Microwave Hydrothermal Synthesis of In$_2$O$_3$-ZnO Nanocomposites and Their Enhanced Photoelectrochemical Properties

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Indium oxide (In$_2$O$_3$) doped zinc oxide (ZnO) nanocomposites were successfully synthesized through a facile microwave hydrothermal method. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), N$_2$ adsorption–desorption isotherms (BET) and UV-Vis diffuse reflectance spectroscopy. The morphology of In$_2$O$_3$-ZnO composites was observed to be like flowers, and the diameter of particles constituting the porous petal was about 30 nm. The photoelectrocatalytic test showed that the photoelectrocatalytic methylene blue (MB) degradation efficiency using In$_2$O$_3$-ZnO nanocomposites as photocatalysts under visible light irradiation and a certain voltage could reach above 95.3% after 60 min, much higher than that of In$_2$O$_3$ particles and ZnO particles. The enhanced photoelectrocatalytic activity was attributed to the doping of In$_2$O$_3$ and applied voltage, which beneficially reduced the recombination of electrons and holes in the photoelectrocatalytic process, therefore, it promoted the production of active species ($\bullet$OH and $\bullet$O$_2$.)

In recent years, water pollution problems are becoming more and more serious due to the fast development of technology and world economy.1–4 Among various sources of pollution, dyes have a wide range of applications and are difficult to decompose, causing the most serious water pollution. Many methods of sewage treatment, such as biodegradation, adsorption, and catalysis, have been used in the treatment of printing and dyeing wastewater.5–13 Among them, photocatalysis and photoelectrocatalysis are regarded as the most effective and low-cost ways to solve the water pollution problems.14

Semiconductor-based photocatalysts have received enormous attention, such as TiO$_2$, ZnO, CuO, CeO$_2$, In$_2$O$_3$ etc.15–23 Among many kinds of oxide semiconductor materials, ZnO seems to be the most promising for use in environmental issues on account of its distinguished photoelectrochemical properties, low cost, high bio-safety, nontoxicity and long-term photostability. In recent years, ZnO has received extensive attention as photoelectrocatalyst and photocatalyst.24 For example, Lai et al. synthesized flower-like nano-ZnO photocatalysts with an excellent photocatalytic activity by a facile hydrothermal process.25 Xue et al. prepared ZnO nanoparticles-reduced graphene oxide (rGO) materials by a novel one-step photochemical method and the ZnO/rGO nanocomposite effectively degraded MB dye solution under the UV-light.26 Unfortunately, the bandgap of monocomponent ZnO photocatalyst is about 3.2 eV, therefore it can only be activated by ultraviolet (UV) light. However, the content of ultraviolet light is no more than 5% in the total solar spectrum on the earth, which restricts its utilization rate of light energy, especially in the practical applications in the field of photocatalysis.25 Another disadvantage of pure ZnO photocatalyst is the rapid recombination of photogenerated electrons ($e^-$) and holes ($h^+$), which results in the insufficient yield of reactive radicals in the photocatalytic reaction.26 The above two characteristics of ZnO make it difficult to be widely used in industry.

Semiconductor composites have attracted much attention due to their unique properties and simple fabrication.27 Heterostructures and heterojunctions are formed by compounding two or more different semiconductors together, which can effectively inhibit the recombination of electron-hole pairs.28 More and more composite materials with heterostructures and heterojunctions are used in photocatalytic fields, such as ZnO/CdS, MnS/TiO$_2$, and Co$_3$O$_4$/BiVO$_4$.29–31 In addition, the combination of ZnO with other transition metals can also enhance the absorption of ZnO in the visible light region and improves the utilization rate of light energy to meet the requirements of practical applications. Several composite materials about ZnO have been reported, e.g., ZnO/SnO$_2$, Er/ZnO, Mn/ZnO, CdS/ZnO, etc., and proved that their photocatalytic performances are better than that of ZnO under the same experimental conditions.32–34 For example, Yu et al. synthesized ZnO and Er-doped ZnO composites using a chemical precipitation method and the ability of Er-doped zinc oxide nanoparticles to degrade methylene blue (MB) was significantly higher than that of pure ZnO.35 Parihasheemi et al. prepared ZnO/CoMoO$_3$ nanocomposites through refluxing method and the nanocomposites successfully photodegrade many dyes including RhB, MB and MO.36 In$_2$O$_3$ is an indirect band semiconductor with a bandgap of 2.56 eV, and has been proved as highly effective sensitizer to extend the absorption spectra of the transition metal oxide photocatalysts from ultraviolet to the visible region.37–39 In addition, the p-n junctions could also be formed at the interface of ZnO phase and In$_2$O$_3$ phase in the In$_2$O$_3$-ZnO composites, which are beneficial to the separation of electrons and holes.28 Consequently, the fabrication of In$_2$O$_3$-ZnO composites has attracted extensive attention. Many In$_2$O$_3$-ZnO composites have already been synthesized and applied for gas sensors, conductive films, hydrogen production and light-emitting diodes through several
methods. For example, Espid et al. fabricated ZnO-In₂O₃ composites via facile co-precipitation method and applied it to the field of gas sensor. Minami et al. synthesized high transparent and conductive In₂O₃-ZnO system thin films via the rf magnetron sputtering method.

