Isotopic Effects in Photocatalysis: An Underexplored Issue

Günemann, C., Bahnemann, D. W., & Robertson, P. K. J. (2021). Isotopic Effects in Photocatalysis: An Underexplored Issue. ACS Omega, 6(17), 11113−11121. https://doi.org/10.1021/acsomega.1c00178

Published in:
ACS Omega

Document Version:
Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
Copyright 2021 the authors. This is an open access article published under a Creative Commons Attribution License (https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution and reproduction in any medium, provided the author and source are cited.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Download date:15. Jul. 2021
Isotope Effects in Photocatalysis: An Underexplored Issue

Carsten Günemann, Detlef W. Bahnemann, and Peter K. J. Robertson

ABSTRACT: In order to improve the performance of well-established photocatalysts and to develop new potential photocatalyst materials, an understanding of the underlying mechanisms of photocatalytic reactions is of the utmost importance. An often neglected method for studying the mechanism is the investigation of isotope effects. Although just a few studies related to isotope effects exist, it has been shown to be a powerful tool for exploring mechanisms of photocatalytic processes. Most of the reports are focused on TiO₂, which is the most studied photocatalyst, while there is a lack of data for other photocatalyst materials. This mini-review represents an overview of research utilizing isotope effects in the area of photocatalysis. The benefits and the importance of these studies will be highlighted, and the potential for these processes to be applied for the study of further photocatalytic reactions and different photocatalyst materials will be shown.

INTRODUCTION

Semiconductor photocatalysis is a versatile technology that has been applied to a broad range of applications from treatment of contaminated water and air to energy conversion and storage. In designing and developing this process for practical commercial applications, it is critical to have a robust understanding of fundamental mechanistic processes that are occurring on the surface of the semiconductor material. A broad range of physical and chemical methods have been used in developing our understanding of these surface processes over the past four decades. One area that has not been applied to the same extent is the application of isotope effects to probe photocatalytic processes and mechanisms.

For this purpose, it is always necessary to perform two sets of experiments. In one experimental run one species (e.g., the photocatalyst) is labeled, and in a further run the same reaction is performed but with the same species unlabeled. This allows a comparison of both runs to make conclusions related to the mechanism of the investigated reaction.

The labeling of reactant molecules or the photocatalyst allows us to study the transfer of atoms between both species. For a correct interpretation of the obtained results, several points need to be considered. Besides a reaction during illumination, also a reaction in the dark needs to be performed since it might be possible that an exchange of atoms occurs spontaneously between the photocatalyst and the reactant molecules, which could lead to wrong conclusions for the reaction under illumination. Further, it is important to consider all possible reaction products that might be produced. For example, if CO₂ is the reaction product and the incorporation of O is expected, it is necessary to detect C¹⁶O₂, C¹⁶O¹⁸O, and C¹⁸O₂.

In the case of the investigation of solvent isotope effects, the effect of the exchange of H₂O by D₂O on the rate constant is investigated. It can be recommended not only to perform experiments in pure H₂O or D₂O but also to consider mixtures of both solvents.

This paper explores the areas in which these techniques have been used successfully to date and also looks at the scope for more extensive application of such methods to studying the photocatalytic process promoted by semiconductor materials. In this mini-review, works from our groups as well as works from other groups are considered.

ISOTOPIC LABELING OF SEMICONDUCTOR PHOTOCATALYST MATERIALS AND TARGET MOLECULES FOR REACTION

Isotopic labeling is a method to investigate the incorporation of atoms from reactant molecules into the surface of the photocatalyst and vice versa during a reaction, which allows the mechanism of chemical processes on surfaces to be followed. In the case of TiO₂ as a photocatalyst, oxygen labeling (exchange of O by ¹⁸O) is commonly used. For this, two different methods exist, since the reactant molecules can be either isotopic labeled or TiO₂ itself.

Courbon et al. showed that after ¹⁸O₂ adsorption on TiO₂ and following UV illumination ¹⁶O¹⁸O and ¹⁶O₂ can be detected in the gas phase, while the ¹⁸O₂ content decreases.

Received: January 11, 2021
Accepted: April 5, 2021
which proves the incorporation of \(^{18}\text{O}^2\) into the surface of TiO\(_2\). Furthermore, they were able to confirm that only one surface oxygen anion is involved in the exchange at a time. The proposed mechanism of the oxygen isotopic exchange (OIE), as described by Pichat et al., is depicted in Figure 1. After the excitation with light, with an energy equal to or higher than the band gap energy of TiO\(_2\), electron–hole pairs are formed. The conduction band electrons are able to reduce \(^{18}\text{O}_2\), which leads to the formation of superoxide radicals (\(^{18}\text{O}_2^\cdot\)). Since the additional electron is in an antibonding orbital, the O–O bond is weakened in the superoxide radical. In the lattice of the oxide, an \(^{16}\text{O}^2\) anion transfers an electron to the conduction band, forming an \(^{16}\text{O}^\cdot\) radical, which causes a weakened bond to the neighboring Ti\(^4^+\) cations. Further, the generated species react with each other, leading to the incorporation of \(^{18}\text{O}_2\) in the surface and the release of \(^{16}\text{O}^\cdot\) to the gas phase. However, Pichat et al. pointed out that there is, to the best of their knowledge, no proof for the existence of a complex between \(^{18}\text{O}^\cdot\) and \(^{16}\text{O}^\cdot\).

