A survey of photogeochemistry

Timothy A. Doane*

Abstract
The participation of sunlight in the natural chemistry of the earth is presented as a unique field of study, from historical observations to prospects for future inquiry. A compilation of known reactions shows the extent of light-driven interactions between naturally occurring components of land, air, and water, and provides the backdrop for an outline of the mechanisms of these phenomena. Catalyzed reactions, uncatalyzed reactions, direct processes, and indirect processes all operate in natural photochemical transformations, many of which are analogous to well-known biological reactions. By overlaying photochemistry and surface geochemistry, complementary approaches can be adopted to identify natural photochemical reactions and discern their significance in the environment.

Keywords: Atmosphere, Minerals, Natural photoreactions, Photocatalysis, Photochemistry, Soil, Surface geochemistry, Water

Background
Photogeochemistry has been defined as the photochemistry of Earth-abundant minerals in shaping biogeochemistry [1], and this can be extended to the entire interface between photochemistry and geochemistry to include any chemical reaction induced by sunlight among naturally occurring substances. The term has been used previously on only several other isolated occasions [2, 3], but if existing research is surveyed for studies that fit this definition, an appreciable body of knowledge emerges.

The context of a photogeochemical reaction is implicitly the surface of the earth, since that is where sunlight is available (ignoring other sources of light such as bioluminescence). Reactions may occur among constituents of land such as minerals, plant residue, and the organic and inorganic components of soil; constituents of surface water such as sediment and dissolved organic matter; and constituents of the atmospheric boundary layer directly influenced by contact with land or water, such as organic aerosols, mineral aerosols, and gases. Figure 1 shows some examples of photochemical reactions among these substances. Sunlight penetrates up to approximately 0.3 mm in soils and particulate minerals, depending on the wavelength of light and the nature of the particles [4], and many meters in clear water, depending on the concentration of light-absorbing molecules [5, 6]. Light of wavelengths less than about 290 nm is completely absorbed by the present atmosphere and therefore does not reach Earth’s surface [7, 8].

Photogeochemistry describes photochemical reactions on Earth that are not facilitated by living organisms. The reactions that comprise photosynthesis in plants and other organisms, for example, are not included, since the physiochemical context for these reactions is installed by the organism, and must be maintained in order for the reactions to continue (the photoreactions cease if the organism dies). However, if a certain substance is produced by an organism, and the organism dies but the substance remains (e.g., plant residue or biogenic mineral precipitates), photoreactions involving this substance still contribute to photogeochemistry.

History
The most famous example of a photochemical reaction involving natural compounds is the production of indigo dyes from the secretions of marine mollusks, known since antiquity [9]; the role of sunlight was emphasized in a study by William Cole in 1685 [10]. The development of modern photochemistry in general was fostered by similar adventitious observations of the effect of sunlight on natural compounds. For example, Hyde Wollaston in 1811 [11] observed that guaiac, a tree resin, rapidly...
turned green in the air when exposed to sunlight (due to photooxidation). Natural photodegradation was also known, as described by Berzelius in 1829 [12]: “Light fades and destroys the majority of plant colorants. Every day we see that of the sun weakening the dyes of our fabrics”. This phenomenon was also mentioned by John William Draper in 1845 [13]. Georges Witz in 1883 described the degradation of cellulose by sunlight, remarking on the influence of air and moisture, and further noted that degradation was greatly accelerated by ferric oxide [14]. By the end of the 19th century, photodegradation of organic matter in natural waters was recognized as a universal phenomenon [15]. In addition to degradation, other light-induced transformations were also recorded. Louis Pasteur described how a dark-colored material is produced in cinchona bark under the influence of sunlight, an observation that he confirmed in the laboratory with specific compounds [16], and Hermann Trommsdorff [17] and Karl Fritzsche [18] were also among those who observed changes in natural organic substances when they were illuminated. Many inorganic substances were also known to change (e.g., in color or crystal structure) upon exposure to light [13]. For example, since 1881 it has been known that zinc sulfide, normally white, becomes dark when exposed to sunlight [19]; John Cawley remarked that “I have prepared pigments so sensitive as to be turned almost black when exposed to bright sunlight for one or two minutes” [20]. Investigation of the light-induced reactions of this compound [21], which occurs as a natural mineral, provided some additional empirical contributions to photochemistry and the “photochemical metallurgy” of zinc, and its photocatalytic properties are still studied at present [22, 23]. Many natural inorganic compounds used throughout the ages as pigments in painting also slowly degrade by exposure to sunlight; artists like Van Gogh were aware of this [24]. Some of these compounds, such as mercury(II) sulfide, undergo a number of light-mediated reactions [25] which are environmentally relevant.

Around the time of these and other observations, experiments increased in an effort to reproduce natural processes. The hypothesis of von Baeyer in 1870 [26], in which formaldehyde was proposed to be the initial product of plant photosynthesis followed by polymerization into sugars, inspired numerous attempts to obtain formaldehyde from carbon dioxide and water. For example, the formation of lower uranium oxides was observed upon irradiation of a solution of uranium acetate and carbon dioxide, implying the formation of a reducing agent assumed to be formaldehyde [27]. Some experiments included reducing agents such as hydrogen gas [28], and others reportedly detected formaldehyde and other products in the absence of additives [29, 30], suggesting that reducing power was produced from the decomposition of water during exposure to light. In addition to this main focus on the synthesis of formaldehyde and simple sugars, other light-driven reactions were occasionally noted, such as the decomposition of formaldehyde and subsequent release of methane [28]. Many experiments explored the effect of a catalyst in converting light energy into chemical energy; some effective “transformers” (as they were sometimes called) were similar to naturally occurring minerals, including iron(III) oxide or colloidal iron(III) hydroxide [30–32], zinc oxide [33], and cobalt,
copper, nickel, and iron carbonates [30, 33]. By this time, interest had spread to other light-induced reactions involving naturally occurring materials. These studies sometimes reported photoreactions analogous to biological processes, such as oxidation of simple carbon compounds [34] or nitrification in soil [35].

Overview of photogeochemical reactions
Table 1 presents a selection of documented photochemical reactions (with light >290 nm) among naturally occurring substances, ranging from general reactions such as mineralization of organic matter to specific reactions such as methylation and demethylation of mercury. This compilation is by no means exhaustive, either in reactions or references, but illustrates the general scope and diversity of abiotic photochemical reactions that may occur at the surface of the earth.

Classification of photogeochemical reactions
The same principles that form the foundation of photochemistry can also be used to describe and explain photogeochemical reactions. If specific reactions are known, they may be distinguished as either photosynthetic reactions, photocatalytic reactions, or uncatalyzed reactions. In the most general sense, photosynthesis refers to any photochemical reaction for which the change in energy (ΔG) is positive. The energy of the products is greater than that of the reactants, and therefore the reaction is thermodynamically unfavorable, except through the action of light in conjunction with a catalyst [36] or a chromophoric system, for example, that mimics what occurs in plants [37]. Examples of photosynthetic reactions include the production of H2 and O2 from water and the reaction of CO2 and water to form O2 and reduced carbon compounds such as methane and methanol. Photocatalysis refers to photochemical reactions, accelerated by the presence of a catalyst, that have a negative change in energy and are therefore thermodynamically favored [36], such as the reaction of organic compounds with O2 to form CO2 and water. Finally, uncatalyzed photoreactions proceed through the action of light alone. For example, many organic compounds absorb light and suffer decomposition as a result. Figure 2 depicts a simple scheme for classifying photoreactions based on the requirement for a catalyst and whether a reaction proceeds by a direct or indirect mechanism, as further described below. Figure 3 shows some of the processes that operate in these reactions, also discussed below.

Catalysis
A catalyst is a substance that increases the rate of a chemical reaction due to a change in mechanism, but does not experience any net change itself during the course of the reaction [37, 38]. A photocatalyst does this by absorbing light, but as described below, other substances that do not absorb light may nevertheless catalyze light-induced reactions. Strictly speaking, the term catalysis should not be used unless it can be shown that the number of product molecules produced per number of active sites on a substance (the turnover number) is greater than one [39]; this is difficult to do in practice, although it is often assumed to be true if there is no loss in the activity of the substance for an extended period of time [36]. Reactions which are not definitively catalytic may be designated as assisted photoreactions [36, 38] or photosensitized reactions. Photosensitized reactions involve transfer of energy from a light-absorbing species (photosensitizer) to another, nonabsorbing species, and therefore facilitate reaction of this nonabsorbing species [40]. If the photosensitizer remains intact it is effectively a photocatalyst. Furthermore, a substance may initially act as a photocatalyst in a reaction even if it eventually suffers light-induced decomposition. Descriptors such as those given here are most applicable when all of the participants in a specific reaction can be identified, not just individual reactants or products. In contrast, it is hard to classify observations in complex matrices such as soil if the complete reactions responsible for the observations are not first discerned.

Direct reactions
Photochemical reactions can be further categorized as either direct or indirect. Direct reactions involve the substance that initially absorbs light [41–43] which reacts with other substances or is itself changed. Many photochemical reactions on Earth may be directly mediated by naturally occurring semiconductors that absorb ultraviolet and visible radiation. These are mostly transition metal oxides and sulfides and include abundant, widely distributed minerals such as hematite (Fe2O3), magnetite (Fe3O4), goethite and lepidocrocite (FeOOH), anatase and rutile (TiO2), pyrolusite (MnO2), pyrite (FeS2) chalcopyrite (CuFeS2), and sphalerite (ZnS) [44, 45]. Other types of minerals are also known to absorb light and directly participate in photoreactions, including silicates such as Ag6Si2O7 [46] and phosphates such as Cu3(OH)PO4 [47]. Light of energy equal to or greater than the band gap of a semiconductor is sufficient to promote electrons from the valence band to a higher energy level in the conduction band, leaving behind electron vacancies or holes (Fig. 3a). The excited electron and hole in the semiconductor can then, respectively, reduce and oxidize other compounds having appropriate redox potentials relative to the potentials of the valence and conduction bands [48]. The band gaps and absolute energy levels of many minerals are suitable, in theory, for a diverse array of
| Reaction                                                                 | Descriptor                                                                 | Facilitators                                | References                                      |
|-------------------------------------------------------------------------|----------------------------------------------------------------------------|---------------------------------------------|------------------------------------------------|
| Carbon compounds                                                        |                                                                            |                                             |                                                |
| Plant material $\rightarrow$ CO$_2$                                      | (Oxidative) photochemical decomposition (mineralization)                    |                                             | [124, 125, 166 (CO$_2$ implied), 167]           |
| Plant material (litter and living foliage) $\rightarrow$ CO$_2$         | Photochemical decomposition (mineralization)                               |                                             | [125, 168–171]                                 |
| Plant material (litter) $\rightarrow$ CH$_4$                            | (Reductive) photochemical decomposition (mineralization/methanification)    |                                             | [172–174]                                      |
| Plant material (foliage) $\rightarrow$ CH$_4$                          | (Reductive) photochemical mineralization                                    |                                             | [171, 173–176]                                 |
| Plant material $\rightarrow$ ethane, ethene, propene, butane, other hydrocarbons | (Reductive) photochemical decomposition                                   |                                             | [171, 177]                                    |
| Solid organic matter $\rightarrow$ CO$_2$                               | (Oxidative) photochemical decomposition (mineralization)                    |                                             | [180]                                          |
| Solid organic matter $\rightarrow$ CH$_4$                               | (Reductive) photochemical decomposition (mineralization/methanification)    |                                             | [181]                                          |
| Sorbed or particulate organic matter $\rightarrow$ dissolved organic matter | Photochemical dissolution                                                 |                                             | [115]                                          |
| Dissolved and colloidal organic matter $\rightarrow$ amino acids        | Photochemical decomposition (depolymerization)                             |                                             | [115]                                          |
| (Nonspecific) decomposition of dissolved organic matter $\rightarrow$ CO$_2$ | Photochemical decomposition                                                 |                                             | [70, 109, 185–187]                             |
| Dissolved organic matter $\rightarrow$ CO$_2$                          | (Oxidative) photochemical decomposition (mineralization)                    |                                             | [188–191]                                     |
| Dissolved organic matter $\rightarrow$ CH$_4$                          | (Oxidative) photochemical decomposition (mineralization)                    |                                             | [190, 192–194]                                 |
| Dissolved organic matter $\rightarrow$ biologically more labile compounds | Photochemical priming (encouraging subsequent biotic decomposition)        |                                             | [195]                                          |
| Dissolved organic matter $\rightarrow$ biologically more labile compounds with increased carboxylic acid content | Photochemical priming (encouraging subsequent biotic decomposition)        |                                             | [134, 135, 196]                                |
| Dissolved organic matter $\rightarrow$ organic matter with increased aliphatic content | Photochemical aliphatization                                                |                                             | [83, 193]                                      |
| Humic substances $\rightarrow$ humic substances with increased hydrophobicity of remaining organic matter | Photochemical decomposition + acidification                                  |                                             | [135, 186]                                    |
| Humic substances $\rightarrow$ simple carbonyl compounds (e.g., formaldehyde, acetone, pyruvate) | Photochemical decomposition                                                |                                             | [189, 197]                                    |
### Table 1 continued

