



Application of Co₃O₄ in Photoelectrocatalytic Treatment of Wastewater Polluted with Organic Compounds: A Review

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Abstract: The negative effects of refractory organic substances in water on the environment and life have aroused worldwide attention. The efficiency of using photoelectrocatalysis (PEC) to degrade refractory organic pollutants depends to a large extent on the properties of the photoanode semiconductor. Therefore, the selection of a satisfactory photoanode semiconductor material to promote the production of intermediate reactive species (hydroxyl radicals and superoxide radicals) has become a key issue in improving the efficiency of PEC. Among the available catalysts, transition metal oxides have received a lot of attention in recent years due to their low price and significant advantages. Due to its outstanding photoelectrocatalytic properties, Co_3O_4 has emerged as a candidate to serve as a photoelectrocatalyst specifically for the oxidation of water with oxygen in these materials. This paper summarizes in detail the recent advances in Co_3O_4 materials for PEC, both pure Co_3O_4 and Co_3O_4 -based composites. In addition, this review discusses the impact of strategies on the performance of photoelectrocatalysts, such as synthesis methods, crystal surface structures, and composites. Finally, this review concludes with a presentation of the challenges and workable solutions for Co_3O_4 -based materials in PEC, along with a discussion of their potential for future research.

Keywords: hierarchical nanostructure; Co₃O₄; wastewater treatment; photoelectrocatalysts

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1. Introduction

Wastewater is a global issue that has seriously harmed both human survival and ecology. Among various organic pollution sources in wastewater, the discharge of dyecontaining effluents into water systems is a critical issue. Organic dyes and their intermediate products may be subjected to various chemical reactions, which may cause in these products becoming carcinogenic, mutated, or abnormal, and can have adverse effects on micro-organisms, aquatic life, soil, and water [1,2]. Research by type shows that since the beginning of the 20th century, the textile and pharmaceutical industries [3], which produce a large number of pollutants in the water environment, have experienced significant growth [4,5]. It is well known that wastewater containing intractable organic dyes has a high chemical oxygen demand (COD), high color, a high amount of total dissolved solids (TDS), uneven pH, and low biodegradability [6]. Undoubtedly, a clean and secure environment without the contamination of air, water, and soil is essential for people's health and survival. Research shows that traditional water treatment technology cannot solve the problems of sludge and other secondary pollutants, resulting in the incomplete removal of pollutants and the transport of pollutants to other media [7]. In contrast, advanced oxidation processes (AOPs) are effective in degrading harmful and high-resistance pollutants by producing powerful oxidizing agents in situ, such as hydroxyl radicals (OH), which have the capability of fully mineralizing toxic organic pollutants. In AOPs, there are four known methods [8–10], including biological oxidation [11,12], chemical oxidation [13,14], photochemical oxidation [15,16], and electrochemical oxidation processes [17,18]. Nevertheless, the single technical method is not entirely effective and successful in treating dyed

wastewater due to its non-degradability and volatility. In practice, different methods are often combined to achieve the desired water quality in the most cost-effective way.

In recent years, photocatalysis (PC) has performed well in the treatment of pollution such as staining [19,20], drugs [21,22], and other endocrine disruptors [23–26]. Electrochemical (EC) catalysis is considered a highly efficient, sustainable, and low-cost technology for the degradation of wastewater [27]. AOPs are also a sub-class of photoelectrocatalysis (PEC). PEC aims to achieve a synergistic effect by combining photocatalysis with electrocatalysis. PEC has several advantages over PC and EC, including the ease of reuse of electrodes concerning catalyst power. For instance, in sewage, the rate of synthesis can be reduced and the degradation of organic compounds can be achieved by applying a bias voltage. PEC also provides an opportunity to generate reactive oxygen species at the cathode, which is beneficial for organic decomposition. To make full use of this free energy, it is possible to use the sun's rays to power the PEC, which is called Solar PEC [28]. Fujishima and Honda established the cornerstone of PEC technology by using the n-type TiO_2 and Pt electrodes in 1972 as the anode and cathode for water decomposition. This approach opened a vital door to the PEC field [29]. Then, Vinodgopal et al. first degraded organic pollutants in the PEC process using a particulate TiO₂ film electrode in 1993 [30]. This success was extended to the degradation of dyes using many various semiconductor materials in PEC processes, such as TiO₂ [31,32], WO₃ [33], ZnO, α -Fe₂O₃ [34], Sn₃O₄ [35], and Co₃O₄.