Photoelectrocatalysis has gradually become a hot spot for people to study. Compared with traditional photocatalysis, photoelectrocatalysis has many advantages, such as high efficiency, environmental protection, economy, and most importantly, convenient recovery of active substances. However, the preparation of In₂O₃-ZnO composites with excellent photoelectrocatalytic performance by microwave hydrothermal method has rarely been reported. In this work, ZnO nanoparticles, In₂O₃ particles and In₂O₃-ZnO composites were successfully synthesized by a microwave hydrothermal method. The photoelectrocatalytic performance of the samples was examined by MB degradation in aqueous solution under the visible light irradiation and a suitable bias voltage (0.2 V). Compared with ZnO, In₂O₃-ZnO composites exhibited a higher photoelectrocatalytic performance. At the same time, we also discussed the mechanism of photoelectrocatalysis and the influence of In₂O₃ dopant.

### Experimental

**Materials.**—Zn(CH₃COO)_2·2H₂O and CO(NH₂)_2 were obtained from Tianjin Bodi Reagent Co. Ltd. (AR, Tianjin, China). In(NO₃)₃·4.5H₂O and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co. Ltd. (AR, Shanghai, China). All the chemical reagents were analytical grade and there was no further refinement.

**Fabrication of In₂O₃-ZnO composites.**—The experiment adopted the microwave-hydrothermal method to synthesize the In₂O₃-ZnO composites. First of all, Zn(CH₃COO)_2·2H₂O (1.098 g) and CO(NH₂)_2 (0.095 g) were dissolved in the 50 mL ionized water and stirred them for 30 minutes in an ice water bath. Then 2 g CO(NH₂)_2 was added into the mixed solution and kept stirring. After 30 min, the above mixed solution was diverted into the microwave hydrothermal parallel synthesizer (Beijing XiangHu Science and Technology Development Co., Ltd, XH-800S, China). The power of the microwave hydrothermal parallel synthesizer was set to 800 W and the temperature of the mixed solution would rise from room temperature to 120 °C in 15 min. Then it was maintained for 30 min at 120 °C. When the solution in the microwave reactor was cooled naturally at 120 °C down to room temperature, the precipitates were washed three times by deionized water and absolute ethanol, respectively. Finally, the dried samples were calcined at 550 °C with a ramp rate of 1.5 °C per minute and maintained at 550 °C for 2 h. In addition, for comparison, pure ZnO, In₂O₃ and other proportions of In₂O₃-ZnO composites were produced via the same method. The proportion and abbreviations of various materials are summed up in Table I.

### Characterizations.

The information of microstructure and elementary mapping of the products were tested by scanning electron microscope (SEM, S-4800, Hitachi, Japan). Transmission electron microscopy was measured using a JEOL JEM-2100F system (TEM, JEM-2100F, Japan) at an accelerating voltage of 200 kV. The crystalline phases (20–80°) of the samples were determined by X-ray diffraction (XRD, ultima IV, Rigaku, Japan) with Cu Kα radiation (λ = 0.1540 nm) at a scanning rate of 8°/min. Element information of the products was examined by an X-ray photoelectron spectrometer (XPS, Thermo Scientific, USA) with Al Kα radiation (1486.6 eV, 12 kV, and 3 mA). The bandgap energy information of the products was determined from the UV-Vis absorption spectrum on a UV-Visible diffuse reflectance spectrophotometer (UV-Vis DRS, UH4150, Hitachi, Japan). The specific surface area and pore volume information were calculated by the Brunauer–Emmett–Teller (BET, TriStar II 3020, USA) method. The transient photocurrent, current density versus potential (I–V) curves and electrochemical impedances spectroscopy (EIS) were analyzed using an electrochemical workstation (Autolab, Metrohm Co. Ltd.).