| Reaction | Descriptor | Facilitators | References |
|----------|------------|--------------|------------|
| Dissolved organic matter → condensed aromatic structures (soluble and particulate) | Photochemical condensation | With and without ZnO | [193] |
| Carbohydrates and lipids → oxidized products (Non-specific) decomposition of cellulose | Photochemical oxidation | No facilitator | [198] |
| Cellulose → less polymerized cellulose with increased carbonyl and carboxyl content (Non-specific) decomposition of cellulose | Photochemical depolymerization + oxidation | Fe(III) compounds, ZnO, ZnS, TiO$_2$ | [96, 200] |
| Cellulose | Photochemical decomposition | No facilitator | [99] |
| Cellulose | Photochemical decomposition | No facilitator | [98, 202, 203] |
| Lignin → CH$_4$, ethane | (Reductive) photochemical decomposition | | [204] |
| Lignin → quinones | (Oxidative) photochemical decomposition | | [99, 204, 205] |
| Lignin → aromatic and aliphatic aldehydes | (Oxidative) photochemical decomposition | | [206] |
| Proteins → larger, aggregated proteins e.g., via intermolecular tyrosine dimerization | Photochemical crosslinking | | [207] |
| Unconjugated unsaturated lipids → conjugated unsaturated lipids + insoluble material | Photochemical isomerization, condensation | Observed in seawater | [208] |
| Polysaturated lipids → humic substances (proposed reaction) | (Oxidative) photochemical crosslinking | | [209] |
| Fatty acids → CO$_2$, alkenes, aldehydes, ketones, fatty acid dimers | Photochemical oxidation, cleavage, dimerization, condensation | No facilitator | [210, 211] |
| Hydrocarbons e.g., ethane, ethene, propane, butane, paraffin → CO$_2$ | Photochemical oxidation | TiO$_2$ | [211, 212] |
| Long-chain alkanes → ketones, alcohols, acids | Photochemical oxidation | Naphthal, xanthone, anthraquinone | [213] |
| Dienes + NO$_x$ → carboxylic acids | Photochemical oxidation | | [214–218] |
| Aromatic compounds + NO$_x$, NO$_3^-$, or NO$_2^-$ → nitrated aromatic compounds (Non-specific) decomposition of polycyclic aromatic hydrocarbons | Photochemical decomposition | No facilitator | [195] |
| Polycyclic aromatic hydrocarbons → quinones | Photochemical oxidation | Al$_2$O$_3$ | [78] |
| Condensed aromatic compounds (dissolved black carbon) → non-specific products, CO$_2$ | (Oxidative) photochemical decomposition | Sand containing magnetite and ilmenite | [220, 221] |
| Soot → oxygen-containing species | Photochemical oxidation | | [222] |
| Crude oil → CO$_2$ | Photochemical oxidation (mineralization) | Cu(I) (aq) | [223] |
| Amino acids → CO$_2$ | Photochemical oxidation (mineralization) | | [224, 225] |
Table 1 continued

| Reaction | Descriptor | Facilitators | References |
|----------|------------|--------------|------------|
| Amino acids and peptides → smaller carboxylic acids, amines, amides, NH₃, CO₂ | (Oxidative) photochemical decomposition, mineralization | [226] |
| Lysine → pipercolinic acid ornithine → proline | Photochemical cyclization | HgS, ZnS, CdS | [227, 228] |
| Phenolic ketones and aldehydes → brown carbon | Photochemical oxidation, oligomerization | [155] |
| Phenol → hydroquinone, catechol → further oxidation products, CO₂ | Photochemical oxidation | Fe₂O₃, TiO₂ | [211, 229, 230] |
| Decomposition of aqueous phenol, naphthal, methylene, methoxyphenols, anilines | Photochemical oxidation | Humic and fulvic acids, flavins (algae live or dead) | [219, 231, 232] |
| Phenols → phenol dimers | Photochemical coupling/dimerization | Fe(III) (aq) | [102] |
| Phenols → quinones, naphthols, aminonaphthols → naphthoquinones | Photochemical oxidation | No facilitator | [217, 233, 234] |
| Quinones → quinone dimers | Photochemical coupling/dimerization | | [235, 236] |
| Quinones + benzocyclic olefins → addition products | Photochemical coupling | | [237] |
| Ketones → carboxylic acids | Photochemical cleavage + acidification | | [238–240] |
| Ketones → CH₄, ethane | photochemical reduction | | [174, 240] |
| Aromatic ketones → condensed aromatic ring systems | Photochemical condensation | | [241] |
| Vicinal diols → ketones, aldehydes, carboxylic acids | Photochemical cleavage + oxidation | Fe(III) porphyrins | [242] |
| Cinnamic acid → cinnamic acid dimer | Photochemical coupling/dimerization | | [243] |
| Acetic acid → CH₄ + CO₂ | Photochemical disproportionation/dismutation | TiO₂, α-Fe₂O₃, Fe₂O₃ on montmorillonite (in the absence of O₂), TiO₂, Fe₂O₃, SrTiO₃ plus an electron acceptor | [1, 21, 122, 244] |
| Acetic acid → CO₂, CH₄, ethane, ethanol, propionic acid, other products | Various | α-Fe₂O₃, TiO₂, Fe₂O₃, SrTiO₃, WO₃ plus an electron acceptor | [1, 22, 211, 244] |
| Acetate, terpenes + O₂ → organic (hydro)peroxides | Photochemical peroxidation | No facilitator | [245–247] |
| Unsaturated lipids + O₂ → lipid hydroperoxides | Photochemical peroxidation | ZnO, organic sensitizers | [248, 249] |
| Propionic acid → ethane + CO₂ | Photochemical decarboxylation | Fe₂O₃ alone or on montmorillonite | [1, 22, 250] |
| Butyric acid → propane + CO₂ | | Algae (live or dead) | |
| Salicylic acid → phenol + CO₂ | | | |
| Lactic acid → pyruvic acid + H₂ | Photochemical oxidation + dehydrogenation | ZnS | [251] |
| Lactic acid → acetaldehyde + CO₂ | (Oxidative) photochemical decarboxylation | Aqueous Cu(II) and Fe(III) | [251, 252] |
| Glucose → CO₂ | Photochemical oxidation | TiO₂ | [211] |
| Oxalic acid → CO₂ | Photochemical oxidation | TiO₂, sand, ash, α-Fe₂O₃, γ-Fe₂O₃, α-FeOOH, β-FeOOH, γ-FeOOH, δ-FeOOH | [71, 211, 253, 254] |
Table 1 continued

| Reaction | Descriptor | Facilitators | References |
|----------|------------|--------------|------------|
| Tartaric, citric, oxalic, malonic acids → oxidized products | Photochemical oxidation | Ferritin | [2,55] |
| Pyruvic acid → pyruvic acid oligomers | Photochemical oligomerization | | [2,56] |
| Salicylic acid → humic-like substances | Photochemical condensation | Accelerated in the presence of algae | [2,50] |
| Syringic acid and other methoxybenzoic acids → methanol | Photochemical decomposition | | [2,57] |
| Syringic acid and related compounds + Cl⁻ → CH₃Cl | Photochemical decomposition + chlorination | ZnS in the absence of air | [2,57] |
| Methanol → ethylene glycol + H₂ | Photochemical coupling + dehydrogenation | | [2,58] |
| Ethanol → butane-2,3-diol + H₂ | Photochemical decomposition | | [2,59] |
| Isoprene → methyldithiole and methyldithiole (aerosols) | Photochemical oxidation | | [2,60, 261] |
| (Specific) plant compounds → compounds toxic to other organisms | Phototoxicity | | |
| CO₂ → CO, HCOOH, HCHO, CH₃OH, CH₄ | Photochemical reduction (one-carbon products) | Fe(III) oxides, FeCO₃, NiCO₃, CoCO₃, CuCO₃, Mn(II) (aq), ZnO, TiO₂, ZnS, CdS, ZnO, WO₃, CaFe₂O₄, BVO₃, hydrous Cu₂O, transition metal ions and oxides in zeolites | [30, 31, 33, 262–268] |
| CO₂ + H₂ → CH₄ | Photochemical reduction | α-Fe₂O₃ and Zn-Fe oxide in the presence of water, NiO | [2,69, 270] |
| CO₂ + H₂ → CO, HCOOH, CH₃OH | Photochemical reduction | α-Fe₂O₃ and Zn-Fe oxide in the presence of water | [2,69] |
| CO₂ → HCOOH | Photochemical reduction | Paraphyrins, phthalocyanines Elemental Cu on silicate rocks such as granite and shale | [2,71, 272] |
| CO₁ → ethanol | Photochemical reduction (products with more than one carbon) | SIC, ZnS, BVO₃, montmorillonite-modified TiO₂ | [2,73–277] |
| CO₂ → ethane, ethene, propane, propene | | | |
| CO₁ → tartaric, glyoxylic, oxalic acids | | | |
| CH₄ → HCOOH | Photochemical oxidation | TiO₂ | [2,11, 278] |
| CH₄ → CO, CO₂ | | | |
| CH₄ → ethane + H₂ | Photochemical coupling + dehydrogenation | SiO₂-Al₂O₃-TiO₂ | [2,79] |
| Nitrogen compounds | | | |
| Plant foliage → NOₓ | | | [2,80] |
| Plant foliage → N₂O | | | [2,81] |
| Particulate organic N → dissolved organic N and NH₄⁺ | Photochemical decomposition (dissolution + mineralization) | | [1,15] |
| Dissolved organic N → biologically more labile N | Photochemical priming | | [2,82] |
| Amino acids and other organic N (including biologically recalcitrant organic N) → NH₄⁺ | Photochemical decomposition (mineralization/ammonification) | No facilitator Organic matter, Fe₂O₃, soil | [1,32, 184, 193, 194, 283–286] |
| Humic substances → NO₃⁻ | (Oxidative) photochemical decomposition (mineralization) | | [1,04, 287] |
Table 1 continued

