h^{-1}	_	
40%Ag/AgBr/BiOIO ₃	$2 \times 10^{-2} mM (D)$	0.554 h^{-1}		
80%Ag/AgBr/BiOIO ₃	10 ppm (ND)	$1.856 \mathrm{h^{-1}}$	_	
150% Ag/AgBr/BiOIO ₃	500-W XeL, c-oF (> 420 nm)	$2.736 \ h^{-1}$	2,4-DCP = 31.4%, phenol = 34.2%, Cl_tetracyc. = 47.8%, tetracyc. = 40.0%,	107
$300\% \Delta \sigma / \Delta \sigma Br/BiOIO_2$	5-h irr.	2.604 h^{-1}	bisphenol $A = 20.0\%$	
Ag/AgBr	-	$\frac{2.004 \text{ h}}{0.361 \text{ h}^{-1}}$	_	
bulk g-C ₃ N ₄	C _{i(MB)} : 0.02 mM vis: 300-W	<i>MB</i> : $0.34 \times 10^{-3} \text{ min}^{-1}$	<i>H</i> ₂ evolution (& in- situ Pt deposition) 11.1 µmol (5 h irr.)	108
HGCNF/SNG/MoS ₂ & bulk g-C ₃ N ₄	XeL, c-oF (> 400 nm)	$1.24 \times 10^{-3} \mathrm{min}^{-1}$	44.9 µmol (5 h irr.)	
CdS-SnS (Sn/Cd = 0)	Ci: 5 ppm	MB:80%; RhB:67%	phenol: 61%	
CdS-SnS (Sn/Cd = $1/3$)	150W, c-oF	MB:92%;RhB:95%	phenol: 74%	109
CdS-SnS (Sn/Cd = 1)	(>420 nm)	MB:99%; RhB:99%	phenol: 84%	

Table 2. The comparison of photocatalytic effect investigated under vis irradiation for dyes (D) and non-dye (ND) compounds

Ag ₂ ZnGeO ₄	C _{i(D)} : 12 ppm	<i>RhB:</i> 100%	O_2 evolution:	
	300-W XeL,	(6h irr.)	8.5 µmol (14 h irr.)	- 110
$\Delta \sigma_2 7 n GeO $	c-oF	Orange II: 68%		110
	$(\lambda > 420 \text{ nm})$	(6 h irr.)		
0.10	Ci: 5 ppm	MB: 80%,		
Cas	t = 3 h	RhB: 67%	pnenol: 61%	
	— 150-W L., -	MD. 080/		- 111
CdS-Ag ₂ S	c-oF	MD. 90%	phenol: 81%	
	(>420 nm)	<i>RnB</i> : 90%	•	
	C _i : 10 ppm			
$\Delta \sigma / \Delta \sigma C l / SrTiO_{2}$	$t = 0.5_{(D)}/4h_{(ND)}$	<i>RhB</i> : 97%	nhanal: 70%	
(21.60)	vis: 300-W	<i>MO</i> : 93%	high an al A : 820/	112
(21.0%)	XeL, c-oF	MB: 97%	Disphenoi A. 85%	
	$(\lambda > 420 \text{ nm})$			
	Ci: 10(D)/			
	20(ND) ppm			
$\Lambda \sim C_{2} V O$	$t = 5_{(D)}/4h_{(ND)}$	<i>RhB</i> : 78%	1 1 210/	112
$Ag_2Cav_4O_{12}$	vis: 300-W	MB: 93%	pnenol: 21%	115
	WhL, c-oF			
	$(\lambda > 400 \text{ nm})$			
$T_{O_{1}}^{*}/D_{2}^{*}(II)$	$C_i: 10^{-4} M_{(D)}$	DhD,000/	phanal, 25%	
110 ₂ /Ft(11)	2 x 10 ⁻⁴ M _(ND) /	<i>KnD</i> : 90%	phenol: 25%	
$T' \cap D_{I}(U)$	$t = 2_{(D)}/3h_{(ND)}$	DLD: 400/	11. 100/	100
$110_2/Pt(1V)$	vis: 300-W	KNB: 40%	phenol: 10%	100
T_{0}^{*}	XeL, c-oF	DLD, 200/	r h a l 170/	-
$110_2/Pl(0)$	$(\lambda > 450 \text{ nm})$	KNB: 80%	pnenoi: 17%	

 C_i – initial concentration, Cl_tetracyc.- chlortetracycline hydrochloride, c-oF – cut-off filter, D – dye, HGCNF – hollow g-C₃N₄ nanofiber, irr. – irradiation, L – lamp, ND – non-dye compound, SNG – sulfur/nitrogen co-doped graphene, tetracyc. - tetracycline hydrochloride, WhL – tungsten halogen lamp, XeL – xenon lamp

6. Spectrophotometric Analysis for Photocatalytic-Activity Test without Dye and Its Challenge

Based on the above-mentioned drawbacks of using dyes, it might be concluded that most problems are caused by interaction of dyes with light. As a result, it is not easy to evaluate photocatalyst performance reliably under vis irradiation. Therefore, the use of substrate with less or no absorption (the best) of vis is necessary for reliable photocatalytic-activity evaluation under vis. However, colorimetric analysis of colorless compounds is not as common as that of dyes. The possible reason is probably there are some criteria that should be fulfilled in the selection of colorimetric analysis method, i.e., simplicity, selectivity, precision, sensitivity and agreement with Lambert-Beer's law [114]. However, there is another important aspect that should be considered related to the selection of non-dye compound for photocatalytic activity testing, i.e., reliability of the method for photocatalytic activity test under vis irradiation, which will be discussed in this section.

Colorless organic compounds are often considered as 'ideal' substrates for photocatalytic activity evaluation, especially under vis irradiation. There are three main reasons for this statement,

as follows: (i) photocatalytic reactions used for activity testing have a clear stoichiometry (hence it is easy to estimate AQE), (ii) there is no sensitization under vis irradiation, and (iii) they produce less intermediates than that of dyes [86]. However, there are also some problems, which must be considered, especially during the selection of suitable colorless organic compound for photocatalytic activity tests, as discussed further.

Molecule-to-band charge transfer (MBCT) is a phenomenon where the colorless organic compound might induce vis absorption. Although both UV-active photocatalyst and colorless organic compound do not absorb vis, the surface complexation of colorless organic compound and semiconductor might result in absorption of visible light. Unlike dye sensitization, in MBCT, electron is photoexcited from the HOMO of the adsorbed organic compounds (surface adsorbates) directly to the CB of the photocatalyst, i.e., without involving the LUMO [115]. Since CB of photocatalyst has mainly metal orbital character, this charge transfer is also named as ligand-to-metal charge transfer (LMCT) or charge-transfer complex (CTC) [116,117]. Commonly, adsorbed organic compounds with hydroxyl or carboxyl functional group might form MBCT complex on the surface of photocatalyst. To allow LMCT/MBCT, the level of the HOMO should be lower (more positive in energy) than that of CB of photocatalyst. Additionally, the energy gap between HOMO and CB should be narrow enough to enable the charge transfer under vis irradiation [118]. The illustration of MBCT is shown in **Figure 6**.



Figure 6. Illustration of MBCT mechanism from the HOMO of adsorbed organic compound to the CB of photocatalyst. Reproduced from Park, H., et al. [116]. Copyright under the terms of the Creative Commons Attribution License.