 Co_3O_4 is a typical spinel-type oxide, where Co(II) cations occupy tetrahedrally (Co(II)Td) [36,37]. On the other hand, Co(III) cations occupy octahedrally (Co(III)OH) [38,39]. This gives the oxidation–reduction pair Co(II)/Co(III). It has been reported that the bond of Co with other atoms is better suited to the process of water oxidation. This can provide a redox pair Co(II)/Co(III) that is well suited to several redox reactions and electron transfers. It has been reported that the binding force between Co atoms and other atoms is more suitable. Because of its superior catalytic activity, low cost (in comparison with Au, Ag, Pt), and high permanence, O₂ has little capability to prevent "toxicity" (readily adsorbed into an intermediate, hard to desorb), which influences the catalysis [40,41]. One-dimensional (1D) Co_3O_4 is currently attracting a great deal of attention because of its high conductivity, large surface area, wide optical response range, chemical stability [42,43], and its expected synergistic effect with PC and EC [44,45]. Spinel Co_3O_4 may be a promising candidate to replace precious metals as anode materials. Similarly, in recent years, more articles have been published on Co_3O_4 than any other spinel oxide. Among them, Fe_3O_4 , NiO, and CuO are less active and have smaller electrochemical active surface areas (ECSA) than Co₃O₄. To enhance the PEC performance of the Co₃O₄ photoanode, different strategies have been utilized, such as facet engineering [46,47], heteroatom doping, heterojunction construction, and the deposition of particles of noble metals [48]. They identified a number of active sites that benefit OER in catalysis [49,50]. For instance, Yang and his colleagues prepared hollow Co₃O₄ dodecahedrons, which were designed by the calcination of a ZIF-67 precursor under various conditions of argon and oxygen. It had a high percentage showing good photoelectrocatalytic properties for oxygen evolution reaction (OER) [51]. Yan and colleagues synthesized highly conductive, Ag-doped Co₃O₄ nanowires via electrodeposition. Ag-Co/FTO is a kind of OER material with good catalytic performance [52]. Recently, Li and colleagues reviewed the latest advances in cobalt-based materials as bi-functional photoelectrocatalysts for oxygen reduction reaction (ORR) [53]. There are a few types of research on the degradation of pollutants using different anode materials.

This paper presents a summary of the methods and ideas for the design and synthesis of materials and provides a perspective on methods to improve the performance of cobalt-based materials. These studies are more conducive to the development of photoelectrocatalytic hydrolysis.

2. Co₃O₄: Synthesis Routes

The physical and chemical properties of a substance are a reflection of its properties, and we usually learn about the properties of a substance through observation, experimentation, and analysis. However, we can also learn about a substance in terms of its physical, chemical, and biological properties and its patterns of change. We have investigated the properties of Co_3O_4 (Table 1) to gain a fuller understanding of its properties and to select a suitable synthesis method. Up to now, several physics and chemistry methods have been used to synthesize Co_3O_4 . Table 2 summarizes the synthesis pathway and the advantages and disadvantages of Co_3O_4 .

| | Single isotope mass | 240.779258 Da |
|----------------------------------|---------------------------|---|
| Molecular structure | Nominal mass | 241 Da |
| | Average mass | 240.7972 Da |
| | Molecular weight | 240.7972 |
| | Melting point | 895 °C (dec.) (lit.) |
| | Boiling point | 3800 °C |
| | Density | 6.11 g/mL at 25 °C (lit.) |
| Physical and chemical properties | Laser particle size | 5–10 um |
| | Tension | 0 Pa at 20 °C |
| | Colour | Dark Gray |
| | Proportion | 6.11 |
| | Water solubility | Soluble in acids and alkalis. Insoluble in water. |
| | Exposure Limits | ACGIH: TWA 0.02 mg/m ³ |
| | Merck | 142,429 |
| | InChIKey | LBFUKZWYPLNNJC-UHFFFAOYSA-N |
| Information search | CAS database | 1308-06-1 (CAS DataBase Reference) |
| | NIST Chemical Information | Cobalt oxide (1308-06-1) |
| | EPA Chemical Information | Cobalt tetraoxide (1308-06-1) |

Table 1. Characteristics of Co₃O₄.