| Reaction | Descriptor | Facilitators | References |
|----------|------------|--------------|------------|
| NH₃ → NO₂⁻ | Photochemical oxidation (nitrification) | TiO₂, ZnO, Al₂O₃, SO₂, MnO₂, soil | [288–290] |
| NH₃ → NO₃⁻ | Photochemical oxidation | TiO₂ | [290, 291] |
| NH₄⁺ + NO₂⁻ → N₂ | Photochemical oxidation + reduction (denitification) | TiO₂, ZnO, Fe₂O₃, soil | [292, 293] |
| NH₄NO₃ → N₂O | Photochemical reduction (denitrification) | TiO₂, ZnO, SiO₂ | [294] |
| NO₂ → NO₃⁻ | Photochemical oxidation | TiO₂ | [295, 296] |
| NO₂ → HONO, NO, NO₂ | Photochemical reduction | ZnO, Fe₂O₃, sand | [94, 95, 151, 312] |
| NO₃⁻ → NO₂⁻ | Photochemical oxidation | TiO₂, plus electron acceptor | [298] |
| NO₃⁻ → NH₃ | Photochemical reduction | ZnO, TiO₂, SiO₂, α-Fe₂O₃, ZnO, CuCrO₂, Na zeolite, sand | [299–305] |
| NO₃⁻ → NO2⁻ (± O₂) | Photochemical reduction (+oxidation) | No facilitator | [103, 306–309] |
| NO₂ → HONONO | Photochemical reduction | Humic acids, soot, soil | [157, 310, 311] |
| N₂O → N₂ | Photochemical reduction | ZnO, Fe₂O₃, sand, Humic and fulvic acids | [94, 95, 151, 312] |
| N₂O → N₂ + O₂ | Photochemical dissociation | ZnO, Cu(I) zeolites | [313, 314] |
| N₂ → NH₃ | Photochemical reduction/(reductive) photochemical fixation | ZnO, Al₂O₃, Fe₂O₃, NiO₂, CuO, Fe(III) in TiO₂, Fe₂O₃-Fe₃O₄, MnO₂, Sand, soil | [2, 229, 315–321] |
| N₂ + H₂O → NH₃ + O₂ | Photochemical reduction + oxidation | TiO₂, in the absence of O₂, α-Fe₂O₃, Fe(III)-doped TiO₂ | [58, 321, 322] |
| N₂ → N₃H₄ | Photochemical reduction | Sand | [2] |
| N₂ + H₂O → N₃H₄ + O₂ | Photochemical reduction + oxidation | TiO₂, in the absence of O₂ | [322] |
| N₂ + O₂ → NO | Photochemical oxidation (oxidative) photochemical fixation | TiO₂ in air | [323] |
| N₂ → NO⁻ | Photochemical oxidation (oxidative) photochemical fixation | Suspension of ZnO in the absence of O₂ | [320, 324, 325] |
| N₂ → NO₃⁻ | Photochemical oxidation (oxidative) photochemical fixation | Aerated suspension of hydrous iron(III) oxide | [320, 324, 325] |
| N₂ + H₂O → NO⁻ + H₂ | Photochemical oxidation + reduction | ZnO-Fe₂O₃ under N₂ | [326] |
| Metal compounds | Organic complexes of Fe, Al, Co, Ni (aq) → ionic Fe, Al, Co, Ni (aq) | Photochemical decomposition + decomplexation | [327, 328] |
| Reaction | Descriptor | Facilitators | References |
|----------|------------|--------------|------------|
| Organic complexes of Fe, Cu, Cr, Pb, V (aq) → colloidal Fe, Cu, Cr, Pb, V | Photochemical decomposition + precipitation | | [328] |
| Organic matter (aq) + iron (aq) → organic matter + iron (s) | Photochemical flocculation | | [193, 329] |
| Fe(OH)₂ (aq) → FeOOH | Photochemical oxidation | | [330] |
| Fe(III) (hydr)oxides (s) → Fe(II) (aq) | (Reductive) photochemical dissolution of FeOOH + photochemical oxidation of organic matter (if present) | No facilitator | Coprecipitated or dissolved organic matter, HSO₄⁻, montmorillonite Accelerated in ice |
| Fe(II) (aq)/Fe(OH)₂ + H₂O → Fe(III) + H₂ | Photochemical oxidation + reduction | No facilitator | Chromophores such as chlorophyll |
| Fe(III)-carboxylate complexes (aq) → Fe(II) (aq) | Photochemical reduction + decomplexation | | [66, 70, 341, 342] |
| Mn(IV) oxide → Mn(II) (aq) | (Reductive) photochemical dissolution | Dissolved organic matter | [337, 343–347] |
| Mn(II) (aq) → MnO₂ (x = 1 to 2) | Photochemical oxidation | Organic matter, TiO₂ | [348, 349] |
| Cu(II) (aq) → Cu(I) | Photochemical reduction | Amino acids | [224, 225] |
| Cr(VI) (aq) → Cr(III) (aq) | Photochemical reduction | Ferritin, phenol | [350, 351] |
| ZnS + H₂O → H₂S + H₂ | Photochemical reduction + dissolution | | [21, 251] |
| ZnS → Zn(0) + S(0) | Photochemical oxidation + reduction | | [21] |
| CdS → Cd(0) + S(0) | Photochemical oxidation | | [211] |
| HgS → Hg(II) (aq) + H₂S | Photochemical dissolution | | [228, 352] |
| HgS → Hg(0) + S(0) | Photochemical oxidation + reduction | Cl⁻ | [25] |
| HgS → [Hg₂Cl₂ and other intermediates] → HgCl₂ | Photochemical oxidation, reduction/ photochemical dissolution | Cl⁻ | [25] |
| Hg(III) (aq) → Hg(II) (aq) | Photochemical oxidation | | [352, 353] |
| Hg(III) (aq) → Hg(0) (aq) | photochemical reduction | Fe(III) species, TiO₂, organic matter Observed in freshwater, seawater, and snow | [352, 354–357] |
| Hg(II) (aq) → HgCH₃⁺ | Photochemical methylation | | [358] |
| HgCH₃⁺ → Hg(II) | Photochemical demethylation | | [359, 360] |
| HgCH₃Cl → Hg(II) + Hg(0) + CHCl₃ + HCHO | Photochemical demethylation + reduction | | [361] |
| Other elements | | | |
| Plant material → H₂ | (Reductive) photochemical decomposition | | [362, 363] |
| Dissolved organic P → inorganic phosphate | Photochemical decomposition (mineralization) | | [364] |
| Phosphate adsorbed to Fe(III) oxides or Fe(III)-organic matter complexes → free phosphate | Photochemical desorption | | [161, 365, 366] |
| HS⁻/S²⁻ → H₂ | Photochemical reduction | CdS, α-Fe₂O₃ | [367, 368] |
| SO₄²⁻ → SO₃²⁻ | Photochemical oxidation | TiO₂, Fe₂O₃, ZnO, CdS | [369–372] |
| Thiols and SO₃²⁻ → oxidized products | Photochemical oxidation | Ferritin | [255] |
| Alkyl sulfides + NO₃⁻ → aldehydes, sulfonic acids, SO₄²⁻ | Photochemical oxidation | | [373] |
| Reaction | Descriptor | Facilitators | References |
|----------|------------|--------------|------------|
| \( \text{O}_2 \rightarrow \text{H}_2\text{O} \) | Photochemical reduction | ZnO, TiO₂, sand in the presence of organic electron donors | [34, 107, 246, 298, 374–376] |
| \( \text{O}_2 \rightarrow \text{H}_2\text{O} \) | Photochemical reduction | Aqueous Fe(III)-carboxylic acid complexes, Tryptophan and tyrosine, Porphyrins and phthalocyanines, Algae (live or dead) | |
| \( \text{H}_2\text{O} \rightarrow \text{H}_2 \) | Photochemical reduction | Numerous catalysts, usually in the absence of \( \text{O}_2 \) e.g., TiO₂, ZnS, α-Fe₂O₃, hydrated Cu₂O, tungstosilicate on TiO₂, Ti(III)-zeolite, graphite oxide | [21, 22, 262, 315, 377–382] |
| \( \text{H}_2\text{O} \rightarrow \text{O}_2 \) | Photochemical oxidation | α-Fe₂O₃, Fe(III) (aq), BiVO₄, + electron acceptor, Mn₂O₃, λ-MnO₂, Mn₃O₄, Co₃O₄, + sensitizers, AgCl, layered double hydroxide minerals, Fe(OH)²⁺ | [383–390] |
| \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2 \) | Photochemical water splitting (oxidation + reduction) | TiO₂, Fe₂O₃-Fe₃O₄, Fe₂O₃-FeS₂, Cu₂O, ZrO₂, Ag zeolite, diverse two-mineral systems | [60, 137, 321, 322, 391–393] |
| As(III) (aq) → As(V) (aq) | Photochemical oxidation | No facilitator | [158, 394, 395] |
| As₂S₄ → As₂S₆ (polymorph) | Photochemical structural (crystal) modification | Ferricyanide, kaolinite | [396] |
| As₂S₃ → [As + S] + O₂ → As₂O₅ | Photochemical oxidation/dissolution | Water | [396, 397] |
| Volatile organic compounds + NO₃ → O₃ | Photochemical oxidation | Chlorophyll, Hg(II) | [398] |
| Cl⁻ → Cl₂⁻ (dichloride radical anion) | Photochemical oxidation | Chlorophyll, Hg(II) | [399] |
| Cl⁻ + O₃ → Cl₂ | Photochemical oxidation | | [400] |

A suggested descriptor is given for each reaction as well as substances reported to facilitate the reaction (if any) and some relevant notes. These facilitating substances also occur naturally, or (in just a few instances) are reasonably similar to something that might occur naturally. About 15% of the studies cited here can be considered field studies, which means that a reaction was observed with both natural sunlight and natural substances as well as under representative environmental conditions, as opposed to the use of artificial light and/or laboratory-prepared equivalents of natural compounds.

Note on terminology: The term “photochemical” can be used to maintain a clear distinction between abiotic photoreactions and analogous reactions involving light and living organisms (phototrophy). For example, “iron(III) photooxidation” can refer to either a biological process driven by light (photobiological/phototrophic iron(III) oxidation) or a strictly chemical, abiotic process (photochemical iron(III) oxidation). Similarly, an abiotic process that converts water to \( \text{O}_2 \) under the action of light may be described as “photochemical oxidation of water” rather than simply “photooxidation of water” (even though the latter is shorter and often understood to mean a photochemical reaction); this distinguishes it from light-induced biological oxidation of water that might occur simultaneously in the same environment.
photoreactions at interfaces with water, gases, and other solids. Naturally occurring semiconductors are almost exclusively inorganic compounds, with notable exceptions (notable because they occur widely) being melanin [49] and possibly cellulose [50, 51] and peptides [52–54]. Natural semiconducting minerals, like most minerals, are rarely pure; additional metals are almost always present [44], and these substitutional impurities can cause changes in energy levels and conductivity [44, 55]. Such alterations are manifested in photocatalytic activity. For example, the band gap of TiO$_2$ decreases due to Fe impurities [56, 57], which extends its response to a wider range of solar radiation compared to pure TiO$_2$; the efficiencies of photochemical oxidation and reduction reactions of TiO$_2$ are also greater if Fe impurities are present [57, 58]. Similarly, the presence of Ti or V in magnetite enhances its photocatalytic activity relative to pure magnetite [59]. In addition to atoms of foreign elements, another common “defect” in minerals is deviation from stoichiometry due to vacancies (missing atoms), and this can also affect photochemical properties. For example, sulfur deficiencies in ZnS crystals impart increased photocatalytic activity under visible light to a material that normally absorbs little or no visible light [23]. In addition to chemical alterations, the photocatalytic activity of materials like these is also influenced by physical properties such as crystal structure and specific surface area [23, 56, 60].

Like inorganic minerals, many natural organic compounds also absorb sunlight and can react directly with other compounds or undergo reactions themselves (Fig. 3b); these include dissolved organic matter [61–63], “bioorganic” substances [64], chlorophyll [65], atmospheric humic-like substances [42], and soot or black carbon [42, 66]. Moreover, two species may combine to form a new species with even greater propensity to undergo direct photoreactions, as is often the case with intramolecular or intermolecular charge-transfer complexes among components of organic matter [67] or between transition metals and organic matter [68]. Sometimes this even leads to catalytic or autocatalytic cycles [69–71].

Finally, materials that do not absorb sunlight, such as silica, may nonetheless enable direct photoreactions. These materials are usually catalysts and act primarily via surface adsorption, which can alter the bond lengths and energies of a substance when it is bound to the catalyst [72, 73] and consequently alter the amount or wavelengths of sunlight absorbed by this substance [74, 75].

---

**Fig. 2** Photogeochemical reactions, if enough information is known, can be classified using general principles of photochemistry. Examples are given for each of four categories in a simple scheme of classification based on the mechanism of reaction. Light-absorbing materials are shaded and catalysts are shown in italics. Intermediate processes in indirect reactions are indicated as separate reactions below the main reaction arrow. For additional explanation of these mechanisms, see the text and the references for specific reactions listed in Table 1.
Fig. 3  Simplified representations and some examples of processes that occur in photochemical reactions of natural substances: a promotion of electrons ($e^-$) and generation of electron vacancies (holes, $h^+$) upon irradiation of a semiconductor, which may then reduce and oxidize other substances; b excitement of organic compounds by sunlight which then directly react with other substances or are themselves altered, with examples of photochemical acidification, dissolution, and crosslinking; c photocatalysis via surface adsorption, which makes a species, here N$_2$O, susceptible to the effect of light; d indirect generation, via a photosensitizer, of electrons and holes in a semiconductor: the difference between the highest occupied molecular orbital (HOMO) of the sensitizer and its lowest unoccupied molecular orbital (LUMO) is smaller than the band gap of the semiconductor, and therefore less energy is required to excite the sensitizer; e cooperative generation of transient reactive species by compounds that do not individually absorb sunlight; f generation of transient reactive species by light-absorbing compounds. Arrows with shadows indicate reactions induced by light (hν), asterisks (*) indicate excited species (electrons promoted to higher energy levels), single brackets (I) indicate mineral surfaces, and dotted lines (…) indicate surface adsorption. The references cited in the text offer additional, detailed explanations of these processes.
The bound substance then becomes susceptible to photolysis and other photo reactions (Fig. 3c). Depending on the nature of a substance, however, adsorption onto materials such as clay and ash can sometimes impede rather than facilitate photoreactions [76–78].

**Indirect reactions**

Indirect photochemical reactions are initiated by substances that absorb radiation and subsequently facilitate other reactions that do not involve the original light-absorbing substance [42]. For example, excited electrons and holes can be indirectly generated in semiconductors by light of lower energy than the band gap: the semiconductor itself does not absorb this light, but another substance (possibly even another semiconductor) that does absorb this light may be excited, and if this substance is in contact with the semiconductor and has appropriate energy levels, electrons can then be transferred between the excited substance and the semiconductor [48, 68, 79–81] (Fig. 3d). The semiconductor, now carrying additional electrons or holes, can participate in redox reactions that would not otherwise occur. For example, TiO$_2$ has a large band gap and is not normally excited by visible light; however, organic matter and natural chlorophyll derivatives are excited upon absorption of visible light, and in proximity to TiO$_2$ can transfer electrons to TiO$_2$ [82, 83]. This process is called charge injection, and is an example of photosensitization—reactions of TiO$_2$ with additional substances are facilitated by the initial presence of organic matter or chlorophyll derivatives.