The proof of MBCT for the interaction of UV-active photocatalyst and colorless compound is shown in **Figure 7**. First, photoabsorption properties (the DR spectra) of titania photocatalyst before and after adsorbing organic compounds are shown in **Figure 7** (a). It has been found that adsorption of aromatic compounds on the surface of titania, i.e., 4-chlorophenol (4-CP), 2,4-dichlorophenoxyacetate sodium salt (2,4-D), phenol (PhOH), and 2,4-dichlorophenol (2,4-DCP), results in an appearance of photoabsorption in vis region. However, adsorption of dichloroacetate (DCA) hardly changes photoabsorption property of titania. Therefore, it has been proposed that phenolate linkage (see eq. 07), formed on the photocatalyst surface between aromatic compound and titania, causes an enhanced photoabsorption at vis range, induced by MBCT [119].

$$\equiv Ti - OH + HO - Ph \rightarrow \equiv Ti - O - Ph + H_2O \qquad eq. 7$$

It has been suggested that hydroxyl groups on photocatalyst surface play an important role in the complexation with the hydroxyl groups of aromatic compounds. This is supported by the fact that fluorine-modified titania with lower content of hydroxyl groups has similar photoabsorption spectrum as pristine titania (see **Figure 7** (b)), i.e., without obvious MBCT-induced vis photoabsorption.



Figure 7. Diffuse reflectance spectra of UV-titania (ST-01, Ishihara) and substrate/UV-titania with (a) different substrates (b) surface fluorination. (c) Action spectra of photoinduced current 4-CP degradation on titania. Reprinted with permission from Kim, S. and Choi, W. [119]. Copyright 2005 American Chemical Society.

Of course, MBCT-based mechanism could not be confirmed only by investigation of absorption spectra, and thus, respective action spectra have also been studied. Indeed, action spectrum of photocatalytic degradation of 4-CP correlates well with photoabsorption spectrum of TiO₂/4-CP (see **Figure 7** (c)) rather than with that of pristine titania, suggesting that adsorbed 4-

CP on the titania surface initiates photocatalytic activity under vis, confirming the MBCT-induced vis activity of titania.

Interestingly, it should be noted that not only colorless organic compounds can cause MBCT, but also inorganic ones. For example, Kuncewicz et al. have found MBCT between chromate and titania [120], as presented in **Figure 8**. EPR spectrum of P25 with adsorbed Cr^{VI} in DMSO under vis irradiation indicates the presence of 'OH. However, there is no proof for 'O₂⁻ formation. Therefore, it has been proposed that during excitation of chromate (VI), positive holes are injected to the VB of titania followed by formation of 'OH. The absence 'O₂⁻ is probably because an electron transfer from excited chromate (VI) to the CB of titania is not possible (due to the lower reduction potential of chromate (VI) than that of CB), as well as a direct reduction of oxygen by Cr (V). After positive holes transfer, it is probable that the reduced chromate (VI), i.e., chromate (V), reduced the organic compound produced from photolyzed suspension and Cr(VI) was regenerated. Another possibility is that regeneration of Cr(VI) occurs through disproportionation of Cr(V) to form Cr(VI) and Cr(III) [120].



Figure 8. Positive holes transfer mechanism between chromate and titania. Reprinted with permission from Kuncewicz, et al. [120]. Copyright 2012 American Chemical Society.

Many studies have been performed on examination of MBCT with titania, as summarized in Table 3. As presented in Figure 7, efficient light harvesting is observed due to additional photoabsorption caused by MBCT. There are several factors that might affect the intensity of MBCT. Agrios et al. have found that the higher-chlorinated phenol and mixture of polymorphic phases (anatase and rutile) of titania result in higher intensity of MBCT photoabsorption than that of less-chlorinated phenol and pure anatase, respectively [117]. In the case of titania P25 (mixture of anatase and rutile) and pure anatase, 2,4,5-trichlorophenol (2,4,5-TCP) has shown the highest MBCT absorbance, followed by 2,4,6-trichlorophenol (2,4,6-TCP), 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP) and finally for phenol. Furthermore, evaluation of wavelengthdependence degradation of chlorophenols on P25 has also been performed. It has been found that under dark conditions, the higher the number of chlorines in chlorophenols is, the higher is adsorption on titania surface. More importantly, it has been found that degradation of chlorophenols is much more efficient under irradiation (430 nm) than that under dark conditions, confirming the MBCT activities. On the other hand, another study reveals that specific surface area (SSA) of photocatalyst is more important in MBCT effect than crystalline-phase composition since pure anatase (ST-01) but with very high SSA (340 m² g⁻¹) exhibits higher photoinduced

activity of 4-CP degradation than mixed phase titania (P25) with smaller SSA (50 m² g⁻¹) [119]. Hence, MBCT activity is difficult to estimate considering only one property of photocatalyst (which is typical also for all other photocatalytic activity tests) [43]. Additionally, the conditions during photocatalytic reaction, e.g., pH value, could also affect the formation of MBCT between titania and colorless substrate [121].

No.	titania type	substrate	Ref.
1	ST-01 (anatase)	4-CP	119
		2,4-DCP	
		2,4-dichlorophenoxyacetate sodium salt	
		(2,4-D)	
		phenol	
2	P25	hydrogen peroxide (H ₂ O ₂)	122
3	P25 and anatase titania	2,4,5-TCP	117,123
		2,4,6-TCP	
		2,4-DCP	
		4-CP	
		phenol	
4	P25	Brij	124
5	synthesized titania	benzyl alcohol	125
6	synthesized titania	terephthalate acid	126
7	P25	arsenic (III) solution	121
8	P25	humic acid	127
		pyrocatechol	
9	P25	glucose	128
10	titania	tetracycline	129
11	P25 and tytanhydrat-0	chromate(VI) ion	120

Table 3. Examples of MBCT between UV-active titania and chemical compounds

Summarizing, it might be concluded that the main difference between photosensitization and MBCT is based on the wavelength region of enhanced photocatalytic activity. In the case of photosensitization, "apparent" vis activity occurs usually at wavelength of maximum absorption by a sensitizer (dye), whereas for MBCT, the enhanced activity usually occurs in red edge of photocatalyst photoabsorption. Moreover, a sensitizer must absorb light at longer wavelengths than semiconductor (i.e., usually vis), whereas in the case of MBCT, photoabsorption properties of both components could be similar (both could exhibit only UV response) and the difference is based only on redox properties (oxidation and reduction levels). Additionally, MBCT tends to occur for photocatalysts with high content of hydroxyl groups on its surface.

7. Prospective Colorimetric Method for Reliable Photocatalytic Activity Evaluation

As presented above, many colorless compounds could cause "apparent" vis activity due to MBCT effect. Therefore, their use as testing molecules is not reliable for some photocatalysts, especially those enriched with hydroxyl groups (i.e., the majority of titania samples). However, it should be pointed out that the study on MBCT is still very rare (examples shown in **Table 3**), mostly limited to organic compounds containing phenolic groups. Therefore, in this section,

several colorimetric analyses are presented, which could be used for proper evaluation of photocatalytic activity, especially under vis irradiation. However, of course, further examination for their reliability is necessary to exclude any possibility of MBCT effect.

Photocatalytic activity methods based on spectroscopic analysis could be devided into two main groups, as follows: (i) direct, and (ii) indirect analyses. The direct analysis means the measurement of absorption of reaction product, i.e., formed by reaction of photogenerated electrons or holes with substrate molecules. In the case of indirect analysis, an introduction of another compound, which could react either with reactants or products (forming spectroscopically-active compounds), to the reaction system is necessary.

