

Chapter 15

MoS₂ Applications in Photo-Fenton Technology



15.1 The Brief Introduction of Fenton Technology

Wastewater arising from different chemical industries like resin manufacturing, petrochemical, oil refineries, paper making, and textile industry has high concentration of organics and their derivatives which are extremely toxic and refractory to the environment. The presence of organic compounds in wastewater, surface water, and groundwater poses serious threat to humans' health. Thus, its removal from contaminated water is of high priority. The conventional treatment methods like biotechnology are not effective in some fields. Consequently, the need of more efficient treatment methods is imperative. In recent years, oxidation processes are preferred to degrade pollutants.

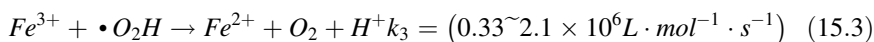
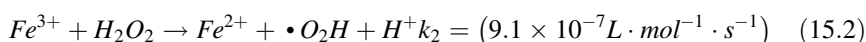
Advanced oxidation processes (AOPs) have been described as a promising choice to remove persistent pollutants from contaminated water. Additionally, AOPs require less energy than direct oxidation [1–3]. Typically, AOPs are operated under ambient temperature and pressure, which involve the generation of hydroxyl radicals in sufficient quantity to achieve water purification [4]. The hydroxyl radicals as highly reactive species are able to break the structure of most organic molecules with rate constants in the order of 10^6 – 10^9 mol/L• [5]. The reduction potential of various oxidants is shown in Table 15.1. Hydroxyl radical is the second strongest oxidant followed fluorine, and it reacts about 1000 times faster than ozone depending on the substrate to be degraded [6]. Classified by the reactive phase, AOPs contain homogeneous and heterogeneous phases. One of the most commonly used AOPs for dealing contaminants is Fenton process. The generated hydroxyl radicals in Fenton process possess inherent properties that enable it to achieve a complete mineralization of organic molecules into CO₂, water, and mineral acids such as sulfuric, hydrochloric, and nitric acids [7–9].

Fenton's reagent was discovered about 100 years ago, but its application as an oxidation process for decomposing toxic organics was not applied until the late

Table 15.1 Standard reduction potential of common oxidants [10]

Oxidant	Oxidation potential (eV)
Fluorine (F ₂)	3.03
Hydroxyl radical (OH)	2.80
Atomic oxygen (O)	2.42
Ozone (O ₃)	2.07
Hydrogen peroxide (H ₂ O ₂)	1.77
Potassium permanganate (KMnO ₄)	1.67
Chlorine dioxide (ClO ₂)	1.5
Hypochlorous acid (HClO)	1.49
Chlorine (Cl ₂)	1.36
Oxygen (O ₂)	1.23
Bromine (Br ₂)	1.09

1960s [11]. Commonly, the accepted Fenton mechanism is presented by Eqs. (15.1), (15.2), and (15.3), and its reaction rates were well reported in the literature [12].



Typically, Eq. (15.1) is considered as the core step in Fenton chemistry and implies the oxidation of ferrous to ferric ions to decompose H₂O₂ into hydroxyl radicals. Eq. (15.2) is usually called Fenton-like reaction. This step allows Fe²⁺ regeneration in an effective cyclic mechanism. Apart from ferrous ion regeneration, hydroperoxyl radicals ($\cdot O_2H$) are also produced.

15.2 Photo-Fenton Technology

15.2.1 UV Light-Assisted Fenton Process

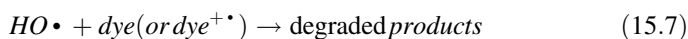
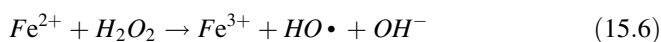
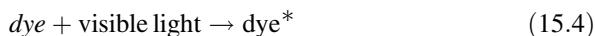
Photo-Fenton process has attracted much attention among researchers. Several studies have reported that Photo-Fenton process has good influence on degradation of organic pollutants under UV irradiation, for instance, anisole [13], phenols [14–16], Orange II [17], and xylydine [18]. Because the majority of sunlight is visible light, therefore, it must be of great importance in the environmental field to utilize visible light for the degradation of pollutants.