A substance may also participate indirectly in photochemical reactions by generating reactive species upon irradiation; these reactive species then engage in other reactions that do not involve the original light-absorbing substance [42]. For example, some aluminosilicates (e.g., zeolites) and non-transition-metal oxides (e.g., SiO$_2$, Al$_2$O$_3$, MgO) can react with the oxygen in air upon irradiation to produce reactive oxygen species (ROS) such as singlet oxygen and superoxide [84, 85]. Photodegradation of an organic compound was observed in the presence of kaolinite and montmorillonite, for example, and was attributed to the formation of ROS on the surface of these minerals in the presence of molecular oxygen and water [86]. Since the organic compound in question does not absorb sunlight and the ROS are produced in a separate reaction, this is an indirect photoreaction, facilitated by the clay minerals which presumably act as catalysts by generating ROS from O$_2$ upon exposure to light (Fig. 3e).

Along with minerals [87], other substances can indirectly facilitate photoreactions by generating reactive species in sunlight: dissolved and particulate organic matter [88–95], dissolved organic matter and silicate minerals in synergy [63], cellulose [50, 96, 97], lignin [98, 99], leaves of phototoxic plants [100], chlorophyll [101], nitrate and nitrite [102–104], flavins [41, 105], tryptophan and tyrosine [99, 106, 107], and aqueous iron(III) species [108–110]. In contrast to the typically strong oxidizing action of ROS, a strongly reducing species can also be generated which is usually represented as $e^-$ (aq), a hydrated electron, although its true nature and features are not completely understood. Hydrated electrons are evident upon irradiation of dissolved organic matter, for example [94, 95]. As might be expected, reactive species are formed on exposed soil surfaces [111, 112]; both the mineral and organic components of soil contribute to this process [113]. Indirect photolysis of organic compounds in soil has been observed to occur at depths of up to 2 mm due to migration of reactive species; in contrast, direct photolysis (in which the degraded compound itself absorbs light) is restricted to a photic depth of about ten times less [114, 115]. Both light penetration and transport processes such as diffusion influence the extent to which compounds are degraded by light in soil and similar media [116]. Indirect processes may operate during photodegradation of plant material as well [117]. In certain instances, however, the same substances listed above may also inhibit the formation of reactive species and therefore retard indirect photoreactions, as observed for chlorophyll [118], carotenoids [119], and organic matter in soil and water [76, 120].

**Experimental approaches**

Studies in photogeochemistry may take several different paths, depending on the source of inspiration for identifying and investigating natural photochemical reactions (Fig. 4). Oftentimes photogeochemistry distinctly parallels biogeochemistry. As mentioned above, early research sometimes intentionally used biological phenomena as a starting point to search for analogous photochemical reactions. Other studies simply explored the effect of light on different materials, and as a result also discovered photochemical reactions analogous to biological processes. Photochemical counterparts have since been confirmed for many well-known biochemical reactions. These include photochemical disproportionation of acetic acid [121, 122] which is analogous to acetoclastic methanogenesis, and light-induced depletion of O$_2$ via a catalytic cycle involving iron and organic matter [123], analogous to consumption of O$_2$ by microorganisms. Estimates of the environmental significance of photochemical reactions relative to biological reactions have been offered on occasion, as for photochemical production of gases from plant litter [124, 125], and the photofixation of N$_2$ in deserts, estimated as 20 kg N ha$^{-1}$ year$^{-1}$, which is about one third of that fixed by lightning and about 10% of that fixed biologically on Earth [126]. In contrast to these processes, in which
biological reactions predominate (at least on a global level), the rate of degradation of dissolved lignin in rivers by photochemical mechanisms was found to be several times larger than by biological mechanisms [127]. Witz, based on his (nonbiological) studies with cellulose and other plant fibers [14], concluded that light is indeed an integral participant in natural decomposition: “In nature, once the life of plants is extinguished, cellulosic matter and other structured matter must no doubt pass progressively under the influence of light, air, and humidity ... and are eventually transformed into gaseous compounds and colored humic materials.”

**Extension of known photoreactions**

The most obvious experimental precedent in photogeochemistry is a natural photoreaction that has already been ascertained. Known reactions may be further investigated as to their context, mechanisms, and environmental significance. For example, the greenhouse gases CO$_2$, CH$_4$, and N$_2$O are the subject of a large amount of ongoing interdisciplinary research. Natural production and consumption of these gases at the earth’s surface are ascribed largely to biological activity [128–131], which remains the focus of most research, in spite of studies that have demonstrated photochemical production and consumption (see Table 1). Similarly, mineralization of organic carbon, nitrogen, and phosphorus in soil and water, the biological drivers of which are extensively studied, may also proceed photochemically. It is interesting to note that biologically recalcitrant portions of organic matter can be quite susceptible to photodegradation [132, 133]; the consequent release of labile organic and inorganic compounds can stimulate biological activity [134–136].

Sometimes a particular reaction, when placed in a certain environmental context, may even affect existing paradigms. For example, it is generally (and logically) assumed that in water classified as anoxic there can be no reactions involving molecular oxygen, including aerobic metabolism. However, some naturally occurring minerals are known to facilitate the photochemical oxidation of water to molecular oxygen; such “photochemical sources of oxidizing power in low-oxygen environments” [137] may be active alongside or in place of other sources of oxygen such as air or photosynthetic organisms. Similarly, organic acids known to be produced during the photodecomposition of organic matter may form a connection between light exposure and soil acidity, a simple but unestablished possibility next to the usual factors that determine soil pH.

While investigation of known natural photoreactions can be extended by pursuing additional work with the same substances, knowledge of natural photoreactions may also support inquiry into photoreactions of distinct but related substances. For example, the susceptibility to photodegradation of polycyclic aromatic hydrocarbons and related condensed aromatic compounds has been reported [e.g., 78, 138–140]. These studies focus on relatively simple molecules which are either regarded as naturally occurring pollutants or are components of dissolved organic matter. At the same time, the incomplete
combustion of natural organic materials leaves solid residues (“charcoal”, “biochar”, or “pyrogenic black carbon”) that contain analogous extended aromatic structure [141–143]. It may therefore be suggested that this ubiquitous material, commonly deemed environmentally persistent [63, 140, 143, 144] and therefore paradoxical (since it does not accumulate in the environment) [145, 146], is also degraded upon exposure to sunlight.

The study of photogeochemistry, while purely chemical in nature, may even venture into the domain of biology and identify more of the ways in which compounds derived from living organisms can influence abiotic photochemistry [e.g., 81], as well as more of the unique relationships between photochemical reactions and biological metabolism known as photobiocatalysis [147–149].

Observation of natural phenomena

Specific photo reactions are often planned and conveniently observed in the laboratory, using artificial light sources or sunlight itself, where it is easy to confirm the identity of the substances involved, design reaction vessels, characterize the light, and adjust the reaction environment. However, observations of natural phenomena can offer opportunities to consider unknown photochemical reactions possibly associated with these phenomena. For example, by the 1970s it was generally agreed that nitrous oxide (N₂O) has a short residence time in the troposphere, although the explanation for its removal was incomplete. Since N₂O does not absorb light of wavelengths greater than 290 nm, direct photolysis had been discarded as a possible explanation. It was then observed that light would decompose chloromethanes when they were adsorbed on silica sand [150], and this occurred at lower energies (longer wavelengths) than the absorption spectra for the free compounds. The same phenomenon was observed for N₂O on natural sand, leading to the conclusion that particulate matter in the atmosphere is responsible for the destruction of N₂O via surface-sensitized photolysis [151]. Indeed, the idea of such a sink for atmospheric N₂O was supported by reports of low concentrations of N₂O in the air above deserts, where there is a large amount of suspended particulate matter [152].

In general, simple atmospheric gases (e.g., CO₂, CO, CH₄, N₂O, H₂O, H₂, O₂) do not absorb ultraviolet and visible sunlight at the earth’s surface, and the cooperation of particulate matter is necessary for photo reactions involving these gases; such reactions are therefore heterogeneous. Other gases, however, such as some of the volatile compounds emitted from living plants [153, 154], burning plants [155] and soils [156], do absorb sunlight and can undergo homogeneous as well as heterogeneous reactions.

As another example, the observation that the amount of nitrous acid in the atmosphere greatly increases during the day led to insight into the surface photochemistry of humic acids and soils and an explanation for the original observation [157]. Fluctuations such as this are often a clue to the existence of photochemical reactions, which operate only during the day. Diurnal photogeochemical cycles often have a significant influence on the amounts of redox-sensitive elements in aqueous environments [70, 158–160]. Furthermore, multiple elemental cycles can be linked via photoreactions that directly affect both elements, as occurs during the concurrent oxidation of organic matter and reduction of iron [92]. The effect of light on one element can also indirectly affect other elements: a daily cycle of photoreduction, reoxidation, and precipitation of iron(III) species affects dissolved As, Cu, and P, which adsorb to iron(III) oxides as they reappear at night and may be subsequently released the next day upon photoreduction of the same iron oxides [158, 159, 161].

Contextualization of nonnatural photoreactions

Although photogeochemistry describes reactions among substances known to occur naturally, studies of similar substances may nonetheless point towards greater understanding of natural processes. A general example demonstrates this: it has been shown that samples of clay minerals found in soils can accelerate the photodegradation of synthetic chemicals via production of reactive oxygen species [e.g., 86]; it may therefore be assumed that many naturally occurring compounds are similarly affected. The conversion of N₂ to NH₃ and NO₃⁻ has been observed upon irradiation with visible light in the presence of Fe₂Ti₂O₇ [162, 163]. While such a compound is not known to occur naturally, it is related to known minerals like ilmenite (FeTiO₃), ulvospinel (Fe₂TiO₄), pseudorutile (Fe₂Ti₃O₉), and various titanium-substituted iron oxides, and can form when ilmenite is heated [162, 164]; these naturally occurring minerals might therefore also react with N₂ under certain conditions.

Outlook

Principles of photochemistry can be readily merged with geochemistry in investigation as well as education. Given the broad response of natural substances to light, recognizing photochemical reactions in the environment is part of understanding its fabric of interconnected processes, particularly on land, where this has not been explored as much as in water or the atmosphere. As remarked by Formenti and Teichner [40] concerning heterogeneous photochemistry, “there are so many different possibilities”, an outlook reiterated by Cooper and Herr [165] for aqueous photochemistry which is
easily extended to photogeochemistry: “there are a seemingly endless number of combinations and permutations to study.” This does not enjoin an unattainable research agenda, but rather affirms ample opportunity for geoscientists to incline their curiosity toward what happens on Earth when the sun appears.

Acknowledgements
It is a pleasure to acknowledge discussions with colleagues and guidance from the editor and three reviewers which helped me considerably improve this paper.

Competing interests
I have no competing interests.