7.1 Direct analysis

7.1.1 *Iodide*

During photocatalytic oxidation of iodide (I⁻) to iodine (I₂; eq. 8), the formation of I₂ can be analyzed by colorimetric analysis of triiodide (I₃⁻), formed in the presence of excess of iodide (eq. 9). Even though this reaction is often conducted under aerobic conditions, no formation of iodate, i.e., IO⁻ or IO₃⁻, is observed [130]. Triiodide can be detected at wavelength of 352 nm ($\epsilon = 2.64 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$) or 288 nm ($\epsilon = 4 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$) [131-134].

The use of iodide as a photocatalytic substrate has been reported for photocatalytic-activity evaluation under vis irradiation [92]. However, it has been found that negligible I_3^- generation was observed even on non-vis-absorbing P25 titania under vis irradiation ($\lambda > 420$ nm) [135]. Therefore, it could be expected that this "apparent" activity might be caused by titania modification with iodine during activity testing. Unfortunately, there are no reports about MBCT or sensitization-type effects for this kind of activity testing.

7.1.2 Methyl viologen

Methyl viologen (MV^{2+} , $E^0MV^{2+}/MV^{+*} = -0.44 \text{ eV}$, pH independent) has been proposed as another colorless compound for activity testing. Reduction of methyl viologen (paraquat) results in formation of blue-colored methyl viologen radical (MV^{+*}) [136,137]. A sacrificial electron donor, e.g., ethanol, is utilized to scavenge photogenerated holes, and experiments are performed under anaerobic conditions to avoid reoxidation of MV^{+*} (forming MV^{2+}) [138]. The spectrophotometric analysis of MV^{+*} is conducted by measuring absorption at 395 nm ($\varepsilon = 4.2 \times 10^4 \text{ L}^{-1} \text{ mol cm}^{-1}$) [139]. However, it should be pointed that experiments are carried out in absence of oxygen, and thus mostly reductive properties of photocatalysts could be estimated. Accordingly, for novel photocatalysts with vis response, and thus less negative CBB (in many cases due to bandgap narrowing), the estimated activity could be very low.

Although, as a colorless compound, methyl viologen could be considered as photosensitization-free under vis irradiation, the further examination of MBCT possibilities should be studied. Additionally, though, paraquat is commonly used for some photocatalytic tests (e.g., estimation of quasi-Fermi level by a Roy method), its broad application for activity testing is rather not expected due to its high toxicity.

- 7.2 Indirect Analysis
- 7.2.1 Formaldehyde

Formaldehyde (HCHO) has been utilized as a model compound for photocatalytic activity evaluation, i.e., its oxidative decomposition. A common evaluation method is usually performed by analyzing the mineralization product, i.e., carbon dioxide (CO₂) by a gas chromatograph (GC). However, the analysis of HCHO consumption has also often been performed, either in gas or aqueous phases [140,141].

To determine HCHO concentration in an aqueous phase by colorimetric analysis, Hantzsch reaction has been proposed, in which a colorless HCHO solution is derived into a yellow one, because of 3,4-diacetyl-1,4-dihydrolutidine (DDL) formation ($\varepsilon = 8 \times 10^3 \text{ mol}^{-1} \text{ L cm}^{-1}$ at 412 nm) in the presence of acetylacetone as a source of β -diketone [142]. The derivatization of HCHO into pyridine compound is characterized by a relatively high stability of color and a low interference by reagents. The use of other β -diketone sources has also been reported, such as acetoacetanilide, benzoylacetone, benzoyltrifluoroacetone and 2-thenoyltrifluoroacetone [143]. A short summary of colorimetric analysis of HCHO during photocatalytic activity estimation is presented in **Table 4**. There are several photocatalytic systems, which might utilize this colorimetric analysis, because HCHO might be used either as a substrate or a product of different photocatalytic reactions.

	photocatalytic	β-		.01	
No.	system	diketone	λ_{max}	substrate	light source
		source			
					UV/vis (HgL)
	methanol	acetyl_	412 nm		[144,145];
1	ovidation	acetone	in	methanol	UV/vis (450-W XeL):
	UXIUALIUII	acetone	water		$\lambda > 320 \text{ nm} [146];$
					UV (365 nm, 6W) [147]
	m oth on ol	a satula	412 nm		UV/vis (HgL) [145];
2	methanoi	acetyla-	in	methanol	solar simulator
	oxidation	cetone	water		(AM 1.5 filter) [148]
	carbon dioxide		412	CO ₂ [149],	
2	(or related	acetyla-	412 nm	Na ₂ CO ₃ &	UV/vis
3	compounds)	cetone	in	K ₂ CO ₃ [150-	(500-W WL) [149-152]
	reduction		water	152]	
4	Tris	acetoace	368 nm	Tris	UV
	decomposition	-tanilide			(20-W BLBL) [153,154]
	^a H ₂ evolution	acatul		amethanol	LIV & vie
5	^b HCHO	acetono		^b formaldehyda	$(I ED & H_{eff})$ [155]
	decomposition	accione		Tormaluenyue	(LED & HgL) [133]

Table 4. Photocatalytic systems with formaldehyde as a key compound for colorimetric analysis via dipyridine formation

BLBL - black light blue lamp, HgL - mercury lamp, XeL - xenon lamp, WL - tungsten lamp

A detailed study on colorimetric analysis of HCHO under both UV and vis irradiation, for two photocatalytic systems, i.e., methanol dehydrogenation and HCHO oxidative decomposition, has been investigated to confirm the lack of photosensitization effect [155]. The reliability of colorimetric analysis has been studied by a comparison of GC analysis (evolution of H₂ and CO₂ in the case of methanol dehydrogenation and oxidative decomposition of HCHO, respectively) with colorimetric analysis (HCHO). Successfully, it has been confirmed that colorimetric analysis shows similar trends with GC analysis, confirming its reliability under both UV (UV LED) and vis (green LED) irradiation for both photocatalytic systems (**Figure 9**). Additionally, in contrast to RhB-decoloration analysis, no photoinduced reaction proceeded under vis on UV-absorbing titania (ST-G1), suggesting that photosensitization and MBCT do not occur with HCHO.



Figure 9. Summary of photocatalytic activity tests for three photocatalytic systems (RhB decoloration – first row, methanol dehydrogenation – second and third rows, and oxidative decomposition of HCHO – fourth and fifth rows) under UV or vis (green LED) irradiation on UV-absorbing titania (ST-G1) and vis-absorbing titania (Sample A and Sample B); "-RhB" – decrease in concentration of RhB (spectroscopic analysis (SA)), "H₂" and "CO₂"– H₂ and CO₂ evolution, respectively (GS analysis), "HCHO" and "-HCHO" – change in concentration of HCHO (SA). Reproduced from Amalia, F. R., et al. [155]. Copyright under the terms of the Creative Commons Attribution License.

7.2.2 Methanol

The utilization of methanol (or other aliphatic alcohols) as a sacrificial electron donor (a hole scavenger) is common during photocatalytic dehydrogenation of water [156]. Even though, adsorption of methanol (or other aliphatic alcohols) on the titania surface has been reported, to the best of the authors' knowledge, there are no reports about MBCT-induced vis activity yet [157]. In the utilization of methanol as a photocatalytic substrate (methanol dehydrogenation or even methanol photooxidation), the photocatalytic activity could be evaluated by colorimetric analysis of HCHO, i.e., analysis of oxidation product, instead of hydrogen (H₂) evolution by GC (see **section 7.2.1**) [155]. It should be pointed out that this photocatalytic reaction is usually performed

in the presence of co-catalysts (e.g., photodeposited platinum or other noble metals) to enhance the photocatalytic activity, but such surface modification of titania could inhibit the MBCT [45,87,158,159]. Accordingly, though methanol dehydrogenation system could be also one of possible systems for reliable evaluation of photocatalytic activity, the confirmation of MBCT-free is still necessary. Fortunately, photosensitization has not been reported in the case of alcohol use [155]. The colorimetric analysis of HCHO could be conducted by utilizing Hantzsch reaction as described in the **section 7.2.1** [160].