Table 2. Various synthesis methods and advantages and disadvantages of Co₃O₄.

| Entry | Name of the Synthetic Process | Advantages | Disadvantages | Reference |
|-------|-------------------------------|---|--|-----------|
| 1 | Hydrothermal reaction | The crystalline powder can be obtained directly without high-temperature sintering, the crystallinity is high, and it is easy to control the particle size of the produced crystal | Strong dependence on production equipment | [23] |
| 2 | Thermal decomposition | Thermal instability; pyrolysis products are different | The combustible gas is large and the residual carbon slag is small | [24] |
| 3 | Solution combustion | The process is simple, the operation is convenient, the purification efficiency is high, and the heat energy can be recovered | When the combustible component content is low, preheating energy consumption is required | [25] |
| 4 | Vapor deposition method | The film-forming device is simple and raw materials are easy to obtain | High reaction temperature | [54] |
| 5 | Co-precipitation | The process is simple, the cost is low, the preparation conditions are easy to control, and the synthesis cycle is short | The precipitate produces agglomeration or uneven composition | [27] |
| 6 | Sol-gel | Easy doping, uniform composition, low reaction temperature required | Film density is poor; volume shrinkage | [31] |
| 7 | Template method | Easy synthesis and size control, especially for nanomaterials | The pH and ionic strength of the solution are required to be higher | [32] |
| 8 | Chemical reduction method | Simple reagents and equipment; low cost | The reaction process is not easy to control; impurities easily appear | [55] |
| 9 | Wet synthesis | Simple operation; can be a large number of syntheses | There are hidden dangers in emissions and cooling methods | [56] |
| 10 | Ionic-liquid-assisted method | Low melting point, good thermal stability | The process is complex, the cost is high. and the conductivity is low | [57] |

2.1. Hydrothermal

Among the known methods for the synthesis of Co_3O_4 , the hydrothermal process seems to be the most prominent because it produces a highly crystalline Co_3O_4 . Furthermore, it is possible to control the shape of Co_3O_4 by simple optimization of the reaction pressure, temperature, time, and pH of the solution.

Controlled continuous hydrothermal synthesis is one method of obtaining Co_3O_4 nanoparticles. Stripper water containing 0.25% v/v H₂O₂ is fed into the reactor by a high-pressure pump through a preheating device. Experiments at the University of Nottingham have shown that diluted aqueous hydrogen peroxide solutions decompose into a mixture of oxygen and water [58,59]. Cobalt acetate tetrahydrate (II) is added to the reactor at room temperature. In a nozzle reactor, oxygen-enriched water is preheated through an inner tube, and an aqueous solution of cobalt acetate tetrahydrate (II) flows upward [60]. The Nottingham team has previously reported in detail on the design of the nozzle reactor and the mixing of fluids therein. At the outlet of the reactor, the mixture is pumped into the cooling device. A dry powder of Co_3O_4 nanoparticles was obtained by freeze-drying with liquid nitrogen and under low-temperature vacuum (-50 °C) for more than 36 h.

However, this method requires a longer reaction time and is not sufficiently costeffective. Zhao et al. proposed a more energy-efficient solution with lower consumption. Initially, 5 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 10.0 mmol of urea, and 5.0 mmol of NH_4F were dissolved thoroughly into 40 mL of high-purity water at room temperature to form a homogeneous pink solution. The solution was transferred to a 60 mL, Teflon-lined stainlesssteel autoclave, a Ti substrate was inserted as prepared, and the solution was held at 120 °C for 6 h. Subsequently, the Ti substrate having a pink precursor was naturally cooled to ambient temperature and cleaned with deionized water and vacuum dried, followed by annealing at 450 °C for 2 h at 2 °C/min to obtain a Co_3O_4 nanowire array on the Ti substrate. Nanorods of Co_3O_4 were obtained using this method [61] (see Figure 1).