In 2000, Chen et al. reported the photodegradation of methyl orange in methylated solution under both UV and visible irradiations in the presence of ferric ions and H₂O₂ [19]. It was found that different radicals were generated under UV and visible

light irradiations. Besides the organic pollutants, in our daily life, coffee is necessary for many people. At the same time, coffee effluent contains a large amount of dark brown pigments. When coffee effluent is released in aquatic system, it cuts off light and affects photosynthesis due to its intense dark brown color. Furthermore, its high organic load causes eutrophication. Interestingly, Masahiro Tokumura et al. [20] investigated the influence of various operating parameters on the color removal of coffee effluents and found that the UV/Fe²⁺/H₂O₂ system is very efficient.

15.2.2 Visible Light-Assisted Fenton Process

In previous published work, it is well known that the oxidizing power of the Fenton-type systems can be enhanced by visible light. Zhao et al. [21] examined the Photo-Fenton process of malachite green (MG) under irradiation by visible light. It was found that the Fenton degradation of dyes could be accelerated greatly by visible irradiation because of strong absorbance of visible light. This possibly provides another good approach to the treatment of dyes pollutants. Furthermore, Zhao et al. [22] found the mechanism of visible light-induced Fenton reaction. The specific mechanism is shown in Eqs. (15.4), (15.5), (15.6), and (15.7). It is found that the effective electron transfer from the visible light-excited dyes to Fe³⁺ leads to regeneration of Fe²⁺ and easy cycles of Fe³⁺/Fe²⁺. This result represents that much faster degradation and mineralization of various dyes have been achieved in the Photo-Fenton reaction under visible light irradiation, comparing with that in the dark.



15.2.3 Fenton-Like Process

Apart from conventional Fenton degradation, Bokare et al. reviewed the recent experimental attempts to establish the iron-free AOPs based on Fenton reaction chemistry [23]. For example, the use of Ce⁴⁺/Ce³⁺ redox cycle has also been extended to the oxidation of organic pollutants using ceria as a heterogeneous Fenton-like catalyst. In the presence of H₂O₂, Heckert et al. [24] first confirmed the generation of HO•. In terms of its reactivity toward H₂O₂, copper shows similar redox properties like iron [25]. In this work, the performance of the solar

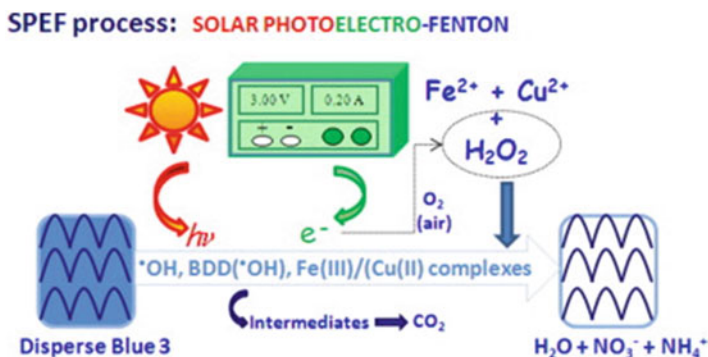


Fig. 15.1 The solar photoelectro-Fenton (SPEF) process. Reprinted with the permission from ref. [25]. Copyright 2012 American Chemical Society

photoelectro-Fenton (SPEF) process with Fe²⁺ and Cu²⁺ as metal cocatalysts and their application in the treatment of Disperse Blue 3 (DB3) dye solution simulating effluents are reported. The whole process is illustrated in Fig. 15.1.

15.3 Transition Metal Catalysts as Fenton Reagents

Among the transition metal catalysts, ruthenium (Ru) is the only member of the platinum group metals that exhibits Fenton-like activity in the presence of H₂O₂. Ruthenium complexes have been widely investigated for various organic transformation reactions like olefin hydroxylation, alcohol dehydrogenation, water oxidation, and alkene epoxidation [26]. Moreover, transition metal dichalcogenides have aroused great interest among the scientists. As to MoS₂ (molybdenum disulfide), a few studies have elucidated its properties in Fenton reaction. In 2010, single-layer MoS₂ was pointed to be as effective as graphene when used as transistor [27]. This finding provoked a stir among scientists. Dai et al. prepared MoS₂/RGO hybrid materials [28], which exhibited superior electrocatalytic activity in the hydrogen evolution reaction (HER), owing to the strong chemical and electronic coupling and the exposed edges of molybdenum disulfide. In 2014, Li et al. reported that electrochemically induced Fenton (electro-Fenton) reaction was used for efficient and controllable preparation of hydroxyl radicals, leading to the generation of luminescent quantum dots through etching of as-exfoliated MoS₂ nanosheets [29]. Apart from these applications, MoS₂ can act as a cocatalyst in the conventional heterogeneous Fenton process. In 2016, Yang et al. [30] synthesized a novel three-dimensional (3D) α -Fe₂O₃/MoS₂ hierarchical nanoheterostructure via a facile hydrothermal method. The zero-dimensional (0D) Fe₂O₃ nanoparticles guide the growth of two-dimensional (2D) MoS₂ nanosheets and formed 3D flowerlike structures, while MoS₂ facilitates the good dispersion of porous Fe₂O₃ with abundant oxygen vacancies. Figure 15.2(a) illustrated the formation process of the 3D α -Fe₂O₃/MoS₂