References
1. Kim JD, Yee N, Nanda V, Falkowski PG (2011) Anoxic photochemical oxidation of siderite generates molecular hydrogen and iron oxides. Proc Nat Acad Sci USA 110:10073–10077
2. Schnauzer GN, Strampach N, Hui LN, Palmer NR, Salehi J (1983) Nitrogen photo-reduction on desert sands under sterile conditions. Proc Nat Acad Sci USA 80:3873–3876
3. Falkowski PG (2015) From light to life. Origins Life Evol B 45:347–350
4. Ciani A, Goss KU, Schwarzenbach RP (2005) Light penetration in soils and particulate minerals. Eur J Soil Sci 56:561–574
5. Kirk JTO (1977) Attenuation of light in natural waters. Aust J Mar Fresh Res 28:497–508
6. Piazena H, Perez-Rodriguez E, Hader DP, Lopez-Figueroa F (2002) Subtropical Atlantic Ocean—optical properties and possible biological consequences. Deep Sea Res Pt II Top Stud Oceanogr 49:3513–3528
7. Semifield JH, Pandis SN (1998) Atmospheric Chemistry and Physics: from Air Pollution to Climate Change. Wiley, New York
8. Madronich S, Flocke S (1999) The role of solar radiation in atmospheric chemistry. In: Boule P (ed) Handbook of environmental chemistry, volume 2 part L: environmental photochemistry. Springer, Berlin
9. McGovern PE, Michel RH (1990) Royal purple dye: the chemical reconstruction of the ancient Mediterranean industry. Acc Chem Res 23:152–158
10. Cole W (1685) A letter from Mr. William Cole of Bristol, to the Philosophical Society of Oxford, containing his observations on the purple fish. Phil Trans 15:1278–1286
11. Wollaston H (1811) Ueber gewisse chemische Wirkungen des Lichts. [On certain chemical effects of light]. Ann Phys 49:291–299
12. Berzelius JJ (1829) Traité de Chimie, Première Partie—Chimie Minérale. Firmin Didot Frères, Paris, p 52
13. Draper JW (1845) A treatise on the forces which produce the organic action, electricity, and the chemical action of light, Chap 10, 2nd edn. Harper and Brothers, New York
14. Witz G (1883) Recherches sur certaines alterations du coton [Studies on certain changes in cotton]. Bulletin de la Société Industrielle de Rouen 11:169–232
15. Whipple GC, Hazen A, Soper GA, Fuller GW, Maiguen JPA, Chester JN, Stearns FP, Fitzgerald D, Dunham HF (1901) The decolorization of water. Am Soc Civ Eng 46:141–181
16. Pasteur L (1853) Alcaloïdes des quinquinas. [Institut Journal Universel 21:249–250
17. Trömmendorff H (1834) Ueber Saponin. Ann Pharm 11:190–207
18. Fritzsche KJ (1867) Ueber die festen Kohlenwasserstoffe des Stein-kohlenteers [On the solid hydrocarbons of coal tar]. J Prakt Chem 101:333–343
19. O’Brien WJ (1915) A study of lithopone. J Phys Chem 19:113–144
20. Cawley J (1891) On the curious behaviour of certain zinc sulphide compounds. Chem News J 63:88–89
21. Job A, Emschwiller G (1922) Sur la réduction photochimique du sulphure de zinc [On the photochemical reduction of zinc sulfide]. CR Hebd Acad Sci 177:313–316
22. Reber JF, Meier K (1984) Photochemical production of hydrogen with zinc sulfide suspensions. J Phys Chem 88:5903–5913
23. Wang G, Huang BB, Li ZJ, Lou ZZ, Wang ZY, Dai Y, Whangbo MH (2015) Synthesis and characterization of ZnS with controlled amount of S vacancies for photocatalytic H2 production under visible light. Sci Rep 2015:8544
24. Everts S (2016) Van Gogh’s fading colors inspire scientific inquiry—lessons learned from the chemical breakdown of pigments in the Post-Impressionist’s masterpieces. Chem Eng News 94:32–33
25. Keune K, Boon JJ (2005) Analytical imaging studies clarifying the process of the darkening of vermilion in paintings. Anal Chem 77:4742–4750
26. von Baeyer A (1870) Ueber die Wasserentziehung und ihre Bedeutung fur das Pflanzenleben unt die Gahrung [On the removal of water and its importance for plant life and fermentation]. Ber Dtsch Chem Ges 3:63–75
27. Bach A (1893) Contribution à l’étude des phénomènes chimiques de l’assimilation de l’acide carbonique par les plantes à chlorophylle [Contribution to the study of the chemical phenomena of carbonic acid assimilation by plants with chlorophyll]. CR Acad Sci 116:1145–1148
28. Berthelot D, Gaudechon H (1910) Synthèse photochimique des hydrates de carbone aux dépens des éléments de l’anhydride carbonique et de la vapeur d’eau, en l’absence de chlorophylle; synthèse photochimique des composés quaternaires [Photochemical synthesis of carbohydrates from the elements of carbonic anhydride and water vapor, in the absence of chlorophyll; photochemical synthesis of quaternary compounds]. CR Acad Sci 120:1690–1693
29. Usher FL, Priestly JH (1911) The mechanism of carbon assimilation: part III. Proc R Soc Lond B 84:101–112
30. Rajvansi AR, Dhar NR (1932) Photosynthesis in tropical sunlight. Part III: synthesis of formaldehyde. J Phys Chem 36:568–574
31. Moore B, Webster TA (1913) Synthesis by sunlight in relationship to the origin of life: synthesis of formaldehyde from carbon dioxide and water by inorganic colloids acting as transformers of light energy. Proc R Soc Lond B 87:163–176
32. Baly ECC (1930) Photosynthesis of carbohydrates. Nature 126:666–667
33. Dhar NR, Ram A (1932) Photoreduction of carbonic acid, bicarbonates, and carbonates to formaldehyde. Nature 129:205
34. Baur E, Neuweiler C (1927) Über photolytische Bildung von Hydroper- oxyd [On the photolytic formation of hydrogen peroxide]. Helv Chim Acta 10:901–907
35. Dhar NR, Bhattacharya AK, Biswas NN (1932) Phototinitration in soil. Soil Sci 35:281–284
36. Mills A, LeHunte S (1994) An overview of semiconductor photocatalysis. J Photochem Photobiol A Chem 83:931–1014
37. Bisalskivy SE, Braun AM, Cassano AE, Emeline AV, Lutter M, Palmisano L, Parmon VN, Serpone N (2011) Glossary of terms used in photocatalysis and radiation catalysis (IUPAC recommendations). Pure Appl Chem 83:931–1014
38. Emeline AV, Otroshchenki VA, Ryabchuk VK, Serpone N (2003) Abiogenesis and photostimulated heterogeneous reactions in the interstellar medium and on primitive earth. Relevance to the genesis of life. J Photochem Photobiol C Photochem Rev 3:203–224
39. Emeline AV, Ryabchuk VK, Serpone N (2007) Photoreactions occurring on metal oxide surfaces are not all photocatalytic. Description of criteria and conditions for processes to be photocatalytic. Catal Today 122:91–100
40. Formenti M, Teichner SJ (1978) Heterogeneous photo-catalysis. In: Kernball C, Dowden DA (eds) Specialist periodical reports, catalysis, vol 2. The Chemical Society (Royal Society of Chemistry), London
41. Larson RA, Weber EI (1994) Reaction mechanisms in environmental organic chemistry. Lewis, Boca Raton
42. George C, Ammann M, D’Anna B, Donaldson DJ, Nikorodov SA (2015) Heterogeneous photochemistry in the atmosphere. Chem Rev 115:4218–4258
43. Kisch H (2015) Semiconductor photocatalysis. Wiley, Weinheim
44. Shuey RT (1975) Semiconductor ore minerals. Developments in economic geology, vol 4. Elsevier, Amsterdam
45. Xu Y, Schoonen MAA (2000) The absolute energy positions of conduction and valence bands of selected semiconducting minerals. Am Miner 85:543–556
46. Lou ZZ, Huang BB, Wang ZY, Ma XC, Zhang R, Zhang XY, Qin XY, Dai Y, Whangbo MH (2014) Ag5Si2O7: a silicate photocatalyst for the visible region. Chem Mater 26:3873–3875
47. Wang G, Huang BB, Ma XC, Wang ZY, Qin XY, Zhang XY, Dai Y, Whangbo MH (2013) Cu2(OH)PO4, a near-infrared-activated photocatalyst. Angew Chem Int Ed 52:4810–4813
48. Schoon MAA, Xu Y, Strongin DR (1998) An introduction to photocatalysis. J Geochim Explor 62:201–215
49. Mostert AB, Powell BJ, Pratt FL, Hanson GR, Sarna T, Gentle IR, Meredith P (2012) Role of semiconductor and ion transport in the electrical conduction of melanin. Proc Nat Acad Sci USA 109:8943–8947
50. Phillips GO, Hinojosa O, Arthur JC Jr, Maes T (1969) Photochemical initiation of free radicals in cotton cellulose. Text Res J 36:822–827
51. Simão CD, Reparaz JS, Wagner MR, Graczykowski B, Kreuzer M, Ruiz-Blanco YB, García Y, Malho JM, Gori AR, Atopjelto J, Sotomayor-Torres CM (2015) Optical and mechanical properties of nanofibrillated cellulose: toward a robust platform for next-generation green technologies. Carbohydr Polym 126:40–46
52. Evans MG, Gergely J (1949) A discussion of the possibility of bands of energy levels in proteins. Biochem Biophys Acta 2:188–197
53. Cardew MH, Eley DD (1959) The semiconductivity of organic substances. Part 7: Haemoglobin and some amino acids. Discuss Faraday Soc 27:115–128
54. Hauser CAE, Zhang SG (2010) Peptides as biological semiconductors. Nature 468:516–517
55. Hu C (2010) Modern semiconductor devices for integrated circuits. Prentice Hall, Upper Saddle River
56. Liu K, Rykov AI, Wang JH, Zhang T (2015) Recent advances in the application of Mossbauer spectroscopy in heterogeneous catalysis. Adv Catal S8:1–142
57. Choi WY, Termin A, Hoffmann MR (1994) The role of metal ion dopants in quantum-sized TiO2: correlation between photoactivity and charge carrier recombination dynamics. J Phys Chem 98:13669–13679
58. Soria J, Conesa JC, Augugliaro V, Palmirosi L, Schiavello M, Scalfani A (1991) Dinitrogen photoelectrodeposition on titanium-dioxide powders doped with ferrocene ions. J Phys Chem 95:274–282
59. Liang XL, Zhong YH, Zhu SY, Ma LY, Yuan P, Zhu JX, He HP, Jiang Z (2012) The contribution of vanadium and titanium on improving methylene blue decolorization through heterogeneous UV-Fenton reaction catalyzed by their co-doped magnetite. J Hazard Mater 199:247–254
60. Osterloh FE (2008) Inorganic materials as catalysts for photochemical splitting of water. Chem Mater 20:353–54
61. Zepp RG, Baughman GL, Schlottzauer PF (1981) Comparison of photochemical behavior of various humic substances in water. 1. Sunlight induced reactions of aquatic pollutants photosensitized by humic substances. Chemosphere 10:109–117
62. Timko SA, Romera-Castillo C, Jaffe R, Cooper WJ (2014) Photo-reactivity of natural dissolved organic matter from fresh to marine waters in the Florida Everglades, USA. Environ Sci Process Impacts 16:866–878
63. Fu HY, Liu HT, Mao JD, Chu WY, Li QL, Alvarez PJ, Qu XL, Zhu DQ (2016) Photochemistry of dissolved black carbon released from biochar: reactive oxygen species generation and photoformation. Environ Sci Technol 50:1218–1226
64. Gomis J, Vercher RF, Amat AM, Martire DO, Gonzales MC, Bianco-Prevot ST (2015) Biological components and bioelectronics interfaces of water splitting photoelectrocatalysts for solar hydrogen production. Chem Eur J 21:4188–4199
65. Vinodgopal K (1994) Environmental photochemistry: electron transfer from excited humic acid to TiO2 colloids and semiconductor mediated reduction of oxazine dyes by humic acid. Res Chem Intermed 20:825–833
66. Gohre K, Miller GC (1985) Artifical photosynthesis. 1. Photosensitization. J Phys Chem 89:5075–5083
67. Gratzel M (1985) Heterogeneous photochemical electron transfer. CRC Press, Boca Raton
68. Kortshagen U, Boschloo G, Sun LC, Kloo L, Pettersson H (2010) Dye-sensitized solar cells. Chem Rev 110:6695–6663
69. Braun A, Boudoire F, Bora DK, Faccio G, Hu YL, Kroll A, Mun BS, Wilson ST (2015) Biological components and bioelectronics interfaces of water splitting photoelectrocatalysts for solar hydrogen production. Chem Eur J 21:4188–4199
70. Sharpless CM, Blough NV (2014) The importance of charge-transfer complexes on heterogeneous photocatalysts for wastewater treatment: sensitizing effect and photo-Fenton-like process. Catal Today 209:176–180
71. Schoonen MAA, Cohn CA, Roemer E, Laffers R, Simon SR, O’Riordan T (2006) Mineral-induced formation of reactive oxygen species. Rev Miner Geochem 64:179–221
72. Katagi T (2004) Photo degradation of pesticides on plant and soil surfaces. Rev Environ Contam Toxicol 182:1–189
73. Thomas JK (1993) Physical aspects of photochemistry and radiation chemistry of molecules adsorbed on SiO2, γ-Al2O3, zeolites, and clays. Chem Rev 93:301–320
74. Kelemen GB, Wehry EL, Mamantov G, Natusch DFS (1980) Resistance to photochemical decomposition of polycyclic aromatic hydrocarbons vapor-adsorbed on coal fly ash. Environ Sci Technol 14:1094–1099
75. Gohre K, Miller GC (1985) Artificial photosynthesis. 1. Photosensitization of TiO2 solar cells with chlorophyll derivatives and related natural porphyrins. J Phys Chem 97:6272–6277
76. Che M, Tench AJ (1983) Characterization and reactivity of molecular oxygen species on oxide surfaces. Adv Catal 32:1–148
77. Gohe K, Miller GC (1985) Photochemical generation of singlet oxygen on non-transition-metal oxide surfaces. J Chem Soc, Faraday Trans 81:793–800
78. Sharpless CM, Blough NV (2014) The importance of charge-transfer interactions in determining chromophoric dissolved organic matter (CDOM) optical and photochemical properties. Environ Sci Process Impacts 16:654–671
79. Appiani E, McNeill K (2015) Photochemical production of singlet oxygen from particulate organic matter. Environ Sci Technol 49:3514–3522
91. Vione D, Minella M, Maurino V, Minero C (2014) Indirect photochemistry in sunlit surface waters: photoinduced production of reactive transient species. Chem Eur J. 20:10590–10606