8. Summary and Future Prospect

Colorimetric analysis is a well-known method due to its simplicity and affordability. However, to utilize the method for photocatalytic-activity-evaluation, the selection of a substrate for photocatalytic reaction should be considered carefully to obtain reliable data. Under vis irradiation, though the use of organic dyes has often been reported, it is improper due to photosensitization, photolysis, and difficulties to assume the stoichiometry, etc. On the other hand, the use of colorless organic compounds seems more superior since there is no photosensitization. However, it should be pointed out that unreliability of the use of colorless compound under vis irradiation might occur due to MBCT on the surface of photocatalyst. Hence, the selection of chemical compounds should be carefully considered, for example by avoiding aromatic compounds with hydroxyl groups that may interact with the photocatalyst surface. Furthermore, it is worth noting that even though colorless compounds might cause MBCT effect, their utilization is still a better option than that of organic dyes, especially due to defined stoichiometry, which allows a correct estimation of AQE of photocatalytic reaction. It is proposed that colorimetric method with HCHO as a reactant (via Hantzsch reaction) is one of the best-known methods to be applied under broad irradiation ranges (UV- and vis-activity testing) for both oxidative- and reductive-based reactions. Further study on efficient utilization of other colorless compounds, e.g., their kinds, further characteristics of properties in correlation with feature of photocatalysts (considering MBCT phenomenon), for reliable colorimetric analysis is highly needed.

Author contributions:

Conceptualization: F.R.A.; B.O and E.K; writing: original draft preparation: F.R.A.; writing-review and editing: F.R.A.; E.K.; and B.O. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest:

The authors declare no conflict of interest.

References

- [1] Liu, M. M.; Hou, L. A.; Xi, B. D.; Zhao, Y.; Xia, X. F. *Appl. Surf. Sci.* 2013, 273, 706-716. DOI: 10.1016/j.apsusc.2013.02.116.
- [2] Zhao, F. P.; Liu, Y. P.; Ben Hammouda, S.; Doshi, B.; Guijarro, N.; Min, X. B.; Tang, C. J.; Sillanpaa, M.; Sivula, K.; Wang, S. B. *Appl. Catal.*, B 2020, 272, 14. DOI: 10.1016/j.apcatb.2020.119033.
- [3] Fiaz, A.; Zhu, D. C.; Sun, J. Z. *Environ. Sci. Eur.* **2021**, 33 (1), 17. DOI: 10.1186/s12302-021-00505-y.

- [4] Bhat, A. P.; Gogate, P. R. J. Hazard. Mater. **2021**, 403, 31. DOI: 10.1016/j.jhazmat.2020.123657.
- [5] Boczkaj, G.; Fernandes, A. J. Chem. Eng. **2017**, 320, 608-633. DOI: 10.1016/j.cej.2017.03.084.
- [6] Wang, C. C.; Li, J. R.; Lv, X. L.; Zhang, Y. Q.; Guo, G. S. Energy Environ. Sci. 2014, 7 (9), 2831-2867. DOI: 10.1039/c4ee01299b.
- [7] Villacres, R.; Ikeda, S.; Torimoto, T.; Ohtani, B. J. Photochem. Photobiol. A 2003, 160, 121-126. DOI: 10.1016/S1010-6030(03)00230-2.
- [8] Wang, K.; Hsieh, Y.; Ko, R.; Chang, C. Environ. Int. 1999, 25, 671-676.
- [9] Kowalska, E. Rau, S. Photoreactors for Wastewater Treatment: A Review, Recent Patent of Engineering 2010, 4 (3). DOI: 10.2174/187221210794578583
- [10] Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Science 2001, 293 (5528), 269-271. DOI: 10.1126/science.1061051.
- [11] Ohno, T.; Akiyoshi, M.; Umebayashi, T.; Asai, K.; Mitsui, T.; Matsumura, M. Appl. Catal. A: Gen. 2004, 265 (1), 115-121. DOI: 10.1016/j.apcata.2004.01.007.
- [12] Kowalska, E.; Abe, R.; Ohtani, B. Chem. Commun. 2009, (2), 241-243. DOI: 10.1039/b815679d.
- [13] Wang, X. C.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. Nat. Mater. 2009, 8 (1), 76-80. DOI: 10.1038/nmat2317.
- [14] Zou, Z. G.; Ye, J. H.; Sayama, K.; Arakawa, H. Nature 2001, 414 (6864), 625-627. DOI: 10.1038/414625a.
- [15] Kong, X. Y.; Tan, W. L.; Ng, B. J.; Chai, S. P.; Mohamed, A. R. Nano Res. 2017, 10 (5), 1720-1731. DOI: 10.1007/s12274-017-1435-4.
- [16] Oregan, B.; Gratzel, M. Nature 1991, 353 (6346), 737-740. DOI: 10.1038/353737a0.
- [17] Yella, A.; Lee, H. W.; Tsao, H. N.; Yi, C. Y.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W. G.; Yeh, C. Y.; Zakeeruddin, S. M.; Grätzel, M. *Science* 2011, 334 (6056), 629-634. DOI: 10.1126/science.1209688.
- [18] Chen, C. Y.; Wang, M. K.; Li, J. Y.; Pootrakulchote, N.; Alibabaei, L.; Ngoc-le, C. H.; Decoppet, J. D.; Tsai, J. H.; Grätzel, C.; Wu, C. G.; et al. ACS Nano 2009, 3 (10), 3103-3109. DOI: 10.1021/nn900756s.
- [19] Braslavsky, S. E. Pure Appl. Chem. **2007**, 79 (3), 293-465. DOI: 10.1351/pac200779030293.
- [20] Chiarello, G. L.; Aguirre, M. H.; Selli, E. J. Catal. 2010, 273 (2), 182-190. DOI: 10.1016/j.jcat.2010.05.012.
- [21] Kudo, A.; Miseki, Y. Chem. Soc. Rev. 2009, 38 (1), 253-278. DOI: 10.1039/b800489g.
- [22] Riente, P.; Noel, T. *Catal. Sci. Technol.* 2019, 9 (19), 5186-5232. DOI: 10.1039/c9cy01170f.
- [23] Hagfeldt, A.; Gratzel, M. Chem. Rev. 1995, 95 (1), 49-68. DOI: 10.1021/cr00033a003.
- [24] Torimoto, T.; Nakamura, N.; Ikeda, S.; Ohtani, B. Phys. Chem. Chem. Phys. 2002, 4 (23), 5910-5914. DOI: 10.1039/b207448f.
- [25] Ohtani, B. Chem. Lett. 2008, 37 (3), 217-229. DOI: 10.1246/cl.2008.216.