Figure 1. Schematic diagram of the hydrothermal synthesis of Co₃O₄ nanorods.

2.2. Sol-Gel

Among the various conditions affecting material properties, the effect of temperature on the material structure is not negligible. Annealing temperature affects the structure, morphology, conductivity, and band gap of nanocrystalline Co_3O_4 films obtained via sol–gel spin-coating. Cobalt acetate tetrahydrate is added into 40 mL methanol and stirred vigorously for 1 h at 60 °C, resulting in a pale pink powder. The as-prepared powder is sintered at various temperatures ranging from 400 to 700 °C with a fixed annealing time of 1 h in ambient air to obtain Co_3O_4 with different crystallite sizes. Table 3 of the revised article illustrates the effect of calcination temperature on the size of the Co_3O_4 crystals. The nanocrystal Co_3O_4 powder is further dissolved in m-cresol, and the solution continues to be stirred at room temperature for 11 h, then filtered. The filtered solution is deposited on a glass substrate by a single-wafer spin processor [62].

| Sr. No. | Annealing Temperature °C | Crystallite Size nm (from XRD) | Thickness μm | Energy Gap E _g , eV | Activation $E_{a\sigma}$, eV | Energy, HT LT | Carrier Concentration, cm ⁻³ | Mobility cm ² , V ⁻¹ ·s ⁻¹ |
|---------|--------------------------------|--------------------------------------|-----------------|-----------------------------------|-------------------------------|------------------|---|--|
| 1 | 400 | 53.40 | 0.7748 | 2.58 | 0.21 | 0.060 | $2.40	imes10^{19}$ | $5.20 	imes 10^{-5}$ |
| 2 | 500 | 58.25 | 0.6887 | 2.34 | 0.36 | 0.062 | $2.75	imes10^{19}$ | $5.78 	imes 10^{-5}$ |
| 3 | 600 | 64.70 | 0.6425 | 2.21 | 0.48 | 0.064 | $3.27	imes10^{19}$ | $6.45	imes10^{-5}$ |
| 4 | 700 | 68.54 | 0.5998 | 2.07 | 0.54 | 0.064 | $4.50	imes10^{19}$ | $7.00 	imes 10^{-5}$ |

Table 3. Effect of annealing on Co₃O₄ thin film properties.

2.3. Vapor Deposition Method

Davide Barreca et al. deposited the film in a low-pressure chemical vapor deposition (CVD) reactor with a heated susceptor. O_2 is used as a carrier and a reactive gas in the process of synthesizing the oxide and removing the organic ligands as oxidation byproducts. The precursor is placed in a vaporizer attached to the tube of the reactor and kept at 90 °C for the entire duration of the film deposition. The gas pipe and the valve between the bubble and the reaction tube are heated to prevent the precursor from condensing. The pressure is measured with a capacitive pressure gauge, and a mass flow controller is used to control the gas flow. Before CVD, the substrates were desorbed in soapy water, washed with water and isopropanol, and then air-dried. In order to minimize carbon contamination, their surfaces were heated by O_2 flow in the reaction chamber for 40 min [33]. Chen et al. show the schematic of the direct liquid injection chemical vapor deposition (DLI-CVD) apparatus. A novel spray atomizing and co-precipitating precursor delivery system was developed; this consisted of a liquid precursor tank, the extraction switch, an atomizer, an evaporator, and some necessary stainless-steel connection tubes. Solid Co(dpm)₃ (DPM; dipivaloylmethanate; Wuhan CVD Science & Technology Co., Ltd., Wuhan, China) was used as the precursor into tetrahydrofuran [63] (see Figure 2).



Figure 2. Schematic of the DLI-CVD.