**Photoelectrocatalytic performance test.**—In order to detect the photoelectrocatalytic activity of the sample, the sample was loaded onto the foamed nickel electrode. The photoelectrocatalytic performance of samples was estimated by photoelectrocatalytic degradation of MB aqueous solution under continuous visible light irradiation. The as-prepared In₂O₃-ZnO photoelectrode was placed in MB aqueous solution (50 mL, 20 mg L⁻¹) and stirred for 1 h in the darkness to achieve the adsorption-desorption dynamic balance between MB and the photoelectrode. Then, assisted by the three-electrode system consisting of working electrode (as-prepared photoelectrode), reference electrode (saturated calomel electrode), and opposite electrode (platinum electrode), the photoelectrocatalysis experiments were conducted under a certain voltage (electrochemical workstation, 0.1~0.4 V) and visible light irradiation with a wavelength of 320~1100 nm (14 V, 15 A, Xe lamp). Finally, after every 10 min, the MB aqueous solution absorbance was measured by a UV-9000 UV-Vis spectrophotometer (maximum absorption wavelength is 664 nm).

### Results and Discussion

**Characterization of the products.**—Fig. 1 shows the SEM images of the obtained ZnO nanoparticles and In₂O₃-ZnO composites. The morphologies of ZnO nanoparticles are shown in Figs. 1a, 1b and 1c. The ZnO nanoparticles display rod shape with 200–300 nm long and 75 nm wide. Figs. 1d, 1e and 1f shows the morphology of 3% In₂O₃-ZnO as shown in Figs. 1j, 1k and 1l. Their morphologies are flaky and each flake is composed of fine particles. It can be seen from the SEM images (Figs. 1g and 1h) that the as-obtained 5% In₂O₃-ZnO has obvious flower like structure which is composed of “porous petals”. The “porous petals” are further composed of rod-shaped particles (Fig. 1i).

The SEM and elemental mapping images of 5% In₂O₃-ZnO are shown in Fig. 2. The K edge mappings of Zn, O, and In elements are shown in Figs. 2b, 2c, respectively. It can be seen that the elemental mapping images of O (red color), Zn (green color) and In (white color) are similar to the SEM image of 5% In₂O₃-ZnO in Fig. 2a. The elemental mapping image of In is not distinct enough compared with the elemental mapping image of O and Zn, this is due to the low content of In relative to O and Zn. Three elements (O, Zn, and In) are uniformly distributed in the sample of 5% In₂O₃-ZnO, which indicates the formation of uniform nanocomposites.

Fig. 3 shows the XRD analyzed data for as-prepared samples. Fig. 3a indicates that ZnO is hexagonal wurtzite crystal structure in ZnO particles, 3% In₂O₃-ZnO, 5% In₂O₃-ZnO, and 7% In₂O₃-ZnO, with characteristic diffraction peaks at 31.77, 34.42, 36.52, 47.54, 56.60, 62.86 and 67.96° indexed to (100), (002), (101), (102), (110), (103), and (112) crystal planes of hexagonal ZnO (JCPDS, No. 36-1451), respectively.

For the In₂O₃-ZnO composites (3% In₂O₃-ZnO, 5% In₂O₃-ZnO, and 7% In₂O₃-ZnO), three new characteristic peaks appeared at 20 values of 30.58, 51.03, and 60.67° can be assigned to (222), (440), and (622) crystal planes of body-centered cubic structure of In₂O₃ (JCPDS, No. 06-0416), respectively.

| Table I. Information of different samples. |
|-------------------------------------------|
| Zn(CH₃COO)₂·2H₂O (g) | In(NO₃)₃·4.5H₂O (g) | n(In):n(Zn) | Abbreviation |
| 1.098 | 0 | / | ZnO particles |
| 0 | 1.910 | / | In₃O₃ particles |
| 1.098 | 0.057 | 0.03:1 | 3% In₃O₃-ZnO |
| 1.098 | 0.095 | 0.05:1 | 5% In₃O₃-ZnO |
| 1.098 | 0.134 | 0.07:1 | 7% In₃O₃-ZnO |
The peaks of mixed metal oxides such as $\text{Zn}_x\text{In}_y\text{O}_z$ cannot be detected, so the samples are heterogeneous structure composites with separated $\text{In}_2\text{O}_3$ and $\text{ZnO}$ phases. As the content of $\text{In}_2\text{O}_3$ in $\text{In}_2\text{O}_3$-$\text{ZnO}$ composites increases, the intensities of typical characteristic peaks of $\text{In}_2\text{O}_3$ also increase. Fig. 3b shows the hexagonal (101) diffraction peaks of the $\text{In}_2\text{O}_3$-$\text{ZnO}$ composites and $\text{ZnO}$ particles. The crystallite size can be obtained according to the Scherrer Formula:

$$D_{hkl} = \frac{0.9k}{b \cos h}$$

where $h$ refers to Bragg angle, $k$ refers to the X-ray wavelength, and $b$ refers to the full width at half maximum. From (101) crystallographic planes in Fig. 3b and Scherrer formula, the crystalline sizes of $\text{ZnO}$ particles, 3% $\text{In}_2\text{O}_3$-$\text{ZnO}$, 5% $\text{In}_2\text{O}_3$-$\text{ZnO}$, and 7% $\text{In}_2\text{O}_3$-$\text{ZnO}$ were calculated to be 32.5, 27.5, 27.8 and 29.1 nm, respectively. This indicates that the as-prepared samples are composed of small particles with a diameter of about 30 nm. The change of crystalline size can be attributed to the difference of coordination structures between the two semiconductor materials.

Fig. 4 shows the TEM photograph of 5% $\text{In}_2\text{O}_3$-$\text{ZnO}$. Figs. 4a and 4b show the representative TEM micrographs of 5% $\text{In}_2\text{O}_3$-$\text{ZnO}$ “porous petals”. Irregular holes are clearly visible in the “porous petals” shown in Fig. 4a. Fig. 4b shows that 5% $\text{In}_2\text{O}_3$-$\text{ZnO}$ is composed of nanoparticles with a particle diameter of 25–30 nm, and the particle size corresponds to the results of XRD. The high-resolution transmission electron microscopy (HRTEM) image of 5% $\text{In}_2\text{O}_3$-$\text{ZnO}$ is shown in Fig. 4c and the clear lattice stripes can be observed, which indicates the high crystallinity of cubic $\text{In}_2\text{O}_3$ and hexagonal $\text{ZnO}$. The clear diffraction ring and interface pattern of selected area electron diffraction (SAED) of 5% $\text{In}_2\text{O}_3$-$\text{ZnO}$ (Fig. 4d) indicate high crystallinity and polycrystalline structure of the sample.
Figure 3. (a) XRD patterns of samples, (b) the (101) planes of samples intercepted from (a).

Figure 4. TEM images (a, b), HRTEM image (c) and a typical SAED pattern (d) of 5% In$_2$O$_3$-ZnO.

this is due to the doping of In$_2$O$_3$ particles.\(^{40,63}\) The bandgap energy values of the products were calculated by Eq. 2:\(^{64}\)

\[(Ahv)^2 = K(\hbar v - E_g)\]

where $E_g$ is the bandgap energy, $A$ stand for absorption coefficient, $hv$ and $K$ stand for photon energy and proportionality constant, respectively. Fig. 6b shows the normalized curves of $(Ahv)^2$ for the photon energy of the products. The bandgap energy of ZnO particles and In$_2$O$_3$ particles is 3.12 and 2.81 eV, respectively. Compared with ZnO particles, the bandgap of In$_2$O$_3$-ZnO composites is lower than that of pure ZnO. The bandgap energy values of 3% In$_2$O$_3$-ZnO, 5% In$_2$O$_3$-ZnO, and 7% In$_2$O$_3$-ZnO are 2.92, 2.87, and 2.89 eV, respectively. Reducing the bandgap energy of the photocatalyst is more conducive to the transition of electrons when exposed to visible light, which leads to an enhanced photoelectricity catalysis performance.\(^{18,40}\)