- [26] Torimoto, T.; Aburakawa, Y.; Kawahara, Y.; Ikeda, S.; Ohtani, B. Light intensity dependence of the action spectra of photocatalytic reactions with anatase titanium(IV) oxide. *Chem. Phys. Lett.* **2004**, 392 (1-3), 220-224. DOI: 10.1016/j.cplett.2004.05.077.
- [27] Gaya, U. I.; Abdullah, A. H. J. Photochem. Photobiol. C: Photochem. Rev. 2008, 9 (1), 1-12. DOI: 10.1016/j.jphotochemrev.2007.12.003.
- [28] Nosaka, Y.; Nosaka, A. Y. *Chem. Rev.* **2017**, 117 (17), 11302-11336. DOI: 10.1021/acs.chemrev.7b00161.
- [29] Khan, M. M.; Adil, S. F.; Al-Mayouf, A. Metal oxides as photocatalysts. J. Saudi Chem. Soc. 2015, 19 (5), 462-464. DOI: 10.1016/j.jscs.2015.04.003.
- [30] Ohtani, B. J. Photochem. Photobiol. C: Photochem. Rev. 2010, 11 (4), 157-178. DOI: 10.1016/j.jphotochemrev.2011.02.001.
- [31] Gratzel, M. Nature 2001, 414 (6861), 338-344. DOI: 10.1038/35104607.
- [32] Hitoki, G.; Takata, T.; Kondo, J. N.; Hara, M.; Kobayashi, H.; Domen, K. Chem. Commun. 2002, (16), 1698-1699. DOI: 10.1039/b202393h.
- [33] Ma, S. S. K.; Hisatomi, T.; Maeda, K.; Moriya, Y.; Domen, K. J. Am. Chem. Soc. 2012, 134 (49), 19993-19996. DOI: 10.1021/ja3095747.
- [34] Wang, X. C.; Maeda, K.; Chen, X. F.; Takanabe, K.; Domen, K.; Hou, Y. D.; Fu, X. Z.; Antonietti, M. J. Am. Chem. Soc. 2009, 131 (5). DOI: 10.1021/ja809307s.
- [35] Bai, Y.; Wilbraham, L.; Slater, B. J.; Zwijnenburg, M. A.; Sprick, R. S.; Cooper, A. I. J. Am. Chem. Soc. 2019, 141 (22), 9063-9071. DOI: 10.1021/jacs.9b03591.
- [36] Shibata, T.; Kabumoto, A.; Shiragami, T.; Ishitani, O.; Pac, C.; Yanagida, S. J. Phys. Chem. 1990, 94 (5), 2068-2076. DOI: 10.1021/j100368a063.
- [37] Yanagida, S.; Kabumoto, A.; Mizumoto, K.; Pac, C.; Yoshino, K. Chem. Commun. 1985, (8), 474-475. DOI: 10.1039/c39850000474.
- [38] Ohtani, B.; Mahaney, O. O. P.; Amano, F.; Murakami, N.; Abe, R. J. Adv. Oxid. Technol. 2010, 13 (3), 247-261. DOI: 10.1515/jaots-2010-0303.
- [39] Kang, J.; Wu, F.; Li, S.; Xia, J.; Li, J. J. Phys. Chem. C 2012, 116, 20765-20768. DOI: 10.1021/jp3067525.
- [40] Choudhury, B.; Choudhury, A. *Physica E Low Dimens. Syst. Nanostruct.* 2014, 56, 364-371. DOI: 10.1016/j.physe.2013.10.014.
- [41] Buchalska, M.; Kobielusz, M.; Matuszek, A.; Pacia, M.; Wojtyla, S.; Macyk, W. ACS Catal. 2015, 5, 7424-7431. DOI: 10.1021/acscatal.5b01562.
- [42] Mikrut, P.; Swies, A.; Kobielusz, M.; Chmielarz, L.; Macyk, W. RSC Adv. 2022, 12, 1862-1870. DOI: 10.1039/d1ra08364c.
- [43] Prieto-Mahaney, O. O.; Murakami, N.; Abe, R.; Ohtani, B. Chem. Lett. 2009, 38 (3), 238-239. DOI: 10.1246/cl.2009.238.
- [44] Nitta, A.; Takashima, M.; Takase, M.; Ohtani, B. Catal. Today 2019, 321, 2-8. DOI: 10.1016/j.cattod.2017.12.020.
- [45] Kowalska, E.; Mahaney, O. O. P.; Abe, R.; Ohtani, B. Phys. Chem. Chem. Phys. 2010, 12 (10), 2344-2355. DOI: 10.1039/b917399d.
- [46] Ryu, J.; Choi, W. Environ. Sci. Technol. 2008, 42 (1), 294-300. DOI: 10.1021/es071470x.
- [47] Wang, K.; Janczarek, M.; Wei, Z.; Raja-Mogan, T.; Endo-Kimura, M.; Khedr, T.; Ohtani, B.; Kowalska, E. *Catalysts* 2019, 9. DOI: 10.3390/catal9121054.

- [48] Rochkind, M.; Pasternak, S.; Paz, Y. *Molecules* **2015**, 20 (1), 88-110. DOI: 10.3390/molecules20010088.
- [49] Molinari, R.; Pirillo, F.; Falco, M.; Loddo, V.; Palmisano, L. Chem. Eng. Process.
 2004, 43 (9), 1103-1114. DOI: 10.1016/j.cep.2004.01.008.
- [50] Sokmen, M.; Allen, D. W.; Akkas, F.; Kartal, N.; Acar, F. Wat. Air and Soil Poll. 2001, 132, 153-163. DOI: 10.1023/a:1012069009633.
- [51] Neppolian, B.; Kanel, S. R.; Choi, H. C.; Shankar, M. V.; Arabindoo, B.; Murugesan, V. Int. J. Photoenergy 2003, 5 (2), 45-49. DOI: 10.1155/s1110662x03000126.
- [52] Rajeshwar, K.; Chenthamarakshan, C. R.; Goeringer, S.; Djukic, M. Pure Appl. Chem.
 2001, 73 (12), 1849-1860. DOI: 10.1351/pac200173121849.
- [53] Wang, Y. Z. Water Res. 2000, 34 (3), 990-994. DOI: 10.1016/s0043-1354(99)00210-9.
- [54] Dung, N. T.; Khoa, N. V.; Herrmann, J. M. Int. J. Photoenergy 2005, 7 (1), 11-15. DOI: 10.1155/s1110662x05000024.
- [55] Kiriakidou, F.; Kondarides, D.; Verykios, X. Catal. Today 1999, 54, 119-130. DOI: 10.1016/S0920-5861(99)00174-1.
- [56] Kansal, S.; Kaur, N.; Singh, S. Nanoscale Res. Lett. 2009, 4, 709-716. DOI: 10.1007/s11671-009-9300-3.
- [57] Zhang, X.; Wang, Y.; Li, G. J. Mol. Catal. A Chem. 2005, 237, 199-205. DOI: 10.1016/j.molcata.2005.03.043.
- [58] Gümüs, D.; Akbal, F. Water Air Soil Pollut. 2011, 216, 117-124. DOI: 10.1007/s11270-010-0520-z.
- [59] Dizge, N.; Aydiner, C.; Demirbas, E.; Kobya, M.; Kara, S. J. Hazard. Mater. 2008, 150, 737-746. DOI: 10.1016/j.jhazmat.2007.05.027.
- [60] Almhana, N.; Al-Najjar, S.; Naser, Z.; Al-Sharify, Z.; Nail, T. Egypt. J. Chem. 2022, 65, 481-488. DOI: 10.21608/EJCHEM.2022.125852.5588.
- [61] Poulios, I.; Aetopoulou, I. *Environ. Technol.* **1999**, 20, 479-487. DOI: 10.1080/09593332008616843.
- [62] Muneer, M.; Philip, R.; Das, S. Rev. Chem. Intermed. 1997, 23, 233-246. DOI: 10.1163/156856797X00448.
- [63] Mohagheghian, A.; Ghaneei-Motlagh, R.; Ayagh, K.; Shirzad-Siboni, M. Int. J. Environ. Anal. Chem. 2023. DOI: 10.1080/03067319.2023.2286307.
- [64] Habibi, M.; Hassanzadeh, A.; Mahdavi, S. J. Photochem. Photobiol. A: Chem. 2005, 172, 89-96. DOI: 10.1016/j.jphotochem.2004.11.009.
- [65] Zielinska, B.; Grzechulska, J.; Kalenczuk, R.; Morawski, A. Appl. Catal. B: Environ.
 2003, 45, 293-300. DOI: 10.1016/S0926-3373(03)00178-4.
- [66] Krishnakumar, B.; Alsalme, A.; Alharthi, F.; Mani, D.; Anandan, K.; Amutha, P.; Sobral, A. Opt. Mater. 2021, 113. DOI: 10.1016/j.optmat.2021.110854.
- [67] Liu, K.; Rouhani, F.; Gao, X.; Abbasi-Azad, M.; Li, J.; Hu, X.; Wang, W.; Hu, M.; Morsali, A. *Catal. Sci. Technol.* **2020**, 10, 757-767. DOI: 10.1039/c9cy02003a.
- [68] Xu, H.; Xiong, J.; Zhang, Y.; Cheng, J.; Yang, B. Inorg. Chem. Commun. 2024, 163. DOI: 10.1016/j.inoche.2024.112327.
- [69] Jena, S.; Sadasivam, R.; Packirisamy, G.; Saravanan, P. Environ. Pollut. 2021, 280. DOI: 10.1016/j.envpol.2021.116964.