92. Voelker BM, Molfet FMM, Sulzberger B (1997) Iron redox cycling in surface waters: effects of humic substances and light. Environ Sci Technol 31:1004–1016

93. Baxter RM, Carey JH (1983) Evidence for photochemical generation of superoxide ion in humic waters. Nature 306:575–576

94. Thomas-Smith TE, Blough NV (2001) Photoproduction of hydrated electron from constituents of natural waters. Environ Sci Technol 35:2721–2726

95. Malesic J, Kolar J, Strlic M, Kocar D, Fromageot D, Lemaire J, Haillant O, Fromageot D, Lemaire J (2000) Photoinduced degradation of cellulose. Polym Degrad Stabil 69:64–71

96. Hon NS (1976) Fundamental degradation processes relevant to solar irradiation of cellulose: ESR studies. J Macromol Sci Chem 10:1175–1192

97. Bellmerd G, Krinast L, Lindfors EL (1978) Singlet oxygen oxidation of lignin structures. In: Ranby B, Rabek JF (eds) Singlet oxygen: reactions with organic compounds and polymers. Wiley, Chichester

98. Rontani JF (1999) Photodegradation of lipidic compounds during the senescence of phytoplankton. In: Boule P (ed) Handbook of environmental chemistry, vol 2 part L: environmental photochemistry. Springer, Berlin

99. Boule P, Bolte M, Richard C (1999) Phototransformations induced in aqueous media by NO₃⁻/NO₂⁻, Fe(III) and humic substances. In: Boule P, Bolte M, Richard C (eds) Handbook of environmental chemistry, vol 2 part L: environmental photochemistry. Springer, Berlin

100. Mack J, Bolten JR (1999) Photochemistry of nitrite and nitrate in aqueous solution: a review. J Photochem Photobiol, A 128:1–13

101. Rontani JF (1999) Photodegradation of lipidic compounds during the senescence of phytoplankton. In: Boule P (ed) Handbook of environmental chemistry, vol 2 part L: environmental photochemistry. Springer, Berlin

102. Ajassa R, Carlotti ME, Vione D (2007) Photochemical processes involving nitrite in surface waters by a photochemical ferrous-ferric catalytic cycle. Environ Sci Technol 15:1089–1095

103. Zepp RG, Braun AM, Hoigne J, Leenheer JA (1987) Photoproduction of oxygen in water samples. Aquat Sci 69:71–85

104. McCormick JP, Thomason T (1978) Near-ultraviolet photooxidation of dissolved organic matter and its size fractions. In: Calza P, Vione D (eds) Surface water photochemistry. Royal Society of Chemistry, Cambridge

105. Zepp RG, Braun AM, Hoigne J, Leenheer JA (1987) Photoproduction of oxygen in water samples. Aquat Sci 69:71–85

106. Denman KL, Brasseur G, Chidthaisong A, Ciais P, Cox PM, Dickinson RE, Drange GS, Fichefet T, Fung I, Gregory KM, Hegglin MI, Houghton RT, Kattsov VM, Lee HD, Lenton TM, Meehl GA, Minster JB, Neelin JD, O’Faffler RA, O’Farrell PJ, Raper SC, Redler RH, Scinocca JF, Seetharaman J, SIA, Stocker TF, Takahashi T, Tomlinson DJ, Trenberth KE, Vancouf S, Weaver AJ, Watanabe K, Wright TC, Yohe GW (2007) Couplings between changes in the climate system and biogeochemistry. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL (eds) Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

107. David D, Cheeseman MS, Harris AJ (2006) The sensitized photodegradation of lignin model compounds. Photochem Photobiol Sci 4:268–274

108. Gellerstedt G, Kringstad K, Lindfors EL (1978) Singlet oxygen oxidation of lignin structures. In: Ranby B, Rabek JF (eds) Singlet oxygen: reactions with organic compounds and polymers. Wiley, Chichester

109. Draper WM, Crosby DG (1983) Photochemical generation of superoxide ion to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

110. Rontani JF (1999) Photodegradation of lipidic compounds during the senescence of phytoplankton. In: Boule P (ed) Handbook of environmental chemistry, vol 2 part L: environmental photochemistry. Springer, Berlin

111. Stumm W, Sulzberger B (1992) The cycling of iron in natural environments. J Geophys Res 97:6023–6038

112. Thomas-Smith TE, Blough NV (2001) Photoproduction of hydrated electron from constituents of natural waters. Environ Sci Technol 35:2721–2726

113. Rontani JF (1999) Photodegradation of lipidic compounds during the senescence of phytoplankton. In: Boule P (ed) Handbook of environmental chemistry, vol 2 part L: environmental photochemistry. Springer, Berlin

114. Boule P, Bolte M, Richard C (1999) Phototransformations induced in aqueous media by NO₃⁻/NO₂⁻, Fe(III) and humic substances. In: Boule P, Bolte M, Richard C (eds) Handbook of environmental chemistry, vol 2 part L: environmental photochemistry. Springer, Berlin

115. Rontani JF (1999) Photodegradation of lipidic compounds during the senescence of phytoplankton. In: Boule P (ed) Handbook of environmental chemistry, vol 2 part L: environmental photochemistry. Springer, Berlin

116. Balmer ME, Goss KU, Schwarzenbach RP (2000) Photolytic transformation of organic pollutants on soil surfaces—an experimental approach. Environ Sci Technol 34:1240–1245

117. McNally AM, Moore EC, McNeill K (2005) Kinetics and mechanism of the sensitized photodegradation of lignin model compounds. Photochem Photobiol Sci 4:268–274

118. Krasnovsky AA, Lopez J, Cheng P, Liddell PA, Blankenship RE, Moore TA, Gust D (1994) Generation and quenching of singlet molecular oxygen by aggregated bacteriochlorophyll d in model systems and chlorosomes. Photophys Res 40:191–198

119. Foote CS, Chang YC, Denny RW (1970) Chemistry of singlet oxygen. Carotenoid quenching parallels biological protection. J Am Chem Soc 92:5216–5218

120. Schrauzer GN (2011) Photoreduction of nitrogen on TiO₂ and TiO₂-containing minerals. In: Zang L (ed) Energy efficiency and renewable energy through nanotechnology. Springer, London

121. Kerstens P, Benner R (2003) Photochemical and microbial degradation of dissolved lignin phenols: implications for the fate of teregenous dissolved organic matter in marine environments. J Geophys Res 108:3291

122. Schoell M (1988) Origins of methane in the earth. Chem Geol 71:1–10

123. Denman KL, Brasseur G, Chidthaisong A, Ciais P, Cox PM, Dickinson RE, Hauglustaine D, Heinze C, Holland E, Jacob D, Lohmann U, Ramachandran S, da Silva Dias PL, Wofsy SC, Zhang X (2007) Couplings between changes in the climate system and biogeochemistry. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averett KB, Tignor M, Miller HL (eds) Climate change 2007: the physical science basis. Contribution of working group i to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

124. Wuebbles DJ (2009) Nitrous oxide: no laughing matter. Science 326:56–57

125. Singh BK, Bardgett RD, Smith P, Reay DS (2010) Microorganisms and climate change: terrestrial feedbacks and mitigation options. Nat Rev Microbiol 8:779–790

126. Wuebbles DJ (2009) Nitrous oxide: no laughing matter. Science 326:56–57

127. fringe B, Bardgett RD, Smith P, Reay DS (2010) Microorganisms and climate change: terrestrial feedbacks and mitigation options. Nat Rev Microbiol 8:779–790

128. Vahatalo AV, Zepp RG (2005) Photochemical mineralization of dissolved organic nitrogen to ammonium in the Baltic Sea. Environ Sci Technol 39:6985–6992

129. Franck DA, Heath RT (1979) Functionally distinct classes of complex phosphorus compounds in lake water. Limnol Oceanogr 24:463–473

130. Moran MA, Zepp RG (1997) Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnol Oceanogr 42:1307–1316

131. Wetzel RG, Hatcher PG, Bianchi TS (1995) Natural photolysis by ultraviolet irradiance of calcilibrant dissolved organic matter to simple substrates for rapid bacterial metabolism. Limnol Oceanogr 40:1369–1380

132. Austin AM, Mendez SM, Ballare CL (2016) Photodegradation alleviates the lignin bottleneck for carbon turnover in terrestrial ecosystems. Proc Nat Acad Sci USA 113:4392–4397

133. Eggelston CM, Stern JR, Strells TM, Parkinson BA (2012) A natural photoelectrochemical cell for water splitting: implications for early Earth and Mars. Am Min 97:1804–1807
186. Brinkmann T, Horsch P, Sartorius D, Fimmel FH (2003) Photoformation of low-molecular-weight organic acids from brown water dissolved organic matter. Environ Sci Technol 37:4190–4198

188. Noorjahan A, Kumari VD, Subrahmanyam A, Panda L (2005) Immobilized Cell-H2/H2: an efficient and stable photo-Fenton catalyst. Appl Catal B 57:291–298

189. Conrad R, Seiler W, Bunse G, Giehl H (1982) Carbon monoxide in sea water (Atlantic Ocean). J Geophys Res 87:8839–8852

190. Mopper K, Zhou XL, Kieber RJ, Sikorski RJ, Jones RD (1991) Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. Nature 353:60–62

192. Miller WL, Zepp RG (1995) Photochemical production of dissolved inorganic carbon from terrestrial organic matter—significance to the oceanic organic carbon cycle. Geophys Res Lett 22:417–420

194. Matthews RW (1986) Photooxidation of organic material in aqueous suspensions of titanium dioxide. Water Res 20:569–578

195. Chen HM, Abdulla HAN, Sanders RL, Myneni SCB, Mopper K, Hatcher PG (2014) Production of black carbon-like and aliphatic molecules from terrestrial dissolved organic matter in the presence of sunlight and iron. Environ Sci Technol Lett 1:399–404

196. Aarnos H, Ylöstalo P, Vähätalo AV (2012) Seasonal phototransformation of dissolved organic matter to ammonium, dissolved inorganic carbon, and labile substrates supporting bacterial biomass across the Baltic Sea. J Geophys Res 117:G01004

197. Zhang Y, Xie H (2015) Photomineralization and photomethanification of dissolved organic matter in Saguenay River surface water. Biogeosciences 12:6823–6836

198. Kieber DJ, McDaniel J, Mopper K (1989) Photochemical source of bio-organic matter in Saguenay River surface water. Biogeosciences 12:6823–6836

199. Kieber RJ, Zhou XL, Mopper K (1990) Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: fate of riverine carbon in the sea. Limnol Oceanogr 35:1503–1515

201. Reine AH, Arthur JC Jr (1970) Photochemistry of cellulose. The reaction of near-ultraviolet light on purified fibrous cotton cellulose. Text Res J 40:90–92

203. Castellan A, Colombo N, Vanucci C, Fornier de Violet P, Bouas-Laurent H (2012) Role of natural organic matter and aromatic ketones in the aquatic environment. Environ Sci Technol Lett 1:399–404

204. Chatterjee S, Sarkar S, Bhattacharyya SN (1994) Photodegradation of phenol by visible light in the presence of colloidal Fe2O3. J Photochem Photobiol, B 2:21–60

205. Niessen MG, Mustafa A, Barakat MZ (1947) Dimerization reactions in liquid phase. Acta Chem Scand 2:63–71

206. Neumann MG, Machado AEH (1989) The role of oxygen in the photodecomposition of anilines and phenols in water. In: Zika RG, Cooper WJ (eds) Photochemistry of Environmental Science. Academic Press, New York, pp 81–90

207. Gellerstedt G, Pettersson E (1975) Light-induced oxidation of lignin. Acta Chem Scand B 29:1005–1010

208. Reine AH, Arthur JC Jr (1970) Photochemistry of cotton cellulose. The direct action of near-ultraviolet light on purified fibrous cotton cellulose. Text Res J 40:90–92

209. Andrady AL, Torikai A, Kobatake T (1996) Spectral sensitivity of chitosan photodegradation. J Appl Polym Sci 62:1465–1471

210. Rossignol S, Tinel L, Bianco A, Passananti M, Brigante M, Donaldson DJ, George C (2016) Atmospheric photochemistry at a fatty acid-coated air-water interface. Science 353:699–702