Tanaka suggested that the OIE reaction proceeds via an \(^{18}\text{O}^\cdot\) radical anion, while Murata et al. were able to confirm the formation of this species. Equation 1 describes the reaction mechanism based on the formation of an \(^{18}\text{O}^\cdot\) intermediate, which thus rules out a direct involvement of a superoxide species as proposed by Pichat et al. Courbon et al. found that the activity for the photooxidation of isobutane correlates with the activity for the OIE and thus concluded that an \(^{18}\text{O}\) species is involved in both reactions, which supports the mechanism.

\[
^{16}\text{O}^\cdot + ^{18}\text{O}_2 \rightarrow [^{18}\text{O}^{18}\text{O}^{16}\text{O}]^\cdot \rightarrow ^{16}\text{O}^\cdot + ^{18}\text{O}^\cdot
\]  

(1)

The isotopic-labeled oxygen can be used also simultaneously with other unlabeled molecules to investigate the effect of the OIE. For example, Liao et al. reported that during UV illumination of a TiO\(_2\) surface no oxygen exchange between \(^{18}\text{O}_2\) and adsorbed CO occurs, while for adsorbed CO\(_2\), CO\(_3^−\), and HCOO species an oxygen exchange was observed.

A further approach is to use directly isotopic-labeled reactant molecules instead of \(^{18}\text{O}_2\). Isotopic-labeled water (H\(_2^{18}\text{O}\)) was used by Nakamura et al. to support their proposed mechanism (Figure 2) for the oxygen evolution of rutile in contact with aqueous solutions during illumination, with Ti–O–O–OH and Ti–O–O–Ti as intermediates. Zhang et al. showed that \(^{18}\text{O}\)-enriched cyclohexanol and benzyl alcohol form in the presence of TiO\(_2\) and \(^{16}\text{O}_2\) during illumination in benzotrifluoride cyclohexanone and benzaldehyde that contain approximately 100\% \(^{16}\text{O}\). Further, they were able to exclude the possibility of oxygen transfer from the TiO\(_2\) to the molecule.

Besides isotopic labeling of the reactant molecules, a further method is to label the photocatalyst. \(^{18}\text{O}\)-enriched surfaces can be prepared via different approaches. The surface of Ti\(^{16}\text{O}_2\) can be \(^{18}\text{O}\)-enriched in contact with \(^{18}\text{O}_2\) at 750 K\(^\circ\) under UV irradiation in H\(_2^{18}\text{O}\) for 12 h, or by applying a potential of 1 V in an \(^{18}\text{O}\)-containing electrolyte during illumination. It needs to be taken into account that the \(^{18}\text{O}\)-enrichment is limited to the surface of TiO\(_2\). Kavan et al. reported the synthesis of isotopically pure Ti\(^{18}\text{O}_2\) by the hydrolysis of TiCl\(_4\) in H\(_2^{18}\text{O}\), yielding anatase, which can be transformed to rutile by heating to 1000 °C in a vacuum. Henderson investigated the formic acid decomposition at an \(^{18}\text{O}\)-enriched (100) TiO\(_2\) crystal without illumination. It was demonstrated that \(^{18}\text{O}\)-containing products are released during the decomposition (H\(_2^{18}\text{O}\), CH\(_2^{18}\text{O}\)\(^{18}\text{O}\), \(^{18}\text{O}\)\(^{18}\text{O}\)), which confirms the incorporation of lattice oxygen into the products. Henderson also investigated the same reaction at an \(^{18}\text{O}\)-enriched (110) TiO\(_2\) crystal in the dark. Similar as for the (100) crystal, the transfer of lattice oxygen to the product molecules was observed.

Figure 1. Proposed mechanism of oxygen isotopic exchange by Pichat et al. Created in analogy to ref 3.

Figure 2. Mechanism for the oxygen evolution of TiO\(_2\) (rutile) in aqueous solutions with a pH between 1 and 12 during illumination. Reprinted with permission from ref 8. Copyright 2004 American Chemical Society.
with adsorbed HCl and water, no OIE was observed. Civis et al. investigated the same interface in the dark and during illumination. As shown in Figure 3, an involvement of oxygen vacancies in the OIE reaction in the dark was found, while the whole process was found to be very fast. One oxygen atom of each C16O2 molecule coordinates to a vacancy, while the carbon atoms coordinate to lattice oxygen (Figure 3a). A CO3 bidentate species is formed with one oxygen atom from the C16O2 molecule being incorporated into the TiO2 lattice (Figure 3b). The major product of the OIE is C18O2 with a minor content of C16O18O. The adsorption of water on the surface did not suppress the OIE, and thus the water is not competing with CO2 for adsorption sites. By laser irradiation of the H216O-treated Ti18O2, it was possible to enhance the OIE reaction with C16O2. Further, as products of the photocatalytic reduction of C16O2, methane and C16O were detected.