- [70] Yong, Y.; Ali, N.; Khan, A.; Khan, S.; Khan, S.; Khan, H.; Shi, X.; Ahmad, W.; Uddin, S.; Ali, N.; et al. *Int. J. Biol. Macromol.* 2021, 167, 169-181. DOI: 10.1016/j.ijbiomac.2020.11.167.
- [71] Bano, K.; Mittal, S.; Singh, P.; Kaushal, S. Nanoscale Adv. 2021, 3, 6446-6458. DOI: 10.1039/d1na00499a.
- [72] Akbal, F. Environ. Prog. 2005, 24, 317-322. DOI: 10.1002/ep.10092.
- [73] Bhattacharyya, A.; Kawi, S.; Ray, M.B.; *Catal. Today* 2004, 98 (3), 431-439. DOI: 10.1016/j.cattod.2004.08.010.
- [74] Fernandes, G.; Silva, W.; Barreto, D.; Lamarca, R.; Gomes, P.; Petruci, J.; Batista, A. Anal. Chim. Acta 2020; Vol. 1135, pp 187-203.
- [75] Tardivo, J. P.; Del Giglio, A.; de Oliveira, C. S.; Gabrielli, D. S.; Junqueira, H. C.; Tada, D. B.; Severino, D.; Turchiello, R. D. F.; Baptista, M. S. *Photodiagnosis Photodyn. Ther.* 2005, 2 (3), 175-191. DOI: 10.1016/s1572-1000(05)00097-9.
- [76] Saenz-Trevizo, A.; Piza-Ruiz, P.; Chavez-Flores, D.; Ogaz-Parada, J.; Amezaga-Madrid,
 P.; Vega-Rios, A.; Miki-Yoshida, M. J. Fluoresc. 2019, 29 (1), 15-25. DOI: 10.1007/s10895-018-2304-6.
- [77] Darwent, J. R.; Lepre, A. J. Chem. Soc., Faraday Trans. 2 1986, 82, 1457. DOI: 10.1039/f29868201457.
- [78] Brown, G.; Darwent, J. J. Chem. Soc., Faraday Trans. 1984, 80, 1631-1643.
- [79] Gorner, H.; Gruen, H.; Schultefrohlinde, D. J. Phys. Chem. 1980, 84, 3031-3039.
- [80] Magennis, S.; Mackay, F.; Jones, A.; Tait, K.; Sadler, P. Chem. Mater. 2005, 17, 2059-2062. DOI: 10.1021/cm048020d.
- [81] Chen, C. C.; Zhao, W.; Lei, P. X.; Zhao, J. C.; Serponer, N. Chem. Eur. J. 2004, 10 (8), 1956-1965. DOI: 10.1002/chem.200305453.
- [82] Watanabe, T.; Takizawa, T.; Honda, K. J. Phys. Chem. 1977, 81 (19), 1845-1851.
 DOI: 10.1021/j100534a012.
- [83] Ohtani, B. Phys. Chem. Chem. Phys. 2014, 16 (5), 1788-1797. DOI: 10.1039/c3cp53653j.
- [84] Ohtani, B. Electrochemistry 2014, 82, 414-425. DOI: 10.5796/electrochemistry.82.414.
- [85] Chiu, Y. H.; Chang, T. F. M.; Chen, C. Y.; Sone, M.; Hsu, Y. J. Catalysts 2019, 9 (5), 32. DOI: 10.3390/catal9050430.
- [86] Yan, X. L.; Ohno, T.; Nishijima, K.; Abe, R.; Ohtani, B. Chem. Phys. Lett. 2006, 429 (4-6), 606-610. DOI: 10.1016/j.cplett.2006.08.081.
- [87] Ohtani, B.; Iwai, K.; Nishimoto, S.; Sato, S. J. Phys. Chem. B 1997, 101 (17), 3349-3359. DOI: 10.1021/jp962060q.
- [88] Wang, W. S.; Ye, M. M.; He, L.; Yin, Y. D. Nano Lett. 2014, 14 (3), 1681-1686. DOI: 10.1021/nl500378k
- [89] Mohammad, T.; Morrison, H. J. Photochem. Photobiol. 2000, 71, 369-381.
- [90] Liu, G. M.; Zhao, J. C. New J. Chem. 2000, 24 (6), 411-417. DOI: 10.1039/b001573n.
- [91] Yang, J.; Chen, C. C.; Ji, H. W.; Ma, W. H.; Zhao, J. C. J. Phys. Chem. B 2005, 109 (46), 21900-21907. DOI: 10.1021/jp0540914.
- [92] Alneyadi, A. H.; Shah, I.; AbuQamar, S. F.; Ashraf, S. S. *Biomolecules* 2017, 7 (1), 18. DOI: 10.3390/biom7010031.