211. Mills A, Davies RH, Worsley D (1993) Water purification by semiconduc-tor photocatalysis. Chem Soc Rev 22:417–425

212. Bridgen CT, Poulston S, Twigg MV, Walker AP, Wilkins AJJ (2001) Photo-oxygenation of short-chain hydrocarbons over titania. Appl Catal B 32:63–71

213. O’Brien RJ, Holmes JR, Bocklan AH (1975) Formation of photochemical aerosol from hydrocarbons. Environ Sci Technol 9:568–576

214. Dione D, Vione D, Maurino V, Minero C (2005) Transformations of benzene photoinduced by nitrate salts and iron oxide. J Atmos Chem 52:259–281

215. Minero C, Bono F, Rubertelli F, Pavino D, Maurino V, Pelizzetti E, Vione D (2007) On the effect of pH in aromatic phototransformation upon nitrate photolysis. Chemosphere 666:650–656

216. Vione D, Maurino V, Minero C, Vincenti M, Pelizzetti E (2001) Aromatic phototransformation in homogeneous and heterogeneous aqueous systems. Environ Sci Pollut Res 10:321–324

217. Niessen R, Lenor D, Boule P (1988) Phototransformation of phenol induced by excitation of nitrate ions. Chemosphere 17:1977–1984

218. Grojean D (1984) Atmospheric reactions of ortho cresol: gas phase and aerosol products. Atmos Environ 18:1641–1652

219. Zepp RG, Schlotzhauer PF (1983) Influence of algae on photolysis rates of chemicals in water. Environ Sci Technol 17:462–468

220. Stubbins A, Spencer RGM, Chen H, Hatcher PG, Mopper K, Hennes PJ, Malmov LA, Mangangu AM, Wabakanghanzi JH, Sw J (2010) Illumi- nated darkness: molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry. Limnol Oceanogr 55:1467–1477

223. Ward CP, Sleighter RL, Hatcher PG, Cory RM (2014) Insights into the complete and partial photodegradation of black carbon in surface waters. Environ Sci Process Impacts 16:721–731

224. Moffett JW, Zika RG (1987) Photocatalysis of copper complexes in sea water. In: Zika RG, Cooper WJ (eds) Photochemistry of Environmental Aquatic Systems. American Chemical Society, Washington DC

225. Haggiage E, Coyle EE, Joyce K, Oelgemoller M (2009) Green photocatalysis. Chem Soc Rev 38:1296–1304

226. Milne PJ, Zika RG (1993) Amino acid nitrogen in atmospheric aerosols: occurrence, sources, and photochemical modification. J Atmos Chem 16:361–398

227. Bharadwaj S, Sathyanarayana SN (2004) Photochemical studies on natural organic compounds in water. In: Zika RG, Cooper WJ (eds) Photochemistry of Environmental Aquatic Systems. American Chemical Society, Washington DC

228. Grace J, Farrow G (1981) Photochemical properties of copper(II) amino acid complexes. Inorg Chem 20:3708–3712

229. Scialfani A, Palmisano L, Schiavello M (1993) N2 photoreduction and production of nitric oxide and nitrogen-containing compounds from UV-induced photolysis of humic substances in natural waters. In: Zika RG, Cooper WJ (eds) Photochemistry of Environmental Aquatic Systems. American Chemical Society, Washington DC

230. Chatterjee S, Sarkar S, Bhattacharyya SN (1994) Photodegradation of phenol by visible light in the presence of colloidal Fe3O4. J Photochem Photobiol, A 81:199–203

231. Larson RA, Ellis DD, Ju HL, Marley KA (1989) Flavin-sensitized pho-totransformation of anilines and phenols. Environ Toxicol Chem 8:1165–1170

232. Schonberg A, Mustafa A, Barakat MZ (1947) Dimerization reactions in liquid phase. Acta Chem Scand 2:63–71

233. Haggagg E, Coyle EE, Joyce K, Oelgemoller M (2009) Green photo-chemistry: solarsynthetic synthesis of 5-amino-1,4-naphthoquinones. Green Chem 11:318–321

234. Konrad K, Litzow K, Weller J (2017) Photochemical degradation of phenol by visible light in the presence of colloidal Fe3O4. J Photochem Photobiol, A 81:199–203

235. Hanson RA, Ellis DD, Ju HL, Marley KA (1989) Flavin-sensitized pho-tochemical processing of anilines and phenols. Environ Toxicol Chem 8:1165–1170
237. Krauch CH, Farid S (1966) Competition between cyclobutane and oxetane formation in the photoaddition of 1,4-naphthaquinone to benzocyclic olefins. Tetrahedron Lett 39:4783–4788
238. Ciamiccan G, Sibber P (1907) Chemische Lichtwirkungen. XI. Mitteilung [Chemical effects of light. XI. Communication]. Ber Dtsch Chem Ges 40:2415–2424
239. Quinkert G (1965) Light-induced formation of acids from cyclic ketones. Angew Chem Int Ed 4:211–222
240. Haas Y (2004) Photochemical a-cleavage of ketones: revisiting acetone. Photoch Photobio Sci 3:6–16
241. Schonberg A, Mustafa A (1947) Reactions of non-enolizable ketones in sunlight. Chem Rev 40:181–200
242. Ito Y, Kunimoto K, Miyachi S, Kako T (1991) Photocatalytic cleavage of 1,2-diols by a cofacially hindered water-soluble iron(III) porphyrin. Tetrahedron Lett 32:4007–4010
243. Hein SM (2006) An exploration of a photochemical pericyclic reaction using NMR data. J Chem Educ 83:940–942
244. Sakata T, Kawai T, Hashimoto K (1984) Heterogeneous photocatalytic reactions of organic acids and water—new reaction paths besides the photo-Kolbe reaction. J Phys Chem 88:2344–2350
245. Schenk GC, Ziegler K (1944) Die Synthese des ascaridols. Naturwissenschaften 32:157
246. Kormann C, Bahnemann DW, Hoffmann MR (1988) Photocatalytic production of H2O2 and organic peroxides in aqueous suspensions of TiO2, ZnO, and desert sand. Environ Sci Technol 22:798–806
247. Chiron F, Chaichat JC, Garry RP, Pilichowski JF, Lacoste J (1997) Photochemical hydroperoxidation of terpenes. I. Synthesis and characterization of α-pinene, β-pinene and limonene hydroperoxides. J Photochem Photobiol A 111:75–86
248. Parlous N, Fey-Forges S (1994) Interest of photochemical methods for induction of lipid peroxidation. Biochimie 76:355–358
249. Khan NA, Lundberg WQ, Holman RT (1954) Displacement analysis of lipids. IX. Products of the oxidation of methyl linoleate. J Am Chem Soc 76:1779–1784
250. Wang WH, Beyerle-Pfnü R, Lay JP (1988) Photoreaction of salicylic acid in aquatic systems. Chemosphere 17:1197–1204
251. Harada H, Ueda T, Sakata T (1989) Semiconductor effect on the selective photocatalytic reaction of α-hydroxycarboxylic acids. J Phys Chem 93:1542–1548
252. Matsuoka M, Ichikawa Y, Kuwabara K (1980) Photooxidation of α-hydroxy acids and organic peroxides in water. Photochem Photobiol, A 11:75–86
253. Styler SA, Donaldson DJ (2012) Heterogeneous photochemistry of oxalic acid on Mauritania sand and Icelandic volcanic ash. Environ Sci Technol 46:8756–8763
254. Leland JK, Bard AJ (1987) Photochemistry of colloidal semiconductor-iron oxide polymorphs. J Phys Chem 91:5076–5083
255. Nikandrov VV, Gratzel CK, Moser JE, Gratzel M (1997) Light induced formation of carbon dioxide to methanol with hydrous cuprous oxide. J Phys Chem 106:8355–8362
256. Guzman MI, Colussi AJ, Hoffmann MR (2006) Photoinduced oligomerization of aqueous pyruvic acid. J Phys Chem A 110:3619–3626
257. Dallin E, Wan P, Krogh E, Gill C, Moore RM (2009) New pH-dependent photoinduction pathways of syringic acid in aqueous solution: relevance in environmental photochemistry. J Photochem Photobiol B 98:207–205
258. Yanagida S, Azumé T, Kawakami H, Kuramoto H (1984) Photocatalytic carbon-carbon bond formation with concurrent hydrogen evolution on colloidal zinc sulfide. J Chem Soc, Chem Commun 4:349–350
259. Ciancio M, Graham B, Vas G, Wang W, Vermeylen R, Pashynska V, Caffmeyer J, Guyon P, Andreau MO, Artaxo P, Maenhaut W (2004) Formation of secondary organic aerosols through photoxidation of isoprene. Science 303:1173–1176
260. Wat CK, Johns T, Towers GHN (1980) Phototoxic and antibiotic activities of plants of the Asteraceae used in folk medicine. J Ethnopharmacol 2:279–290
261. Larson RA, Berenbaum MR (1988) Environmental photoxotoxicity. Environ Sci Technol 22:354–360
262. Tannakone K, Jayatissa AH, Punchihewa S (1989) Selective photoreduction of carbon dioxide to methanol with hydrous cuprous oxide. J Photochem Photobiol, A 49:369–375
263. Matsumoto Y, Obata M, Hombro J (1994) Photocatalytic reduction of carbon dioxide on p-type CaO, powder. J Phys Chem 98:2950–2951
264. Yamashita H, Nishiguchi N, Kamada N, Anpo M, Teraoka Y, Hatano H, Ehara S, Kikui K, Palmissano L, Sclafani A, Schiavello M, Fox MA (1994) Photocatalytic reduction of CO2 with H2O on TiO2 and Cu/TiO2 catalysts. Res Chem Intermed 20:815–823
265. Matsuoka M, Anpo M (2003) Local structures, excited states, and photocatalytic reactivities of highly dispersed catalysts constructed within zeolites. J Photochem Photobiol, C 3:225–252
266. Roy SC, Varghese OK, Paulose M, Grimes CA (2010) Toward solar fuels: photocatalytic conversion of carbon dioxide to hydrocarbons. ACS Nano 4:1259–1278
267. Habibisregten SN, Schmidt-Mende L, Stolarczyk JK (2013) Photocatalytic reduction of CO2 on TiO2 and other semiconductors. Angew Chem Int Ed 52:7372–7408
268. Li KE, An XQ, Park KH, Khrisavliss M, Tang JW (2014) A critical review of CO2 photoconversion: catalysts and reactors. Catal Today 223:3–12
269. Lichtin NN, Vijayakumar KM, Rubio BL (1987) Photoassisted reduction of CO2 by H2 over metal oxides in the absence and presence of water vapor. J Catal 104:264–251
270. Sastre F, Puga AV, Liu LC, Cornia A, Garcia H (2016) Complete photocatalytic conversion of CO2 to methane by H2 under solar light irradiation. J Am Chem Soc 136:6798–6801
271. Premkumar J, Ramaraj R (1997) Photocatalytic reduction of carbon dioxide to formic acid at porphyrin and phthalocyanine adsorbed Nafion membranes. J Photochem Photobiol, A 110:53–58
272. Ohta K, Ueda Y, Nakaguchi S, Mizuno T (1998) Photocatalytic reduction of CO2 using Cu-loaded silicate rock powder suspended in water. Can J Chem 76:228–233
273. Yamamura S, Kojima H, Iyoda J, Kawai W (1987) Formation of ethyl alcohol in the photocatalytic reduction of carbon dioxide by SiC and ZnSe/metal powders. J Electroanal Chem 225:267–290
274. Cook RL, MacDuff RC, Sammells AF (1988) Photocatalytic carbon dioxide reduction to hydrocarbons at ambient temperature and pressure. J Electroanal Soc 135:3096–3070
275. Egger BD, Robertson PKJ, Stewart JH, Woods E (1993) Photooxidation of carbon dioxide on zinc sulfide to give four- and two-carbon acids. J Phys Chem, Chem Commun 4:349–350
276. Liu YF, Huang BB, Dai Y, Zhang XY, Qin XY, Xiang MH, Whangbo MH (2009) Selective ethanol formation from photocatalytic reduction of carbon dioxide in water with BiVO4 photocatalyst. Catal Commun 11:210–213
277. Tahir M, Amin NS (2013) Photocatalytic reduction of carbon dioxide with water vapor over montmorillonite modified TiO2 nanocomposites. Appl Catal B 142:512–522
278. Lien CF, Chen MT, Lin YF, Lin JL (2004) Photooxidation of methane over TiO2. J Chin Chem Soc 51:87–92
279. Yoshida H, Matsushita N, Kato Y, Hatton T (2003) Synergistic active sites on SO2-Al2O3-TiO2 photocatalysts for direct methane combustion. J Phys Chem B 106:8355–8362
280. Hari P, Ravonien M, Vesala T, Munger JW, Pilegaard K, Kulmala M (2003) Atmospheric science: ultraviolet light and leaf emission of NOx. Nature 422:134
281. Bruhn D, Albert KR, Mikkelsen EC, Ambus P (2014) UV-induced N2O emission from plants. Atmos Environ 99:206–214
282. Bushwak KL, Zepp RG, Tarr MA, Schulz-Jander D, Bourbonniere RA, Hodson RE, Miller WL, Bronk DA, Moran MA (1996) Photochemical release of biologically available nitrogen from aquatic dissolved organic matter. Nature 381:404–407
283. Rao GG, Varadanam CI (1938) Photo-ammonification of organic nitrogenous compounds in the soil. Nature 142:618
284. Lundeen RA, Janssen EML, Chu CH, McNeill K (2014) Environmental photochemistry of amino acids, peptides, and proteins. Chima 68:812–817
302. Ndour M, Conchon P, D’Anna B (2009) Photochemistry of mineral dust
307. Milis A, Domenech X (1993) Photoassisted oxidation of nitrite to nitrate
309. Warneck P, Wurzinger C (1988) Product quantum yields for the 305-
311. Rubasinghege G, Grassian VH (2009) Photochemistry of adsorbed
313. Dhar NR, Pant NN (1944) Nitrogen loss from soils and oxide surfaces.
315. Bedjanian Y, El Zein A (2012) Interaction of NO2 with TiO2 surface under
317. Ohtani B, Kakimoto M, Miyadzu H, Nishimoto S, Kagiya T (1988) Effect
319. Miyama H, Fuji N, Nagaye Y (1980) Heterogeneous photocatalytic synthesis of ammonia from water and nitrogen. Chem Phys Lett 72:55–59
321. Khader MM, Lichtin NN, Varens GH, Salmeron M, Somorjai GA (1987) Photocatalytic reduction of atmospheric nitrogen in hydrous iron(II) oxide loaded nanoflms in aerated water. J Chem Soc Chem Comm 55:980–984
323. Khan F, Yue PL, Ruzzuti L, Augugliaro V, Schiavello M (1981) Photochemical synthesis of ammonia over zeolites. J Chem Soc, Chem Commun 20:1049–1050
325. Moore B (1918) The formation of nitrites from nitrates in aqueous solution by the action of sunlight, and the assimilation of the nitrates by green leaves in sunlight. Proc R Soc Lond B 90:158–167
327. Porcal P, Kopacek J, Tomkova I (2014) Seasonal photochemical transformations of nitrogen species in a forest stream and lake. PLoS ONE 9:e116364
329. Helms JR, Mao JD, Schmidt-Rohr K, Abdulla H, Mopper K (2013) Photocatalytic reduction of nitrate using a composite ZnO-Fe2O3 system. Environ Sci Technol 47:7612–7619
331. Monge ME, D’Anna B, Mazzi L, Giroir-Fendler A, Ammann M, Donaldson DJ, George C (2010) Light changes the atmospheric reactivity of soot. Proc Natl Acad Sci USA 107:6605–6609
333. Waite TD, Morel FMM (1984) Photoreductive dissolution of colloidal iron in the water column. Geochim Cosmochim Acta 121:398–413
335. Goldberg MC, Cunningham KM, Weiner ER (1993) Aquatic photolysis: photolytic redox reactions between goethite and adsorbed organic acids in aqueous solutions. J Photochem Photobiol B 14:195–204
337. Finden DAS, Tipping E, Jaworski GHM, Reynolds CS (1984) Light-induced reduction of natural iron(II) oxide and its relevance to phytoplankton. Nature 309:783–784
339. Waite TD, Morel FMM (1984) Photoinduced reduction of colloidal iron oxides in natural waters. Environ Sci Technol 18:860–868
341. Faust BC, Hoffmann MR (1986) Photoinduced reduction of α-Fe2O3 by bisulfite. Environ Sci Technol 20:94–98
335. Pehkonen SO, Siefert R, Erel Y, Webb S, Hoffmann MR (1993) Photoreduction of iron oxyhydroxides in the presence of important atmospheric organic compounds. Environ Sci Technol 27:2056–2062.