Montoya et al. investigated the H216O photooxidation in the presence of Ti18O2 and Ag+ ions as electron scavengers. During illumination, a higher 16O18O/16O2 quadrupole mass spectrometry (QMS) signal ratio as compared to the dark could be detected, which turned back to the initial value after switching off the light (Figure 4). In contrast, by applying Ti16O2 instead, independent from the illumination, no change in the QMS signal ratio appeared. Since in the case of Ti18O2 16O18O was evolved, it could be concluded that the photooxidation of water proceeds via a bridging oxygen from the lattice of TiO2, which is incorporated in the oxygen molecules. In the initial step, a 2-fold-coordinated (symbol: >) bridging oxygen (>Obr) reacts with a photogenerated hole, leading to the formation of a 1-fold coordinated (symbol: −) bridging oxygen radical (−Obr*) and a 1-fold coordinated bridging hydroxyl radical (−OHbr*), respectively. The further steps yielding molecular oxygen according to the water redox photooxidation (WRP) mechanism are described elsewhere.

\[ \text{Obr}^2− + h^+ \rightarrow \text{Obr}^∗ \]  
\[ \text{OHbr}^2− + h^+ \rightarrow −\text{OHbr}^∗ \]  

Melchers et al. employed Ti18O2 to analyze the mechanism of the anaerobic acetaldehyde degradation during illumination. In a previous study of the same authors, the incorporation of lattice oxygen into acetate after the adsorption of acetaldehyde was proposed, which resulted in the formation of CO2 and CH4. The comparison of the C16O18O/C16O2 QMS signal ratio of Ti16O2 and Ti18O2 showed that during illumination no change for Ti16O2 occurs, while for Ti18O2 the ratio increases (Figure 5). Consequently, the incorporation of lattice oxygen into the product molecules, and thus the proposed mechanism (Figure 6), could be proven.

Montoya et al. studied the anaerobic oxidation of benzene in aqueous solutions in the presence of Ti18O2 and Ag+ as electron scavenger. TiO2 with an unlabeled hydrated surface (Figure 7), employing H216O, was used to distinguish between two possible reaction pathways. Either hydroxyl radicals are generated from adsorbed water species (16OHads) or lattice...
oxygen is involved in the generation of radicals (−18O•−/−18OH•) and thus the oxidation of benzene. The C16O18O/C16O2 QMS signal ratio of Ti18O2 is dependent on

higher ratios (Figure 8). For Ti16O2 the ratio under

the water concentration, while a lower concentration yields

higher compared to unlabeled Ti16O2, which indeed con

firms the involvement of bridging oxygens in the mineralization of benzene and the incorporation of these species into the product molecules.

Montoya et al.21 investigated also the oxidation of benzene in acetonitrile with Ti18O2 in the presence of Ag+ as an electron scavenger to prove the incorporation of surface oxygen of TiO2 into the mineralization product CO2. The C16O18O/C16O2 QMS signal ratio of Ti18O2 is dependent on the water concentration, while a lower concentration yields higher ratios (Figure 8). For Ti18O2 the ratio under

causes the formation of a terminal radical (18O•−) (eq 5). A physisorbed benzene molecule (C6H6) coordinates to a terminal radical, and an incipient covalent bond is formed (eq 6). The reaction with a further free photogenerated hole causes the formation of a phenol molecule (C6H518O), which contains an 18O atom that originates from the surface of Ti18O2 and an oxygen vacancy (V[18O−]) (eq 7). The vacancy can be healed by the dissociative adsorption of a H216O molecule, whereby an 18O2− anion is incorporated into the surface of Ti18O2 (eq 8). As shown in eqs 9–11, the incorporated 18O2− anion can also act as a hole scavenger, which finally results in the formation of a phenol molecule that contains an 16O atom (C6H516O). The resulting vacancy V[16O−] is healed by the dissociative adsorption of a further H216O molecule (eq 12). Ag+ ions are able to react with the free photogenerated electrons, which leads to the formation of metallic silver (eq 13). In eq 14, the complete process is summarized, which shows the exchange of an 18O2− anion with an 16O2− anion at the surface of Ti18O2.

Figure 6. Reaction mechanism of the anaerobic degradation of acetaldehyde in the presence of TiO2 under illumination. Adapted from ref 18. Copyright 2020, with permission from Elsevier.

Figure 7. Ti18O2 surface with labeled bridging oxygens (18O) and unlabeled chemisorbed water species (16OH). Reprinted with permission from ref 28. Copyright 2013 American Chemical Society.

Figure 8. C16O18O/C16O2 QMS signal ratio from the anaerobic mineralization of benzene in acetonitrile in the presence of Ti18O2 (1–3) and Ti16O2 (4) under illumination. The following water concentrations were employed: (1) c(H2O) = 0.560 mmol L−1, (2) c(H2O) = 10 mmol L−1, (3) c(H2O) = 24 mmol L−1, and (4) c(H2O) = 24 mmol L−1. Copyright 2014 Wiley. Used with permission from ref 21.

SOLVENT ISOTOPE EFFECTS IN PHOTOCATALYSIS

Solvent isotope studies have been used extensively by organic chemists for decades. In this process, the relative rates of a reaction are compared, when they are carried out in normal water and deuterated water or “heavy” water. The solvent isotope effect (SIE) is the ratio of the rate constant in the “heavy” water (kH) to that observed in normal water (kD):

SIE = kH/kD (15)

Typically the reactions in the heavy water solvent are significantly slower, and hence the rate constants are lower than those observed in normal water. The slower reaction rate in the deuterated solvent is due to the fact that the deuterated solvent has a lower vibrational zero-point energy, and hence a greater activation energy is required to dissociate the OD bond.
compared to OH bonds. Consequently, the rates are slower in deuterated solvents, which are involved in reactions.

Cunningham and Srijaranai were the first to report the use of this technique for a semiconductor photocatalytic process in 1988.23a In their investigation of the photocatalytic degradation of isopropanol (IPA) using TiO$_2$, they observed a primary solvent isotope effect of 3. It was proposed that the reduced rate of IPA destruction in D$_2$O was a result of the lower quantum efficiency for the formation of OD$^+$ radicals on the TiO$_2$ surface in the heavy water solvent. As a result of this, there would be a lower number of OD$^+$ radicals on the TiO$_2$ surface, which would be available to attack the isopropanol. On the basis of this proposal, they suggested that the photogeneration of hydroxyl radicals was the rate-determining step for the photocatalytic process.