- [93] Bibi, I.; Bhatti, H. N.; Asgher, M. Biochem. Eng. J. 2011, 56 (3), 225-231. DOI: 10.1016/j.bej.2011.07.002.
- [94] Robinson-Duggon, J.; Marino-Ocampo, N.; Barrias, P.; Zuniga-Nunez, D.; Gunther, G.;
 Edwards, A. M.; Greer, A.; Fuentealba, D. J. Phys. Chem. A 2019, 123 (23), 4863-4872.
 DOI: 10.1021/acs.jpca.9b03588.
- [95] Wotherspoon, N.; Oster, G. J. Am. Chem. Soc. 1957, 79 (15), 3993-3995.
- [96] Cho, B. P.; Yang, T. L.; Blankenship, L. R.; Moody, J. D.; Churchwell, M.; Beland, F. A.; Culp, S. J. Chem. Res. Toxicol. 2003, 16 (3), 285-294. DOI: 10.1021/tx0256679.
- [97] Lee, J. B.; Kim, M. Food Sci. Biotechnol. 2012, 21 (2), 519-524. DOI: 10.1007/s10068-012-0066-5.
- [98] Dai, K.; Lu, L. H.; Dawson, G. J. Mater. Eng. Perform. 2013, 22 (4), 1035-1040. DOI: 10.1007/s11665-012-0344-7.
- [99] Merka, O.; Yarovyi, V.; Bahnemann, D. W.; Wark, M. J. Phys. Chem. C 2011, 115 (16), 8014-8023. DOI: 10.1021/jp108637r.
- [100] Kowalska, E.; Remita, H.; Colbeau-Justin, C.; Hupka, J.; Belloni, J. J. Phys. Chem. C 2008, 112, 1124-1131. DOI: 10.1021/jp077466p.
- [101] Zhang, T.; Oyama, T.; Aoshima, A.; Hidaka, H.; Zhao, J.; Serpone, N. J. Photochem. Photobiol. A: Chem. 2001, 140, 163-172. DOI: 10.1016/S1010-6030(01)00398-7.
- [102] Jakiminska, A.; Pawlicki, M.; Macyk, W. J. Photochem. Photobiol. A: Chem. 2022, 433,
 8. DOI: 10.1016/j.jphotochem.2022.114176.
- [103] Yogi, C.; Kojima, K.; Takai, T.; Wada, N. J. Mater. Sci. 2009, 44, 821-827. DOI: 10.1007/s10853-008-3151-7.
- [104] Aziz, B. K.; Karim, M. A. H. React. Kinet. Mech. Catal. 2019, 128 (2), 1127-1139. DOI: 10.1007/s11144-019-01677-8.
- [105] Zidan, H. M.; Ei-Ghamaz, N. A.; Abdelghany, A. M.; Waly, A. L. Spectrochim. Acta A Mol. Biomol. Spectrosc. 2018, 199, 220-227. DOI: 10.1016/j.saa.2018.03.057.
- [106] Lee, S. K.; Sheridan, M.; Mills, A. Chem. Mater. 2005, 17 (10), 2744-2751. DOI: 10.1021/cm0403863.
- [107] Chen, F.; Huang, H. W.; Zeng, C.; Du, X.; Zhang, Y. H. ACS Sustain. Chem. Eng. 2017, 5 (9), 7777-7791. DOI: 10.1021/acssuschemeng.7b01259.
- [108] Kang, S.; Jang, J.; Kim, H. J.; Ahn, S. H.; Lee, C. S. RSC Adv. 2019, 9 (29), 16375-16383. DOI: 10.1039/c9ra02074h.
- [109] Alikarami, S.; Soltanizade, A.; Rashchi, F. J. Phys. Chem. Sol. 2022, 171. DOI: 10.1016/j.jpcs.2022.110993.
- [110] Li, X. K.; Ouyang, S. X.; Kikugawa, N.; Ye, J. H. Appl. Catal. A: Gen. 2008, 334 (1-2), 51-58. DOI: 10.1016/j.apcata.2007.09.033.
- [111] Alikarami, S.; Soltanizade, A.; Rashchi, F. Mater. Chem. Phys. 2022, 285. DOI: 10.1016/j.matchemphys.2022.126174.
- [112] Yang, S.; Niu, C.; Huang, D.; Zhang, H.; Liang, C.; Zeng, G. *Environ. Sci. Nano* 2017, 4, 585-595. DOI: 10.1039/c6en00597g.
- [113] Lu, Y.; Wan, Y.; Bi, S.; Weng, H.; Huang, Y.; Qin, L.; Seo, H. Mater. Chem. Phys. 2016, 180, 263-271. DOI: 10.1016/j.matchemphys.2016.06.006.

- [114] Sawicki, E.; Pfaff, J.; Stanley, T. W. Anal. Chim. Acta 1963, 28 (2). DOI: 10.1016/s0003-2670(00)87213-x.
- [115] Ciocarlan, R. G.; Wang, H.; Cuypers, B.; Mertens, M.; Wu, Y.; Van Doorslaer, S.; Seftel, E. M.; Cool, P. Appl. Clay Sci. 2020, 197. DOI: 10.1016/j.clay.2020.105757.
- [116] Park, H.; Kim, H. I.; Moon, G. H.; Choi, W. Energy Environ. Sci. 2016, 9 (2), 411-433.
 DOI: 10.1039/c5ee02575c.
- [117] Agrios, A. G.; Gray, K. A.; Weitz, E. Langmuir 2004, 20 (14), 5911-5917. DOI: 10.1021/la036165d.
- [118] Zhang, G.; Kim, G.; Choi, W. *Energy Environ. Sci.* **2014**, 7 (3), 954-966. DOI: 10.1039/c3ee43147a.
- [119] Kim, S.; Choi, W. J. Phys. Chem. B 2005, 109 (11), 5143-5149. DOI: 10.1021/jp045806q.
- [120] Kuncewicz, J.; Zabek, P.; Kruczala, K.; Szacilowski, K.; Macyk, W. J. Phys. Chem. C 2012, 116 (41), 21762-21770. DOI: 10.1021/jp3040715.
- [121] Yu, S. Y.; Liu, Y.; Ren, H. T.; Liu, Z. Y.; Han, X. Phys. Chem. Chem. Phys. 2022, 24 (22), 13661-13670. DOI: 10.1039/d1cp04752c.
- [122] Li, X. Z.; Chen, C. C.; Zhao, J. C. *Langmuir* **2001**, 17 (13), 4118-4122. DOI: 10.1021/la010035s.
- [123] Agrios, A. G.; Gray, K. A.; Weitz, E. Langmuir 2003, 19 (4), 1402-1409. DOI: 10.1021/la026397x.
- [124] Cho, Y. M.; Kyung, H.; Choi, W. *Appl. Catal. B: Environ.* **2004**, 52 (1), 23-32. DOI: 10.1016/j.apcatb.2004.03.013.
- [125] Zhong, H. L.; Lu, C. J.; Sun, X. L.; Luo, Y. J.; Qian, Q. R.; Xue, H.; Yang, M. Q. ACS Appl. Mater. Interface 2023, 15 (30), 36312-36323. DOI: 10.1021/acsami.3c06701.
- [126] Chen, X. Y.; Peng, X.; Jiang, L. B.; Yuan, X. Z.; Zhang, J.; Yu, H. B. Colloids Surf. A: Physicochem. Eng. Asp. 2020, 603. DOI: 10.1016/j.colsurfa.2020.125188.
- [127] Bui, H. T.; Park, H. Y.; Alvarez, P. J. J.; Lee, J.; Kim, W.; Kim, E. J. *Environ. Sci. Technol.* 2022, 56 (15), 10829-10837. DOI: 10.1021/acs.est.2c02975.
- [128] Kim, G.; Lee, S. H.; Choi, W. Appl. Catal. B: Environ. 2015, 162, 463-469. DOI: 10.1016/j.apcatb.2014.07.027.
- [129] Qin, C. D.; Tang, J. J.; Qiao, R. X.; Lin, S. J. Chin. Chem. Lett. 2022, 33 (12), 5218-5222. DOI: 10.1016/j.cclet.2022.01.067.
- [130] Harvey, P. R.; Rudham, R. J. Chem. Soc., Faraday Trans. 1 1988, 84, 4181-4190. DOI: 10.1039/f19888404181.
- [131] Sakulkhaemaruethai, S.; Pavasupree, S.; Suzuki, Y.; Yoshikawa, S. *Mater. Lett.* 2005, 59 (23), 2965-2968. DOI: 10.1016/j.matlet.2005.03.074.
- [132] Lim, J.; Monllor-Satoca, D.; Jang, J. S.; Lee, S.; Choi, W. Appl. Catal. B: Environ. 2014, 152, 233-240. DOI: 10.1016/j.apcatb.2014.01.026.
- [133] Park, Y.; Kim, W.; Park, H.; Tachikawa, T.; Majima, T.; Choi, W. *Appl. Catal. B: Environ.* 2009, 91, 355-361. DOI: 10.1016/j.apcatb.2009.06.001.
- [134] Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. J. Phys. Chem. 1988, 92 (18), 5196-5201. DOI: 10.1021/j100329a027.