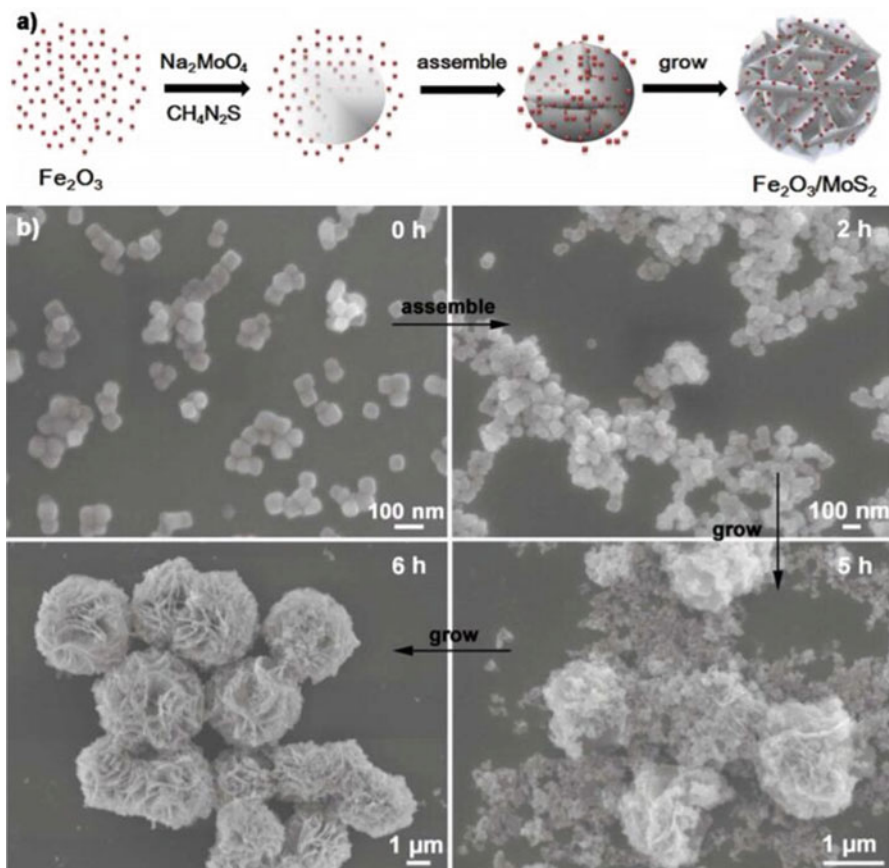


Fig. 15.2 (a) Schematic illustration of formation of the 3D α - $\text{Fe}_2\text{O}_3/\text{MoS}_2$ heterostructures; (b) morphological characterizations of the formation process of the 3D $\text{Fe}_2\text{O}_3/\text{MoS}_2$ heterostructures (3.0MF) with different reaction time [30]

heterostructures. And Fig. 15.2(b) shows the 3D flowerlike structure and the time-dependent growth morphology.

Figure 15.3(a) shows the change of the MO concentration (C/C_0) during the photodegradation process; C_0 and C are the initial concentration and the measured concentration after photodegradation for a certain time, respectively. To quantitatively estimate the reaction kinetics of the MO degradation, the degradation rate is calculated based on Fig. 15.3(a), and the constants k of Fe_2O_3 , MoS_2 , 1.4MF, 2.0MF, 3.0MF, and 4.0MF are 0.01485, 0.00262, 0.175, 0.18021, 0.2301, and 0.16411 per min, respectively [31]. It can be clearly seen that all the $\text{Fe}_2\text{O}_3/\text{MoS}_2$ heterostructures exhibit much higher photocatalytic activities than the pure Fe_2O_3 and MoS_2 . Additionally, the 3.0MF was found to exhibit the highest rate, about 87 times higher than that of MoS_2 and 15 times higher than that of Fe_2O_3 . Figure 15.3 (b) shows the normalized chemical oxygen demand (COD) removal during the