Robertson et al. also observed a solvent isotope effect of 3 for the photocatalytic destruction of the cyanobacterial toxin microcystin-LR using a P25 TiO$_2$ photocatalyst.23b The solvent isotope effect observed by Cunningham for the decomposition of IPA was the same as that reported by Robertson for the cyanotoxin, considering the substantial difference in structure and the molecular mass of the two substrates. Robertson suggested that this was also a confirmation of Cunningham and Srijaranai’s proposal that the hydroxyl radical generation on the photocatalyst surface was also the rate-determining step for the photocatalytic reaction.

In a subsequent study, Robertson and co-workers investigated the solvent isotope effect on the degradation of microcystin-LR (MC-LR) and another cyanobacterial chemical metabolite, geosmin (GSM), using a Hombikat K01/C TiO$_2$ photocatalyst.23b In this case a solvent isotope effect of 1.5 was observed for microcystin and geosmin,23b which was approximately 50% lower than that found in the previous studies by Robertson et al. and Cunningham and Srijaranai (Table 1).

| GSM | MC-LR |
|-----|-------|
| | solvent | k (μM min$^{-1}$) | relative rate | k (μM min$^{-1}$) | relative rate |
| H$_2$O | 1.56 | 1.0 | 8.55 | 1.0 |
| D$_2$O | 0.97 | 0.62 | 5.44 | 0.64 |

"Reprinted from ref 23b. Copyright 2011, with permission from Elsevier.

In this study, Robertson et al. proposed that the solvent isotope effect observed for both molecules was mediated via hydroxyl radicals, generated from the subsequent reduction of the superoxide radical anion, produced at the conduction band. After being generated, the superoxide would be hydrated or deuterated by the solvent to form a hydroperoxide ion (eq 16). The hydroperoxide ions may then interact to form hydroxyl peroxide, which would then generate OH$^+$ (or OD$^+$) radicals following an electron transfer from the conduction band again. This may be rate determining since O$_2$ has to be generated at the conduction band prior to the interaction with the solvent and the subsequent formation of OD$^+$ or OH$^+$ species (eqs 17 and 18).

\[
O_2^{\cdot\cdot} + H^+ \rightarrow HO_2^+ \tag{16}
\]

\[
HO_2^+ + HO_2^+ \rightarrow H_2O_2 + O_2 \tag{17}
\]

\[
H_2O_2 + \epsilon_{cb} \rightarrow OH^+ + OH^- \tag{18}
\]

It was suggested that the observed solvent isotope effect could be a result of the rate of the reaction of the solvent with superoxide species rather than by the rate of reaction of OH$^+$ (or OD$^+$) on the microcystin or geosmin. If the isotope reaction depended on this latter reaction, one would expect it to be the same no matter what photocatalyst or species being oxidized was utilized.

An interesting observation is the fact that the solvent isotope effect is approximately 3 for P-2S and approximately 1.5 for K01/C. They also suggested that since similar kinetic solvent isotope effects were observed for different substrate molecules on the same photocatalyst materials the interaction of the solvent with the photocatalyst and the rate of oxidation of the solvent were probably the rate-determining steps for the photocatalytic reaction, as opposed to conduction band reduction of oxygen as previously proposed by Gersicher and Heller.24 Furthermore, Robertson et al. proposed that the reason the kinetic solvent isotope effect observed in this subsequent work was smaller than that in their previous study and Cunningham’s work was due to the fact that different photocatalyst materials were employed,23b and hence the effect was likely to be dependent on the photocatalyst material.

Belhadj et al. used solvent isotope effects to study the adsorption of water and deuterium oxide on TiO$_2$ surfaces in the dark and under UV(A) irradiation using in situ ATR-FTIR spectroscopy under aerobic and anaerobic conditions.25a Under dark conditions in a mixture of H$_2$O and D$_2$O solvents, an isotope exchange was found to occur on the surface of the TiO$_2$ material. Following irradiation with UV(A) light, the quantity of both OH and OD groups was found to be increasing in the presence of molecular oxygen. Additionally, hydroperoxide was generated through a photocatalytic process under aerobic conditions, which was believed to be produced as a result of the reduction of molecular oxygen adsorbed at the TiO$_2$ surface by the photogenerated conduction band electrons, as opposed to being generated via water oxidation from valence band holes. It was also demonstrated from the spectroscopic studies that under conditions where the percentage of H$_2$O was significantly less than that of D$_2$O there was an exchange of solvent groups on the TiO$_2$ surface with the OD$^-$ ions, having a stronger adsorption affinity to the photocatalyst compared to the OH$^-$ ions. Following illumination with UV light, both OH and OD groups were generated on the photocatalyst surface in the presence of oxygen. The generation of these groups also increased the hydrophilicity of the TiO$_2$ surface. If the experiment was conducted under either a nitrogen or argon atmosphere, there was no evidence of the formation of OH and OD groups, and the hydrophilicity was inhibited (Figure 9). This result indicated that under UV irradiation oxygen played a critical role in both the photocatalytic response and the photoinduced hydrophilicity.