At present, the green synthesis of metal-oxide NPs is one of the most promising fields in green chemistry and nanotechnology. The method of preparing Co_3O_4 nanoparticles from latex at room temperature was studied. In addition, it is unnecessary to apply large quantities of heat, power [64], pressure, or poisonous substances [65,66]. Because of its environmental friendliness, simplicity, rapidity, toxicity, and economy, green synthesis offers a one-step method to synthesize Co_3O_4 NPs [67,68]. The Co_3O_4 NPs are stabilized by combining them with the biological material of amino acids, saponins, enzymes, proteins, steroids, phenol, tannin, vitamins, sugars, flavone, etc. [69,70] (see Figure 3).



Figure 3. A novel green synthesis of cobalt oxide (Co₃O₄) nanoparticles.

3. Crystal Structure Analysis of Co₃O₄ Samples

 Co_3O_4 crystallizes in a cubic regular spinel structure, which consists of Co ions in Co^{2+} , Co³⁺, and Co³⁺, respectively [71]. These are situated in the interstices in the tetrahedral (8a) and the octahedral (16d) positions of the closely packed, face-centered cubic (FCC) lattice formed by oxygen ions (Figure 4). In general, cobalt oxide consists of a spinel structure with an indirect band gap of ~1.5 eV and a direct band gap of 2.2 eV. The common spinel structure is expressed by the formula (A) $[B_2] C_4$, wherein A and B are cations in tetrahedral and octahedral coordination, while C represents anions. The spinal structure is significantly stable when A is divalent and B is trivalent, for instance, $(A^{2+})[B^{3+}]C_4$. Similarly, cobalt oxide (Co_3O_4) is known to follow a spinel structure, such as $(Co^{2+})[Co_2^{3+}]O_4$ [72,73]. The high-spin Co^{2+} occupies the interstitial sites of the tetrahedral (8a) interstices, while the low-spin Co³⁺ is known to occupy the octahedral (16d) interstices of the closely packed, facecentered, cubic lattice of $CoO \cdot Co_2O_3$, as illustrated in Figure 4. It is known that the p-type conductivity of the material $(CoO \cdot Co_2O_3)$ is derived from a gap in the crystal lattice and an excess of oxygen at the interstitial site. However, the concentration of charge carriers is different from the operating temperature or the doping condition. A. Diallo et al. discussed that Co_3O_4 is generally active in the following order: $\{112\} > \{110\} > \{111\} > \{100\}$ [74]. The understanding of Co_3O_4 's crystal structure is further deepened [75,76].

Zhou et al. studied the structure and the action mechanism of Co_3O_4 from the crystal structure and the atomic structure of the crystal surface. Figure 5a is a cell type (cell) structure with a pointed crystal. In Figure 5b–d, the topmost surface atoms and the first atoms, as well as the topmost suspended bonds, are exposed to the environment, and they can react oxidatively in water. Therefore, the main influential factor for the water-oxidizing activity of various well-defined Co_3O_4 crystals lies in the composition of the surface atoms and their respective catalytic active sites [77].



Figure 4. Crystal structure of Co_3O_4 . Unit cell (**left**) and primitive cell (**right**) of Co_3O_4 . Light cyan and navy blue balls indicate Co^{2+} and Co^{3+} ions; red balls indicate O^{2-} ions.



Figure 5. (a) The unit cell structure of spinel Co_3O_4 , green ball is Co^{2+} , blue ball denotes Co^{3+} , and red ball is O^{2-} . The crystal structure model and arrangement of surface atoms of Co_3O_4 with different exposed facets for (b) {100}, (c) {110}, and (d) {112}. The Co_3O_4 structure model is obtained from inorganic crystal structure database (ICSD) with the corresponding JCPDS file.

