Materials Horizons: From Nature to Nanomaterials

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Nanomaterials and Photocatalysis in Chemistry
Mechanistic and Experimental Approaches
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Chapter 1
Introduction

1.1 Historical Background of Photocatalysis

As early as 1901, the experiments were conducted by chemist Giacomo Ciamician to study the influence of light wavelength on chemical reactions [1]. The performed experiments with red and blue lights demonstrated that a chemical effect can be taken place when only blue light was used in chemical reactions. He carefully explored the probability that whether these chemical reactions were powered by temperature (thermal heat) produced via incident irradiated blue light or any other reason. The term “photocatalysis” was first time used in several scientific studies in 1911. In Germany, Eibner introduced the concept in his report on the influence of ZnO on bleaching of Prussian blue [2–5]. This study has motivated subsequent experiments on ZnO photocatalyst for other reactions including reduction of Ag⁺ ion to Ag⁰ under light illumination in 1924 [6]. Although, prior to these effects, the photo-active chemical reactions had long been investigated which did not use light active catalysts [7]. In 1932, TiO₂ and Nb₂O₅ were studied to investigate the photocatalytic decomposition of AgNO₃ to Ag and AuCl₃ to Au [8, 9].

Later in 1938, TiO₂ as photosensitizer was studied for decomposing dyes in the oxygen environment [10]. Interestingly, photocatalytic process continued as a main chemical reaction because of the absence of typical commercial applications. However, this situation modified in early 1970 due to two main reasons. Firstly, the oil crises motivated the researchers to search other renewable energy sources besides fossil fuels [11]. Secondly, the serious environmental effects by large-scale industrialization prompted scientists to explore green and efficient energy resources for the future demand of energy in the world [12]. In 1968, O₂ evolution on TiO₂ was first reported by scientists of the Bell Labs [13]. On the other hand, Fujishima and Honda reported H₂ generation from H₂O oxidation via TiO₂ electrodes under UV photo-illumination in 1972 [14]. Similarly, photocatalysis for water splitting for the production of hydrogen (H₂) and oxygen (O₂) under argon atmosphere was reported.
in 1977 [15]. The authors observed that production of O₂ and H₂ was greatly inhibited in the presence of nitrogen gas because N₂ was reduced to NH₃ and trace amount of N₂H₂ via TiO₂. During the same era of time, TiO₂, ZnO, and CdS photocatalysts were used for the degradation of CN⁻ and SO₃²⁻ in the presence of light by Frank and Bard [16]. Afterward, Fujishima et al. studied the reduction of CO₂ via photocatalysis utilizing variety of inorganic semiconductor-based photocatalytic materials in 1979 [17]. These early reports increased the photocatalysis applications; therefore, lot of research was done in 1980 using especially TiO₂ nanoparticles as photocatalyst [18–20].

After this, major focus of scientists was on the understanding of fundamental principles, improving performance of photocatalysts, searching new photocatalysts, and expending their applications. For example, in 1997, the light-initiated superhydrophilicity phenomenon was explored using TiO₂. Therefore, TiO₂ was used as building material due to its function as self-cleaner and anti-fog agent [21, 22]. Many new materials having photocatalytic activity higher than TiO₂ were developed, which have higher band gap energies and only function under visible-light illumination [23]. Then, in next step, attempts were made to develop visible-light absorbing materials having higher efficiencies [24, 25]. In parallel, scientists gradually learned more about photocatalysis principles and also extended practical applications of photocatalysis. In conclusion, it can be said that photocatalysis has recently emerged as an advanced and efficient technology, providing simple solutions for environmental and energy crises to our today society.