In a subsequent study, the adsorption and photocatalytic degradation of acetate on TiO$_2$ surfaces was investigated in H$_2$O and D$_2$O by both attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR) and EPR spectroscopy.23b Different interactions between the adsorbed acetate and OD groups resulted from the isotopic exchange on the TiO$_2$ surface following adsorption of D$_2$O. The interaction
of the acetate with the TiO₂ surface was found to be strongly influenced by the pH, and a range of surface complexes with the acetate were observed to form. Under acidic conditions, the formation of a bidentate structure involving two distinct Ti atoms appeared to be the preferred complex structure. At pH values close to the point of zero charge for the TiO₂, the acetate favored a monodentate complex, formatted through adsorption to the positively charged TiO₂ anatase material (Figure 10).

Following irradiation with UV(A) light, hydroxyl radicals were observed under alkaline conditions, while methoxy radicals were generated under acidic conditions. Two different degradation pathways were proposed for the acetate under acidic and alkaline conditions (Figure 11), which were supported by the experimental studies performed using ATR-FTIR and EPR spectroscopy. Overall, the results of the EPR study suggested that under alkaline conditions acetate degradation was mainly promoted by attack by valence band generated hydroxyl radicals. Under acidic conditions, the degradation appeared to occur via direct oxidation via photogenerated valence band holes.

Solvent isotope studies were also used for the investigation of the simultaneous photocatalytic degradation of formaldehyde and hydrogen evolution on a platinized TiO₂ material under an oxygen-free atmosphere. Using QMS and ATR-FTIR spectroscopy for analysis, the main reaction products obtained from the photocatalytic degradation of 20% formaldehyde were hydrogen and carbon dioxide in a ratio of 2 to 1. From the solvent isotope study, it was found that the rate of mineralization of formaldehyde to CO₂ is significantly reduced with increasing concentration of D₂O. Following the investigation of the solvent isotope effect on the system using ATR-FTIR analysis, it was proposed that the formaldehyde oxidation was promoted by attack by OD⁺ radicals, formed from the reaction with the photogenerated valence band hole. This reaction generated a surface-adsorbed deuterated formic acid (HCOOD), which subsequently underwent further oxidation by valence band holes in a photo-Kolbe-type reaction. The photogenerated conduction band electrons were proposed to simultaneously reduce H⁺ and D⁺, originating from both formaldehyde and D₂O, to form molecular HD. The yield of the HD gas was found to be strongly influenced by the solvent and was maximized when the ratio of H₂O:D₂O was 20:80%. The proposed mechanism for the simultaneous hydrogen production and formaldehyde oxidation in the presence of D₂O is summarized in eqs 19–26 below:

\[
\begin{align*}
\text{Pt/TiO}_2 & \rightarrow e^- (\text{Pt}) + h^+ (\text{TiO}_2) \\
\text{D}_2\text{O} + h^+ & \rightarrow \text{OD}^+ + \text{D}^+ \\
\text{HCHO} + \text{OD}^+ & \rightarrow \text{HCOOD} + \text{H}^+ \\
\text{H}^+ + h^+ & \rightarrow \text{H}^2 \\
\text{D}^+ + \text{H}^+ + 2\text{e}^- & \rightarrow \text{HD} \\
\text{HCOOD} + 2h^+ & \rightarrow \text{CO}_2 + \text{H}^+ + \text{D}^+ \\
\text{D}^+ + \text{H}^+ + 2\text{e}^- & \rightarrow \text{HD} \\
\text{HCHO} + \text{D}_2\text{O} & \rightarrow \text{CO}_2 + 2\text{HD}
\end{align*}
\]

Figure 9. Evolution of the intensity of the integrated spectral areas of OH and OD stretching groups before and after UV irradiation: effect of dissolved O₂, N₂, and Ar on the adsorption of H₂O−D₂O on the TiO₂ surface. Reprinted from ref 25a. Published by the PCCP Owner Societies.

Figure 10. Schematic representation for the adsorption of acetate on the anatase surface (UV100) in the dark at pH < pH_pzc (A), pH ≈ pH_pzc (B), pH > pH_pzc (C). Reprinted from ref 25b. Copyright 2016, with permission from Elsevier.

Figure 11. Proposed mechanism for the photocatalytic reaction of acetate at pH 9 (A) and pH 3 (B). Reprinted from ref 25b. Copyright 2016, with permission from Elsevier.
SCOPe FOR RESEARCH DEVELOPMENT AND FOCUS

Each of the studies considered in this paper related to the labeling of photocatalyst materials and target molecules have utilized TiO₂ as the photocatalyst. This is also the case for the studies dealing with solvent isotope effects. Although TiO₂ is the most studied photocatalyst material, there has only been a relatively small number of reports related to isotope effects. As has been detailed above, the use of these isotope studies has enabled important insights to be gained for photocatalytic reactions on TiO₂, but there is still significant scope for further studies using these techniques.

For future research, while also investigating the isotope effects of the photocatalytic decomposition of other substrates on TiO₂ materials, it would be important to extend the studies to other photocatalyst materials as well. For example, Fe₂O₃, WO₃, CdS, C₃N₄, and SrTiO₃ are known as photocatalytically active materials, while the labeling of the catalyst or reactant molecules would allow us to get deeper insights into the corresponding mechanisms using these materials.

With respect to TiO₂ itself, there are many more reaction mechanisms that should be investigated based on solvent isotope effects. In particular, the involvement of terminal hydroxyl or oxygen radicals in the photocatalytic mechanism, as one of the initial steps, might be either established or refuted.

The technique could also be used for kinetic studies, particularly in the case of rapidly decomposing intermediates, which may be more easily followed in the heavy water solvent.