4. Co₃O₄: Composites

Despite its unique properties, Co_3O_4 encounters a huge obstacle: the narrow band gap of photoelectrons can recombine easily with holes, resulting in a small quantum efficiency. Particle size and shape effects control the oxidation behavior of the nanostructured photoelectrocatalysis treatment of organic wastewater. The size of the nanoparticles can be altered by changing the cobalt concentration and reaction time. Spherical, cubic, octahedral, and platelike nanoparticles with narrow size distributions and size ranges were formed in high yields via thermal decomposition. These surfactant-free nanoparticles (around 10 nm) form an ideal substrate for the easy deposition of further elements, which in turn increases the efficiency of photoelectrocatalytic degradation (Figure 6). It has been suggested that the formation of composite materials, in which some are heterostructures, may be one of the approaches to improve the photoelectrocatalytic performance of Co_3O_4 (Table 4). The hybridization of Co₃O₄ with metals, non-metals, metal oxides, carbon-based materials, and plasmonic nano-metals such as gold and silver to form heterostructured composites has been extensively explored. The formation of heterogeneous composites by Co₃O₄ hybridization has been extensively studied [78,79]. Doping noble metals into simple metal oxides was shown to improve the photocatalytic activity by Chen et al. Among the noble metals, elemental Ag is widely used due to its lower cost. Its role in improving the catalytic activity mainly involves two aspects. First, Ag doping can separate the photogenerated carriers efficiently because of the formation of a Schottky barrier. Second, it can improve the response to visible light. A new electrochemically modified BiVO₄-MoS₂-Co₃O₄ thin film electrode for environmental applications has been successfully synthesized by Cong et al. [80]. The formation of composites has the potential to promote carrier migration, which leads to the formation of the internal electric field, thus improving carrier separation and finally improving the performance of Co_3O_4 as a photocatalyst. Yang et al. successfully used a simple method to blend Co_3O_4 and CoO on TiO_2 NAs. A series of characterization methods was used to investigate the morphology, structure, and PEC water oxidation properties [81]. It was found that the photocurrent density of the obtained $CoO-Co_3O_4/TiO_2$ photoelectrode was improved and could be maintained with good stability for more than 13 h. The improvement in the properties of CoO-Co₃O₄/TiO₂ is due to the increase in light absorption and reduction in charge transfer resistance, thus improving charge separation.



Figure 6. Shape-selective synthesis of Co₃O₄ nanoparticles.

| Modification Approach | Materials | Reference |
|--|--|-----------|
| Composite | | |
| ·Metal/Co ₃ O ₄ | Cu/Co ₃ O ₄ | [82] |
| ·Metal oxide/Co ₃ O ₄ | ZnO/Co_3O_4 | [83] |
| | Co_3O_4/In_2O_3 | [84] |
| | NiMoO ₄ @Co ₃ O ₄ | [85] |
| | Co_3O_4/TiO_2 | [86] |
| ·Non-metal/Co ₃ O ₄ | Co ₃ O ₄ @C | [87] |
| ·Plasmonic nano-metal/Co ₃ O ₄ | Co ₃ O ₄ -Ag | [88] |

The photo-generated electrons of Co_3O_4 can be channeled into the dopant, thereby reducing the recombination rate [42]. This leads to the production of more oxidizing substances (h⁺ and OH⁻) that break down harmful organic substances. Although the process has some advantages, new electrons may be brought in by dopants, which may have adverse effects. On the other hand, the formation of heterojunction composite materials provides a more effective method for the separation of photogenerated carriers. This technology can increase the photocatalyst's ability to capture light, enhance its charge separation ability, improve its charge utilization ratio, and prolong its service life.

5. Photoelectrocatalytic Application of Co₃O₄ Composites in Water Treatment

To date, Co_3O_4 and its composite materials are mainly used in capacitors and fuel cells. However, there are few studies on its application in dyes and photoelectrocatalysis. Applications in wastewater degradation are described in the following sections.