1.2 Broad Definition of Photocatalysis

The photocatalysis progress was certainly motivated by sunlight-based natural photosynthesis. The photocatalytic process has been extensively used in the literature for two different practices [26]. As shown in Fig. 1.1a, upon absorption of light energy by material, a thermodynamically uphill reaction (Gibbs free energy change (ΔG) > 0) starts usually called photosynthesis. The used material in above process is called “photocatalyst” only if the irradiated light is considered to be a reactant. The major reactions in this category include photocatalytic water splitting and CO₂ conversion [27–29]. On the other hand, if a semiconductor material utilizes light energy for the start of thermodynamically downhill chemical reactions (ΔG < 0, Fig. 1.1b), then in this process material does not alter the reaction thermodynamics but only supports the new reactions via absorption of light. Thus, used material in this reaction would be regarded as true photocatalyst and overall process will be considered as photocatalysis. The phenol oxidation to hydroquinone via oxygen (ΔG° = − 167.96 kJ/mol) or thorough oxidation to CO₂ and H₂O (ΔG° = − 3027.36 kJ/mol) are examples of this category [30, 31]. Besides thermodynamic perspective, the photocatalytic properties including absorption of light, charge transport, and separation are shared by both types of reactions (Fig. 1.1).
1.3 Classification of Photocatalysis

A promising approach uses solar energy to excite a semiconductor photocatalyst that can enable different redox reactions [32]. This broad field is known as photocatalysis. Each potential redox reaction that can occur signifies an individual photocatalytic field. More specifically, it can efficiently utilize solar energy with simultaneous energy conversion and environmental remediation. The energy conversion aspect majorly includes water splitting, carbon dioxide (CO₂) reduction, nitrogen fixation and synthesis of organic molecules (less explored) to develop sustainable and clean energy. Secondly, its environmental remediation applications are more likely to focus on air purification and wastewater decontamination. The overall photocatalysis details in two aspects: Energy conversion and environmental remediation (Fig. 1.2) will be covered in this book.

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**Fig. 1.1** Thermodynamically supported uphill and downhill photocatalysis: a uphill process; b downhill process. Reproduced from ref [26] with permission from ACS, Copyright 2017

**Fig. 1.2** Photocatalysis for energy and environmental applications
References

1. A. Albini, M. Fagnoni, ChemSus chem 1, 63 (2008)
3. A. Eibner, Chem.-Ztg. 35, 753 (1911)
4. A. Eibner, Chem.-Ztg. 35, 774 (1911)
5. A. Eibner, Chem.-Ztg. 35, 786 (1911)
2.1 Photocatalytic Water Splitting

2.1.1 Importance of Photocatalytic Water Splitting

Energy shortage is the most significant problem for the mankind due to the reason that our current society is built on fossil fuels [1]. This fact has motivated researchers to develop clean and renewable energy technologies. For this purpose, hydrogen (H₂) is regarded as one of the cheapest sources of energy, for example, in fuel cell devices, it is used to produce electricity, water, and heat [2]. However, for the production of hydrogen, a complicated process is involved such as hydrocracking of fossil fuels through refinery processes. On the other hand, sunlight is a natural cheapest and clean energy source which can be used to produce hydrogen gas fuel. Therefore, photocatalytic hydrogen production through water splitting reaction has been considered as an excellent method to produce clean hydrogen utilizing earth-abundant sunlight [3].

2.1.2 Basic Principles of Photocatalytic Water Splitting

The direct water splitting into hydrogen and oxygen under solar light irradiation is the final objective of a photocatalytic hydrogen production system. Under ambient conditions, the splitting water is thermodynamically not favorable reaction having net Gibbs free energy change (ΔG⁰) of 237 kJ/mol [4]. However, when semiconductor photocatalyst is irradiated with light in water, then thermodynamic equilibrium can be moved toward the required right direction for H₂ and O₂ production. Moreover, the overall splitting of water and full water splitting reaction is explained in Eqs. (2.1–2.4) [5].
The overall water splitting reaction:

\[ \text{H}_2\text{O} + h^+ \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ \]  \hspace{1cm} (2.1)

\[ 2\text{H}^+ + 2e^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2 \]  \hspace{1cm} (2.2)

The full water splitting reaction:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ \]  \hspace{1cm} (2.3)

\[ 4\text{H}^+ + 4e^- \rightarrow \text{O}_2 + 2\text{H}_2 \]  \hspace{1cm} (2.4)

In general, the water splitting reaction through semiconductor photocatalysis consists of three main steps as shown in Fig. 2.1. The first step involves light absorption by semiconductor photocatalyst to create charge carriers (electrons and holes). In this process, when semiconductor is illuminated with incident light energy higher than its band gap energy (Eg), then electrons are excited from valence band (VB) of