- [135] Shenawi-Khalil, S.; Uvarov, V.; Fronton, S.; Popov, I.; Sasson, Y. J. Phys. Chem. C 2012, 116 (20), 11004-11012. DOI: 10.1021/jp3009964.
- [136] Cabrero-Antonino, M.; Albero, J.; Garcia-Valles, C.; Alvaro, M.; Navalon, S.; Garcia, H. Chem. Eur. J. 2020, 26 (67), 15682-15689. DOI: 10.1002/chem.202003763.
- [137] Park, H.; Choi, W. J. Phys. Chem. B 2004, 108 (13), 4086-4093. DOI: 10.1021/jp036735i.
- [138] Kong, C.; Qin, L. X.; Liu, J. F.; Zhong, X. H.; Zhu, L. Y.; Long, Y. T. Anal. Methods 2010, 2 (8), 1056-1062. DOI: 10.1039/c0ay00201a.
- [139] Jiang, T. F.; Xie, T. F.; Chen, L. P.; Fu, Z. W.; Wang, D. J. Nanoscale 2013, 5 (7), 2938-2944. DOI: 10.1039/c3nr34219k.
- [140] Noguchi, T.; Fujishima, A. *Environ. Sci. Technol.* **1998**, 32 (23), 3831-3833. DOI: 10.1021/es980299+.
- [141] Sekiguchi, K.; Sasaki, C.; Sakamoto, K. Ultrason. Sonochem., 2011; Vol. 18, pp 158-163.
- [142] Nash, T. Biochem. J. 1953, 55 (3), 416-421. DOI: 10.1042/bj0550416.
- [143] Li, Q.; Sritharathikhun, P.; Motomizu, S. Anal. Sci. 2007, 23 (4), 413-417. DOI: 10.2116/analsci.23.413.
- [144] Ahmed, L. M.; Hussein, F. H.; Mahdi, A. A. Asian J. Chem. 2012, 24 (12), 5564-5568.
- [145] Ahmed, L. M.; Ivanova, I.; Hussein, F. H.; Bahnemann, D. W. Int. J. Photoenergy 2014, 2014. DOI: 10.1155/2014/503516.
- [146] Kandiel, T. A.; Robben, L.; Alkaim, A.; Bahnemann, D. *Photochem. Photobiol. Sci.* 2013, 12 (4), 602-609. DOI: 10.1039/c2pp25217a.
- [147] Pradhan, S.; Ghosh, D.; Chen, S. W. ACS Appl. Mater. Interfaces 2009, 1 (9), 2060-2065. DOI: 10.1021/am900425v.
- [148] Mersal, M.; Mohamed, G. G.; Zedan, A. F. *Opt. Mater.* **2021**, 122. DOI: 10.1016/j.optmat.2021.111810.
- [149] Sharma, B. K.; Ameta, R.; Kaur, J.; Ameta, S. C. Int. J. Energy Res. 1997, 21 (10), 923-929. DOI: 10.1002/(sici)1099-114x(199708)21:10<923::aid-er299>3.0.co;2-b.
- [150] Jain, S.; Dangi, G.; Vardia, J.; Ameta, S. C. Int. J. Energy Res. 1999, 23 (1), 71-77. DOI: 10.1002/(sici)1099-114x(199901)23:1<71::aid-er464>3.0.co;2-g.
- [151] Jain, S.; Vardia, J.; Sharma, A.; Ameta, S. C. Int. J. Energy Res. 2001, 25 (2), 107-113. DOI: 10.1002/er.664.abs.
- [152] Jain, S.; Vardia, J.; Ameta, R.; Ameta, S. C. Energy Convers. Manag. 2004, 45 (7-8), 1233-1242. DOI: 10.1016/j.enconman.2003.08.007.
- [153] Diesen, V.; Dunnill, C. W.; Osterberg, E.; Parkin, I. P.; Jonsson, M. Dalton Trans. 2014, 43 (1), 344-351. DOI: 10.1039/c3dt52270a.
- [154] Yang, M.; Jonsson, M. J. Phys. Chem. C 2014, 118 (15), 7971-7979. DOI: 10.1021/jp412571p.
- [155] Amalia, F. R.; Takashima, M.; Ohtani, B. Chem. Commun. 2022, 58 (83), 11721-11724.
 DOI: 10.1039/d2cc04291f.
- [156] Janczarek, M.; Wei, Z.; Mogan, T.; Wang, L.; Wang, K.; Nitta, A.; Ohtani, B.; Kowalska, E. Symmetry-Basel, 2021; Vol. 13. DOI: 10.3390/sym13091682.

- [157] Macyk, W.; Szacilowski, K.; Stochel, G.; Buchalska, M.; Kuncewicz, J.; Labuz, P. Coord. Chem. Rev. 2010, 254, pp 2687-2701. DOI: 10.1016/j.ccr.2009.12.037.
- [158] Wang, K. L.; Wei, Z. S.; Ohtani, B.; Kowalska, E. Catal. Today 2018, 303, 327-333. DOI: 10.1016/j.cattod.2017.08.046.
- [159] Kim, S.; Hwang, S. J.; Choi, W. Y. J. Phys. Chem. B 2005, 109 (51), 24260-24267. DOI: 10.1021/jp055278y.
- [160] Ahmed, A. Y.; Kandiel, T. A.; Oekermann, T.; Bahnemann, D. J. Phys. Chem. Lett. 2011, 2 (19), 2461-2465. DOI: 10.1021/jz201156b.

Biography

Fitri Rizki Amalia

Fitri Rizki Amalia received her M. Sc. and Ph. D. degrees in 2019 and 2022, respectively, from Graduate School of Environmental Science - Hokkaido University - Japan. After finishing her study, she has been working as an assistant professor at Faculty of Chemistry – Jagiellonian University in Poland since 2023. Her research interests are mainly about reliable evaluation of photocatalytic activity, vis-active photocatalysts and inverse-opal photocatalysts. Recently, she has just been awarded for 'Miniatura 8' research grant to conduct research about quantum dots-modified photocatalysts from National Science Centre, Poland.



Ewa Kowalska

Ewa Kowalska is professor at Jagiellonian University (JU). She received PhD degree in chemical technology (GUT, Poland) in 2004. After completing JSPS (2005-2007), GCOE (2007-2009) postdoctoral fellowships in Japan, and Marie Sklodowska-Curie fellowships in France (2002-2003) and Germany (2009-2012), she worked at Institute for Catalysis, Hokkaido University as associate professor (2012-2022). In 2022 she was appointed professor at Faculty of Chemistry, JU. Her research interests focus on environmental protection, AOPs, energy conversion, plasmonic photocatalysis. She has published over 120 papers and has led many research grants (e.g., CONCERT Japan, Bill & Melinda Gates Foundation, European Commission (MSC), NCN, NAWA); https://ewakowalskasapporo.wixsite.com/ewa-kowalska.



Bunsho Ohtani

Since 1981 Dr. Ohtani has been studying photocatalysis and related topics for more than 30 years and published more than 300 original papers. After gaining his Ph. D. degree from Kyoto University in 1985, he became an assistant professor in the university. In 1996, he was promoted to an associate professor in Hokkaido University and was then awarded a full professor position in the Catalysis Research Center (presently Institute for Catalysis), Hokkaido University in 1998. After retirement from Hokkaido University at the end of March 2022, he established Nonprofitable Organization touche NPO in Sapporo to support scientists.



Declaration of interests

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- 1) Spectroscopic analysis as reliable method for photocatalytic activity testing
- 2) Dye sensitization and charge transfer as key-factors limiting molecules' use
- 3) Careful use of dyes and other organic compounds in heterogeneous photocatalysis

Journal Pression