In the PC process, there is a problem with catalyst recycling. Nevertheless, in the photoelectrocatalysis process, the catalytic material is fixed on the surface of the carrier and used as an electrode, which is beneficial to the recycling of the material. In preparing the anodes, it is necessary to have a conductive substrate on which Co_3O_4 is deposited. Titanium plates, anodized TiO₂, and fluoro-doped substrates have been used. Wang and co-workers doped F^- into Co_3O_4 as the conducting substrate. A titanium plate was formed by etching, and cobalt nitrate was made from cobalt. Co₃O₄ nanowires have been prepared using the hydrothermal method and the calcining method on the titanium substrate. The best degradation conditions were obtained by varying the water temperature and electric current during the decomposition [89]. Co_3O_4 is unsuitable as the photoanode material to degrade organic pollutants because conventional Co_3O_4 is a p-type semiconductor. It is well-known that the introduction of F^- can not only promote the morphology of the oxides but can also convert the intrinsic semiconductor to the n-type (e.g., SnO_2) [90–92]. Moreover, the presence of F^- in the crystal plays a key role in reducing the enucleation rate and activating the substrate, which leads to strong mechanical adhesion between the nano-architecture and the substrate. Based on the above results, the possible PEC processes were described as follows (see Figure 7): Firstly, the electrons (e⁻) in the valence band of Co_3O_4 under light irradiation could be excited to the conduction band, leaving the holes (h^+) in the valence band of Co_3O_4 . When applying an anodic bias potential to the semiconductor (i.e., the applied potential is greater than the flat band potential), there will be an increase in band bending. Thus, electrons in the conduction band are flown through the counter electrode via the external circuit, and the holes are transferred to the surface. Thus, the bands are bent downwards, producing an ohmic contact. The band-bending causes no impediment to the motion of the induced electrons from the conduction band of Co_3O_4 into the metal Ti. Then, the electrons are moved to the external circuit faster via an electric field, and the induced charge carriers were effectively separated.

As outlined in the introduction, many different semiconductor materials are used in the PEC process to degrade dyes, such as titanium dioxide, tungsten trioxide, zinc oxide, Sn_3O_4 , and Co_3O_4 . We have compared the photoelectric catalysis degradation capabilities of commonly used compounds. It was found that Co_3O_4 is a suitable material for photoelectric catalysis (Table 5). Coupling two or more different types of semiconductor materials into a single photoanode can improve the photo-carrier transmission efficiency and photo-conversion efficiency. Wang et al. reported one of the first studies on the application of Co_3O_4 in the formation of heterojunction for water treatment. In this paper, a new heterostructure of the PbO₂-tipped Co_3O_4 nanowire array (NW) was prepared by the methods of hydrothermal synthesis and electrochemical deposition. The results show that the as-built PbO₂/ Co_3O_4 composite exhibits a large electro-active area, a low charge-transfer resistance, and a high efficiency in the production of hydroxyl radicals. The photoelectrochemical (PEC) performance of the as-constructed PbO₂/ Co_3O_4 composite has been assessed by the decoloration of dye (Reactive Brilliant Blue KN–R). The PEC test showed that the PbO₂/ Co_3O_4 composite prepared by this process had good repeatability and photoelectric properties. The enhancement of the PEC capability of composites may be attributed to the formation of heterostructures. This work provides a good prospect for using Co₃O₄ NWs doped with lead dioxide as photoanodes for treating refractory organic pollutants. This further reinforces the argument that the PEC is a more effective approach than EC and PC due to the synergy occurring in the PEC [89]. Co₃O₄ heterojunctions have been explored in the remediation of water contaminated with organic pollutants using photoelectric synergy, as outlined in Table 6.



 $E > E_{fb}$

Figure 7. Charge transfer mechanism in the Ti/Co_3O_4 electrode under PEC process.

| Table 5 | 5. S | tudies | on p | hotoe | lectroca | italy | rtic c | legrad | lation | of | toxic | organi | cs |
|---------|------|--------|------|-------|----------|-------|--------|--------|--------|----|-------|--------|----|
|---------|------|--------|------|-------|----------|-------|--------|--------|--------|----|-------|--------|----|

| Materials | Method of Preparation | Analyte | % Removal | Ref. |
|-------------------|----------------------------|---|----------------------|------|
| TiO ₂ | Anodization | Acetaminophen (40 mg/L) | 33.0% after 180 min | [93] |
| ZnO | Spray pyrolytic deposition | Rodamine B dye | 93.0% after 180 min | [94] |
| BiVO ₄ | Electrodeposition | Bisphenol A (BPA) 10 mg/L | 24.2% after 120 min | [95] |
| WO ₃ | Anodization | Methyl orange (MO) 50 µM 12 cm ³ | 70–80% after 180 min | [96] |
| Sn_3O_4 | Hydrothermal | Polyacrylamide (PAM) 20 mg/L | 70% after 180 min | [97] |
| Co_3O_4 | Hydrothermal | Methylene blue (MB) 60 mg/L, 200 mL | 84.0% after 120 min | [89] |