CONCLUSION

The investigation of isotope effects represents a powerful tool in the area of photocatalysis to study the mechanisms of the reactions occurring on the surface of photocatalyst materials. Using this technique, it is possible to elucidate whether photocatalyst surface atoms are transferred into product molecules, while also the incorporation of atoms from reactant molecules into the surface of the photocatalyst can be observed. Furthermore, by exchanging H₂O by D₂O, the ratio of the rate constants between both solvents can be followed to investigate whether the generation of hydroxyl radicals is the rate-determining step of a reaction. Using D₂O as a solvent has a further advantage since it allows the determination of whether hydrogen atoms in product molecules originate from reactant molecules or from the solvent. Consequently, it is important to perform such studies to allow the determination of the mechanistic pathway of the photocatalytic process. It should be noted that isotope effect studies are, however, not enough as the sole process to provide such detail, but in combination with other tools, they can provide important information on such processes.

In conclusion, it is clear that the application of isotope studies is a versatile and useful tool for studying photocatalytic reactions; however, the technique has only been applied in a relatively small number of investigations. There is therefore great scope for the further application of this technique in the field of semiconductor photocatalysis, and it is anticipated that this will be an area of growing interest within the photocatalytic research community over the next few years.

AUTHOR INFORMATION

Corresponding Author
Detlef W. Bahnemann – Institut für Technische Chemie, Leibniz Universität Hannover, D-30167 Hannover, Germany; Laboratory “Photoactive Nanocomposite Materials”, Saint-Petersburg State University, Peterhof, Saint-Petersburg 198504, Russia; orcid.org/0000-0001-6064-6653; Email: bahnemann@iftc.uni-hannover.de

Authors
Carsten Günneßmann – Institut für Technische Chemie, Leibniz Universität Hannover, D-30167 Hannover, Germany; orcid.org/0000-0002-5916-1170
Peter K. J. Robertson – School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast BT9 5AG, U.K.; orcid.org/0000-0002-5217-661X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00178

Notes
The authors declare no competing financial interest.

Biographies

Carsten Günneßmann received his M.Sc. degree in 2017 from the Gottfried Wilhelm Leibniz Universität Hannover under the supervision of Prof. Dr. Detlef W. Bahnemann, and he is currently a Ph.D. student in the same group. His research interests include transient absorption spectroscopy, (photo)electrochemistry, TiO₂ films, and halide perovskites.

Prof. Dr. Detlef W. Bahnemann is Head of the Research Unit “Photocatalysis and Nanotechnology“ at Leibniz University Hannover, Director of the Research Institute “Nanocomposite Materials for Photonic Applications” at Saint Petersburg State University, and Distinguished Professor at Shaanxi University of Science &
Technology, Xi’an (People’s Republic of China). His research topics including photocatalysis, photoelectrochemistry, solar chemistry, and photochemistry focused on the synthesis and physical-chemical properties of semiconductor and metal nanoparticles. His more than 500 publications have been cited over 61,000 times (h-index: 99). He is a Visiting Research Professor at Queens University Belfast, De’Tao Master of Photocatalysis, Nanomaterials and Energy Applications, and holds a Guest Professorship at Tianjin University (China) and several visiting professorships in China, Malaysia, Saudi Arabia, and Britain.

Prof. Dr. Peter K.J. Robertson is Professor of Energy and Environmental Engineering at Queen’s University Belfast. His particular expertise is in the area of photocatalytic technology for both energy and water sustainability. This work has encompassed basic research on photocatalysis through to pilot process development for water treatment and for solar energy conversion and storage. He is also a member of the UK Engineering and Physical Science Research Council’s (EPSRC) Scientific Advisory Committee on Energy and the SUPERGEN High Level Group. He is also a member of sub Panel 8, Chemistry for REF2021 the UK National research assessment exercise. He is Chair of the Royal Irish Academy’s Physical, Chemical and Mathematical Sciences Committee. He holds visiting professor positions at the University of St Andrews, Ulster University, and Robert Gordon University. He is a Chartered Engineer, Chartered Scientist, and Chartered Chemist, a Fellow of the Royal Society of Chemistry, the Institute of Chemistry in Ireland, the Energy Institute, and an Associate Fellow of the Institution of Chemical Engineers.

ACKNOWLEDGMENTS

D.W.B. and C.G. gratefully acknowledge funding by the Federal Ministry of Education and Research (033RC029D). D.W.B. gladly acknowledges financial support by Saint-Petersburg State University (SPBU) within the Project ID: 73032813. The authors acknowledge St. Petersburg State University for the research grant (Pure ID 39054851). The authors also thank the Center for Computational Resources of St. Petersburg State University (Petershof campus) for the provided CPU time.