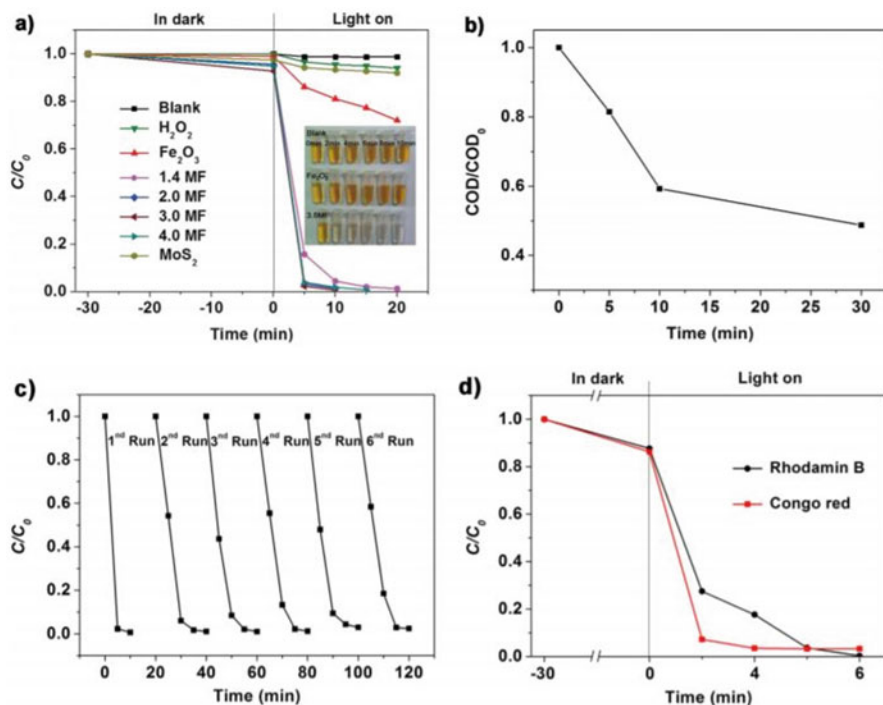


Fig. 15.3 Photocatalytic degradation of MO with different catalysts; **(b)** variations in COD during the photocatalytic (3.0MF) degradation of MO in 30 min. The inset in **(a)** is the photo of the fade of the MO; **(c)** six cycles of the photocatalytic reduction of MO using sample 3.0MF as the photocatalyst under simulated solar light irradiation for 20 min; **(d)** photocatalytic degradation of CR (50 mg L⁻¹) and RhB (20 mg L⁻¹) under simulated solar light with the presence of 3.0MF [30]

photocatalytic treatment with 10 mg of the catalysts. It is observed that more than 56% of COD in the wastewater can be reduced only after 30 min of exposure to the simulated solar light in the presence of 3.0MF. And Fig. 15.3(c) shows that after six cyclic tests, the degradation rate can still keep above 95%. Besides, the generalizability of the Fe₂O₃/MoS₂ heterostructures was also evaluated by the degradation of Congo red (CR, 50 mg L⁻¹) and Rhodamine B (RhB, 20 mg L⁻¹) (Fig. 15.3(d)). This charming 3D structure with perfect match of non-equal dimension exhibits excellent recyclable Photo-Fenton catalytic activity for methyl orange pollutant and other organic pollutants.

In this work, H₂O₂ is added to further enhance the contamination degradation. When irradiated with sunlight, Fe³⁺ would be reduced to Fe²⁺ and generate the •OH. And then, Fe²⁺ would react with the adsorbed oxygen molecules on the surface of the heterostructures to form oxidizing species (O₂•⁻). The superoxide anion radicals (O₂•⁻) generate hydroperoxy (HO₂•) radicals and subsequently produce hydroxyl radicals •OH. Meanwhile, in the presence of H₂O₂, Fe²⁺ is easily oxidized to Fe³⁺

and $\bullet\text{OH}$ is generated at the same time. So the regeneration of $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycles would make more strong oxidant $\bullet\text{OH}$ for the photocatalytic degradation.

15.4 Conclusions

In summary, we have briefly introduced the Fenton technology and specifically clarified the mechanism of Fenton process. Besides that, the application of transition metal dichalcogenides (such as MoS_2) in transistor, hydrogen evolution reaction (HER), and heterogeneous Photo-Fenton process is also introduced. As a unique representative of transition metal dichalcogenides, MoS_2 has been widely explored as a cocatalyst for photodegradation of contaminants. MoS_2 has a broad promising future in Fenton technology.

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