| Table 6. Recent studies or | photoelectrocatal | ytic degradation of | f toxic organics | s involving | Co_3O_4 . |
|----------------------------|-------------------|---------------------|------------------|-------------|-------------|
|----------------------------|-------------------|---------------------|------------------|-------------|-------------|

| Materials | Method of Preparation | Analyte | % Removal | Ref. |
|--|--|------------------------------|----------------------|-------|
| ZnO/Co ₃ O ₄ | Liquid deposition method and calcination treatment | Methylene blue (MB) | 92.5% after 140 min | [53] |
| $Co_3O_4 - Sn_3O_4$ | Hydrothermal | Reactive brilliant blue KN-R | 87.5% in 2 h | [98] |
| Co_3O_4/TiO_2 | Impregnating-deposition-decompositon | Methyl orange (MO) | 90.0% after 90 min | [56] |
| NiMoO ₄ @Co ₃ O ₄ | Two-step hydrothermal | Brilliant blue KN-R | 83.65% in 120 min | [55] |
| PbO ₂ tipped Co ₃ O ₄ | Hydrothermal | Brilliant blue KN-R | 80.0% in 120 min | [66] |
| Co_3O_4/In_2O_3 | Microwave-hydrothermal | Remove Cr(VI) ions | 100% after 120 min | [54] |
| NiFe-LDH/Co ₃ O ₄ | Hydrothermal | Remove Cr(VI) ions | 100% after 120 min | [99] |
| Bi2MoO6@Co3O4 | Hydrothermal | Bright blue KN-R | 88.43% after 110 min | [43] |
| Co ₃ O ₄ @MnO ₂ | Two-step hydrothermal | Bright blue KN-R | 94.8% after 120 min | [38] |
| Co_3O_4/TiO_2-NTs | Anodization and electrodeposition | Methyl orange | 90.7% after 60 min | [100] |

6. Conclusions and Future Perspectives

In recent years, Co_3O_4 has been used in photoelectrocatalysis for wastewater treatment. This material has good light-capturing performance in the visible light regions, so it has good application prospects. The shape and the crystal structure of Co_3O_4 have been reported to affect the photoelectrocatalytic properties of Co_3O_4 , especially the crystal shape, which can change in the course of the application. Accordingly, it is possible to examine the crystalline form or structure of Co_3O_4 before and following a degradation cycle.

In the field of photoelectrocatalysis, further work should focus on the degradation of various types of pollutants. In this paper, the application of Co_3O_4 in PEC for the treatment of organic pollutants in water was shown to be in its initial stages. Indeed, a section of this paper highlights reports that can be compared to other types of semiconductors found in PEC applications. Therefore, it is expected that Co_3O_4 will be widely used as a photoelectrocatalyst. In addition, it would be worthwhile to find basic research on how some pollutants are degraded and how they are treated. Through the discussion of the above problems, we can better reveal its favorable structural form.

Although Co_3O_4 -based catalysts, as frequently used photoelectrocatalysts, have made significant progress in degradation through various effective strategies in recent years, there are still some problems and challenges that cannot be ignored in its application:

(1) Morphology engineering can effectively improve the surface area. Increased porosity is beneficial to the photoelectrocatalytic performance, and an ordered nano-structure is beneficial to catalysis. Therefore, Co_3O_4 -based catalysts with an array structure will be widely studied in the degradation field.

(2) The material lends itself to various synthesis methods, and thus one can expect more novel synthesis routes shortly.

(3) The Co_3O_4 composite exhibits high activity, but its catalytic performance is improved, and its preparation process is also complicated, which is not conducive to industrial applications. Therefore, the preparation technology suitable for practical applications still needs to be studied.

(4) Stability is an important part of the catalyst performance, and corrosion-resistant supports such as Cu, Pt and Ti should be considered as substrates, and cost should also be considered. At the same time, in situ growth technology with binding characteristics can avoid catalyst shedding, so in situ growth will be widely used by researchers in the process of catalyst preparation.

(5) The p–n variability can be exploited in preparing a myriad of heterojunctions with other semiconductors.

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