REFERENCES

(1) (a) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental Applications of Semiconductor Photocatalysis. Chem. Rev. 1995, 95, 69–96. (b) Robertson, P. K. J.; Robertson, J. M. C.; Bahnemann, D. W. Removal of Microorganisms and Their Chemical Metabolites from Water Using Semiconductor Photocatalysis. J. Hazard. Mater. 2012, 211–212, 161–171. (c) Pang, X.; Skillen, N.; Gunaratne, N.; Rooney, D. W.; Robertson, P. K. J. Removal of Phthalates from Aqueous Solution by Semiconductor Photocatalysis: A Review. J. Hazard. Mater. 2021, 402, 123461. (d) Jiang, C.; Moniz, S. J. A.; Wang, A.; Zhang, T.; Tang, J. Photoelectrochemical Devices for Solar Water Splitting – Materials and Challenges. Chem. Soc. Rev. 2017, 46, 4645–4660. (e) Loeb, S. K.; Alvarez, F. J. J.; Brame, J. A.; Cates, E. L.; Choi, W.; Crittenden, J.; Dionysiou, D. D.; Li, Q.; Li-Puma, G.; Quan, X.; et al. The Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset? Environ. Sci. Technol. 2019, 53, 2937–2947. (f) Schneider, J.; Matsouka, M.; Takeuchi, M.; Zhang, J.; Horiiuchi, Y.; Anpo, M.; Bahnemann, D. W. Understanding TiO₂ Photocatalysis: Mechanisms and Materials. Chem. Rev. 2014, 114, 9919–9986. (g) Kisch, H. Semiconductor Photocatalysis-Mechanistic and Synthetic Aspects. Angew. Chem., Int. Ed. 2013, 52, 812–847. (h) Zhu, S.; Wang, D. Photocatalysis: Basic Principles, Diverse Forms of Implementations and Emerging Scientific Opportunities. Adv. Energy Mater. 2017, 7, 1700841. (i) Ahmed, A. Y.; Kandiel, T. A.; Oekermann, T.; Günemann, C.; Bahnemann, D. Mechanistic Investigations of Photoelectrochemical Water and Methanol Oxidation on Well-Defined TiO₂ Anatase (101) and Rutile (110) Surfaces. ACS Appl. Energy Mater. 2019, 2, 5308–5318. (j) Sieland, F.; Schneider, J.; Lippmann, T.; Bahnemann, D. W.; Dong, C.-L. Understanding Charge Transfer Processes on Metal Oxides: A Laser-Flash-Photoysis Study. Proc. SPIE 2016, 9935, 99350G. (k) Rigby, S. J.; Al-Obaidi, A. H. R.; Lee, S.-K.; McStay, D.; Robertson, P. K. J. The Application of Raman and Anti-Stokes Raman Spectroscopy for in Situ Monitoring of Structural Changes in Laser Irradiated Titanium Dioxide Materials. Appl. Surf. Sci. 2006, 252, 7948–7952. (l) Lee, S.-K.; Mills, A.; O’Rourke, C. Action Spectra in Semiconductor Photocatalysis. Chem. Soc. Rev. 2017, 46, 4877–4894. (m) Li, Y.; Lin, B.; Ge, L.; Guo, H.; Chen, X.; Lu, M. Real-Time Spectroscopic Monitoring of Photocatalytic Activity Promoted by Graphene in a Microfluidic Reactor. Sci. Rep. 2016, 6, 28803. (n) Liqiang, J.; Yichun, Q.; Baiqi, W.; Shudan, L.; Baojiang, J.; Libin, Y.; Wei, F.; Honggang, F.; Jiazhong, S. Review of Photoilluminescence Performance of Nano-Sized Semiconductor Materials and Its Relationships with Photocatalytic Activity. Sol. Energy Mater. Sol. Cells 2006, 90, 1773–1787. (o) Mendive, C. B.; Bredow, T.; Blesa, M. A.; Bahnemann, D. W. ATR-FTIR Measurements and Quantum Chemical Calculations Concerning the Adsorption of Oxalic Acid on TiO₂. Phys. Chem. Chem. Phys. 2006, 8, 3232. (2) Courbon, H.; Formenti, M.; Pichat, P. Study of Oxygen Isotopic Exchange over Ultraviolet Irradiated Anatase Samples and Comparison with the Photooxidation of Isobutane into Acetone. J. Phys. Chem. 1977, 81, 550–554. (3) Pichat, P.; Courbon, H.; Enriquez, R.; Tan, T. T. Y.; Amal, R. Light-Induced Isotopic Exchange between O₂ and Semiconductor Oxides, a Characterization Method That Deserves Not to Be Overlooked. Res. Chem. Intermed. 2007, 33, 239–250. (4) Tanaka, K. Intermediate of Oxygen Exchange Reaction over Illuminated Titanium Dioxide. J. Phys. Chem. 1974, 78, 555–556. (5) Murata, C.; Hattori, T.; Yoshida, H. Electrolytic Property of O₂ Photoformed on Isolated Ti Species in Silica Promoting Alkene Epoxidation. J. Catal. 2005, 231, 292–299. (6) Mikhaylov, R. V.; Lisachenko, A. A.; Titov, V. V. Investigation of Photostimulated Oxygen Isotope Exchange on TiO₂ Degussa P25 Surface upon UV-Vis Irradiation. J. Phys. Chem. C 2012, 116, 23332–23341. (7) Liao, L. F.; Lien, C. F.; Shieh, D. L.; Chen, M. T.; Lin, J. L. FTIR Study of Adsorption and Photoassisted Oxygen Isotopic Exchange of Carbon Monoxide, Carbon Dioxide, Carbonate, and Formate on TiO₂. J. Phys. Chem. B 2002, 106, 11240–11245. (8) Nakamura, R.; Nakato, Y. Primary Intermediates of Oxygen Photoevolution Reaction on TiO₂ (Rutile) Particles, Revealed by in Situ FTIR Absorption and Photoluminescence Measurements. J. Am. Chem. Soc. 2004, 126, 1290–1298. (9) Zhang, M.; Wang, Q.; Chen, C.; Zang, L.; Ma, W.; Zhao, J. Oxygen Atom Transfer in the Photocatalytic Oxidation of Alcohols by TiO₂: Oxygen Isotope Studies. Angew. Chem. 2009, 121, 6197–6200.
(10) Henderson, M. A. Formic Acid Decomposition on the \{110\}-Microfaceted Surface of TiO$_2$(100): Insights Derived from $^{18}$O-Labeling Studies. *J. Phys. Chem.* 1995, 99, 15253−15261.