336. Zhu XR, Prospero JM, Savoie DL, Millero FJ, Ziga RG, Saltzman ES (1993) Photoreduction of iron(III) in marine mineral aerosol solutions. J Geophys Res 98:9039–9046.

337. Sherman DM (2005) Electronic structures of iron(III) and manganese(IV) (hydr)oxide minerals: thermodynamics of photochemical reductive dissolution in aquatic environments. Geochim Cosmochim Acta 69:3249–3259.

338. Kim K, Choi W, Hoffmann MR, Yoon HL, Park BK (2010) Photoreductive dissolution of iron oxides trapped in ice and its environmental implications. Environ Sci Technol 44:4142–4148.

339. Weiss J (1935) Photochemical reactions connected with the quenching of fluorescence of dyestuffs by ferrous ions. Nature 136:794–795.

340. Borowska ZK, Mauzerall DC (1987) Efficient near ultraviolet light induced formation of hydrogen by ferrous hydroxide. Origins Life Evol Biol 17:251–259.

341. Balzani V, Carasiti V (1970) Photochemistry of Coordination Compounds. Academic Press, London.

342. Bienfait HF, Scheffers MR (1992) Some properties of ferric citrate relevant to the iron nutrition of plants. Plant Soil 143:141–144.

343. Sunda WG, Huntsman SA, Harvey GR (1983) Photo-reduction of manganese(II) in seawater and its geochemical and biological implications. Nature 301:234–236.

344. Waite TD, Wrigley IC, Szymczak R (1988) Photoassisted dissolution of a colloidal manganese oxide in the presence of fulvic acid. Environ Sci Technol 22:778–785.

345. Bertino DJ, Zepp RG (1991) Effects of solar radiation on manganese oxide reactions with selected organic compounds. Environ Sci Technol 25:1267–1273.

346. Spokes LJ, Liss PS (1995) Photochemically induced redox reactions in seawater. I. Cations. Mar Chem 49:201–213.

347. Kim K, Yoon HL, Choi W (2012) Enhanced dissolution of manganese oxide in ice compared to aqueous phase under illuminated and dark conditions. Environ Sci Technol 46:13160–13166.

348. Alicke B, Amyot M, Kraepiel AML, Morel FMM (2001) Photooxidation of iron oxyhydroxides in the presence of important atmospheric organic compounds. Environ Sci Technol 35:1367–1372.

349. Lozano A, Garcia J, Domenech X, Casado J (1992) Heterogeneous photocatalytic oxidation of manganese(II) over TiO2. J Photochem Photobiol A 69:237–240.

350. Kim I, Hosein H, Strongin DR, Douglas T (2003) Photochemical reactivity of ferritin for (Cr7)2+ reduction. Chem Mater 14:4874–4879.

351. Muytjens, Staassica Z (2004) Photochemical reduction of chromium(VI) by phenol and its halogen derivatives. Appl Catal B 52:167–172.

352. Zhang H (2006) Photochemical redox reactions of mercury. Struct Bond 69:237–240.

353. Lalonde JD, Amyot M, Kraepiel AML (2001) Photooxidation of iron(III) in marine mineral aerosol solutions. J Geophys Res 98:9039–9046.

354. Baltrusaitis J, Jayaweera PM, Grassian VH (2011) Sulfur dioxide adsorption on TiO2 nanoparticles: influence of particle size, coadsorbates, sample pretreatment, and light on surface speciation and surface coverage. J Phys Chem C 115:490–506.

355. Chen J, Pehkonen SO, Lin CJ (2003) Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters. Water Res 37:2496–2504.

356. Lehnerr L, St. Louis VL (2009) Importance of ultraviolet radiation in the photodemetylation of methylmercury in freshwater ecosystems. Environ Sci Technol 43:5692–5698.

357. Chem J, Pehkonen SO, Lin CJ (2003) Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters. Water Res 37:2496–2504.

358. O’Driscoll NJ, Lean DRS, Loseto LL, Carignan R, Siciliano SD (2004) Effect of UV radiation on snow on snow-to-air mercury transfer. Environ Sci Technol 38:2525–2530.

359. Lee H, Rahn T, Throop HL (2012) A novel source of atmospheric H2: abiotic degradation of organic material. Biogeochemistry 94:1411–1419.

360. Xiao W, Aluwihare L, Serpone N (2005) Abiotic production of methylmercury by solar radiation. J Photochem Photobiol A 174:157–164.

361. Chen J, Pehkonen SO, Lin CJ (2003) Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters. Water Res 37:2496–2504.

362. Derendorp L, Quist JB, Holzinger R, Beckmann T (2011) Emissions of H2 and CO from leaf litter of Sequoiaedendron giganteum, and their dependence on UV radiation and temperature. Atmos Environ 45:7520–7524.

363. Lee H, Rahn T, Throop HL (2012) A novel source of atmospheric H2: abiotic degradation of organic material. Biogeochemistry 94:1411–1419.
382. Ismail AA, Bahnemann DW (2014) Photochemical splitting of water for hydrogen production by photocatalysis: a review. Sol Energy Mater Sol Cells 128:85–101
383. Buxton GV, Wilford SP, Williams RJ (1962) The photo-oxidation of water by ferous ion at 25°. J Chem Soc 1962:4957–4962
384. Ohmori T, Takahashi H, Mametsuka H, Suzuki E (2000) Photocatalytic oxygen evolution on alpha-Fe2O3 films using Fe3+ ion as a sacrificial oxidizing agent. Phys Chem Chem Phys 2:3519–3522
385. Silva CG, Boulzi Y, Fornes V, Garcia H (2009) Layered double hydroxides as highly efficient photocatalysts for visible light oxygen generation from water. J Am Chem Soc 131:13833–13839
386. Jiao F, Frei H (2010) Nanostructured cobalt and manganese oxide clusters as efficient water oxidation catalysts. Energy Environ Sci 3:1018–1027
387. Robinson DM, Go YB, Mui M, Gardner G, Zhang ZJ, Mastrogiovanni D, Garfunkel E, Li J, Greenblatt M, Dismukes GC (2013) Photochemical water oxidation by crystalline polymorphs of manganese oxides: structural requirements for catalysis. J Am Chem Soc 135:3494–3501
388. Xu SM, Pan T, Dou YB, Yan H, Zhang ST, Ning FY, Shi WY, Wei M (2015) Theoretical and experimental study on M(II)M(III)-layered double hydroxides as efficient photocatalysts toward oxygen evolution from water. J Phys Chem 119:18823–18834
389. Ashokkumar M, Marignier JL (1999) Hydrogen and oxygen evolution from water using Ag and AgCl colloids. Int J Hydrog Energy 24:17–20
390. Kudo A, Omori K, Kato H (1999) A novel aqueous process for preparation of crystal form-controlled and highly crystalline BiVO4 powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. J Am Chem Soc 121:11459–11467
391. Jacobs PA, Uytterhoeven JB, Beyer HK (1977) Cleavage of water over zeolites. J Chem Soc Chem Comm 4:128–129
392. Reddy VR, Hwang DW, Lee JS (2003) Photocatalytic water splitting over ZrO2 prepared by precipitation method. Korean J Chem Eng 20:1026–1029
393. Hara M, Kondo T, Komoda M, Ikeda S, Shinohara K, Tanaka A, Kondo JN, Domen K (1998) Cu2O as a photocatalyst for overall water splitting under visible light irradiation. Chem Commun 1998:357–358
394. Bhandari N, Reeder RJ, Strongin DR (2011) Photoinduced oxidation of arsenite to arsenate on ferrihydrite. Environ Sci Technol 46:8044–8051
395. Ding W, Wang YJ, Yu YT, Zhang ZX, Li JJ, Wu F (2015) Photooxidation of arsenic(III) to arsenic(V) on the surface of kaolinite clay. J Environ Sci-China 36:29–37
396. Zoppi M, Pratesi G (2012) The dual behavior of the β-As5S4 altered by light. Am Mineral 97:890–896
397. Berkes JS, Ing SW Jr, Hillegas WJ (1971) Photodecomposition of amorphous As2Se3 and As2S3. J Appl Phys 42:4908–4916
398. Atkinson R (2000) Atmospheric chemistry of VOCs and NOx. Atmos Environ 34:2063–2101
399. Oum KW, Lakin MJ, DeHaan DO, Brauers T, Finlayson-Pitts BJ (1998) Formation of molecular chlorine from the photolysis of ozone and aqueous sea-salt particles. Science 279:74–77
400. George IJ, Anastasio C (2007) Release of gaseous bromine from the photolysis of nitrate and hydrogen peroxide in simulated sea-salt solutions. Atmos Environ 41:543–553