(11) Bogdanoff, P.; Alonso-Vante, N. A Kinetic Approach of Competitive Photoelectrooxidation of HCOOH and H$_2$O on TiO$_2$ Anatase Thin Layers via on-Line Mass Detection. *J. Electroanal. Chem.* 1994, 379, 415−421.

(12) Čiviš, S.; Ferus, M.; Kubát, P.; Zukanová, M.; Kavan, L. Oxygen-Isotope Exchange between CO$_2$ and Solid Ti$^{18}$O$_2$. *J. Phys. Chem. C* 2011, 115, 11156−11162.

(13) Kavan, L.; Zukanová, M.; Ferus, M.; Körti, J.; Koltaí, J.; Čiviš, S. Oxygen-Isotope Labeled Titania: Ti$^{18}$O$_2$. *Phys. Chem. Chem. Phys.* 2011, 13, 11583−11586.

(14) Henderson, M. A. Complexity in the Decomposition of Formic Acid on the TiO$_2$(110) Surface. *J. Phys. Chem. B* 1997, 101, 221−229.

(15) Čiviš, S.; Ferus, M.; Zukanová, M.; Kubát, P.; Kavan, L. Photochemistry and Gas-Phase FTIR Spectroscopy of Formic Acid Interaction with Anatase Ti$^{18}$O$_2$ Nanoparticles. *J. Phys. Chem. C* 2012, 116, 11200−11205.

(16) Montoya, J. F.; Bahnemann, D. W.; Salvador, P.; Peral, J. Catalytic Role of Bridging Oxygens in TiO$_2$ Liquid Phase Photocatalytic Reactions: Analysis of H$_2$$^{18}$O Photooxidation on Labeled Ti$^{18}$O$_2$. *Catal. Sci. Technol.* 2017, 7, 902−910.

(17) Salvador, P. Mechanisms of Water Photooxidation at N-TiO$_2$ Rutile Single Crystal Oriented Electrodes under UV Illumination in Competition with Photocorrosion. *Prog. Surf. Sci.* 2011, 86, 41−58.

(18) Melchers, S.; Schneider, J.; Bahnemann, D. W. Isotopic Studies on the Degradation of Acetaldehyde on Anatase Surfaces. *Catal. Today* 2020, 340, 318−322.

(19) Melchers, S.; Schneider, J.; Emeline, A. V.; Bahnemann, D. W. Effect of H$_2$O and O$_2$ on the Adsorption and Degradation of Acetaldehyde on Anatase Surfaces—An In Situ ATR-FTIR Study. *Catalysts* 2018, 8, 417.

(20) Montoya, J. F.; Ivanova, I.; Dillert, R.; Bahnemann, D. W.; Salvador, P.; Peral, J. Catalytic Role of Surface Oxygens in TiO$_2$ Photocatalytic Reactions: Aqueous Benzene Photooxidation with Ti$^{18}$O$_2$ under Anaerobic Conditions. *J. Phys. Chem. Lett.* 2013, 4, 1415−1422.

(21) Montoya, J. F.; Bahnemann, D. W.; Peral, J.; Salvador, P. Catalytic Role of TiO$_2$ Terminal Oxygen Atoms in Liquid-Phase Photocatalytic Reactions: Oxidation of Aromatic Compounds in Anhydrous Acetonitrile. *ChemPhysChem* 2014, 15, 2311−2320.

(22) Cunningham, J.; Srijaranai, S. Isotope-Effect Evidence for Hydroxyl Radical Involvement in Alcohol Photo-Oxidation Sensitized by TiO$_2$ in Aqueous Suspension. *J. Photochem. Photobiol., A* 1988, 43, 329−335.

(23) (a) Robertson, P. K. J.; Lawton, L. A.; Cornish, B. J. P. A.; Jaspris, M. Processes Influencing the Destruction of Microcystin-LR by TiO$_2$ Photocatalysis. *J. Photochem. Photobiol., A* 1998, 116, 215−219. (b) Robertson, P. K. J.; Bahnemann, D. W.; Lawton, L. A.; Bellu, E. A Study of the Kinetic Solvent Isotope Effect on the Destruction of Microcystin-LR and Geosmin Using TiO$_2$ Photocatalysis. *Appl. Catal., B* 2011, 108−109, 1−5.

(24) Gerischer, H.; Heller, A. The Role of Oxygen in Photooxidation of Organic Molecules on Semiconductor Particles. *J. Phys. Chem.* 1991, 95, 5261−5267.

(25) (a) Belhadj, H.; Hakki, A.; Robertson, P. K. J.; Bahnemann, D. W. In Situ ATR-FTIR Study of H$_2$O and D$_2$O Adsorption on TiO$_2$ under UV Irradiation. *Phys. Chem. Chem. Phys.* 2015, 17, 22940−22946. (b) Belhadj, H.; Melchers, S.; Robertson, P. K. J.; Bahnemann, D. W. Pathways of the Photocatalytic Reaction of Acetate in H$_2$O and D$_2$O: A Combined EPR and ATR-FTIR Study. *J. Catal.* 2016, 344, 831−840. (c) Belhadj, H.; Hamid, S.; Robertson, P. K. J.; Bahnemann, D. W. Mechanisms of Simultaneous Hydrogen Production and Formaldehyde Oxidation in H$_2$O and D$_2$O over Platinized TiO$_2$. *ACS Catal.* 2017, 7, 4753−4758.