In order to explore the photoelectrochemical properties and photoelectrocatalytic properties of the samples, the samples were prepared into electrodes.\(^{51}\) The process of preparing electrodes is shown in Fig. 8a. First of all, 12g active substance, 6g PTFE and 2.4g acetylene black were dispersed in 1 mL anhydrous ethanol under ultrasonic treatment for 15 min to form a liquid mixture, and the liquid mixture was dried to black paste mixture at room temperature subsequently. Next the black paste mixture was evenly spread on one side of the foamed nickel (2 × 2 cm$^2$) and was dried at 60$^\circ$C for 8h. Finally, the active substance was compacted on a nickel foam photoelectrode by a pressing machine (6 MP). The photoelectrochemical performance of ZnO particles, 3% In$_2$O$_3$-ZnO, 5% In$_2$O$_3$-ZnO, and 7% In$_2$O$_3$-ZnO were explored by measuring the strength of transient photocurrent. Fig. 8b shows the transient photocurrents for samples measured in Na$_2$SO$_4$ (50 mL, 0.1 mol/L) electrolyte under intermittent visible light irradiation. As shown in Fig. 8b, the transient photocurrents of all photoelectrodes will maintain a constant value when the visible light on.
Figure 5. XPS full survey spectrum of 5% In$_2$O$_3$-ZnO (a), the XPS spectra of Zn 2p (b), In 3d (c) and O 1s (d) in 5% In$_2$O$_3$-ZnO.

light was irradiated, but rapidly decreased to zero as long as the visible light is switched off. Compared with ZnO particles (174 μA/cm$^2$), 3% In$_2$O$_3$-ZnO (231 μA/cm$^2$), and 7% In$_2$O$_3$-ZnO (247 μA/cm$^2$) photoelectrode, the 5% In$_2$O$_3$-ZnO (268 μA/cm$^2$) photoelectrode shows the strongest photocurrent response. The reason for photocurrent density enhancement can be attributed to the more electrons produced by the increased visible light absorption and the fast electron-hole separation.$^{60,67}$ The I-V curves (Fig. 8c) of photoelectrodes were measured under sustained visible light irradiation. As the voltage increases, the photocurrents of all electrodes tend to be stable finally. The stable photocurrents of all the electrodes are 264 μA/cm$^2$ (5% In$_2$O$_3$-ZnO), 249 μA/cm$^2$ (7% In$_2$O$_3$-ZnO), 217 μA/cm$^2$ (3% In$_2$O$_3$-ZnO) and 203 μA/cm$^2$ (ZnO), respectively. This further confirms that the photocurrent density of the 5% In$_2$O$_3$-ZnO photoelectrode is higher than that of other photoelectrodes. Electrochemical impedances spectroscopy (EIS) was applied to test the capability of charge transfer. The test results are shown in Fig. 8d, among those photoelectrodes with different samples loaded, the arc radius of the 5% In$_2$O$_3$-ZnO electrode is the smallest one, suggesting its lowest resistance for interfacial charge transfer.$^{67,68}$

Photoelectrocatalytic activity.—The photocatalytic activities and photoelectrocatalytic activities for the degradation of MB under visible-light irradiation using the products were evaluated, Fig. 9. The photocatalytic degradation rates of MB over ZnO particles, In$_2$O$_3$ particles, 3% In$_2$O$_3$-ZnO, 5% In$_2$O$_3$-ZnO, and 7% In$_2$O$_3$-ZnO are 53.5%, 43.6%, 62.3%, 71.9% and 65.4%, respectively, Fig. 9a. The best performing sample (5% In$_2$O$_3$-ZnO) did not degrade MB solution by more than 71.9% in 60 minutes. Fig. 9b shows the photoelectrocatalytic degradation performance of 5% In$_2$O$_3$-ZnO on MB at different voltages and the results show that different bias voltages have a certain effect on photoelectrocatalytic performance of sample. Among 0.1~0.4V bias voltages, the most suitable bias voltage is 0.2 V. The photoelectrocatalytic degradation rate of 5% In$_2$O$_3$-ZnO for MB solution is 95.3%, and the photoelectrocatalytic activity is increased by about 23% compared with photocatalytic performance. This is because bias voltage with proper intensity can increase the intensity of photocurrents and improve the movement of charges.$^{69}$ The photoelectrocatalytic performance results of samples at 0.2 V bias voltage are shown in Fig. 9c. As we can see from Fig. 9c, the degradation rate of all photocatalysts to MB dye solution is as follows: 5% In$_2$O$_3$-ZnO (95.3%) > 7% In$_2$O$_3$-ZnO (91.7%) > 3% In$_2$O$_3$-ZnO (84.6%) > ZnO particles (75.3%) > In$_2$O$_3$ particles (49.9%). Photoelectrocatalytic performance of all samples is superior to photocatalytic performance under the same conditions, and 5% In$_2$O$_3$-ZnO exhibits the highest photoelectrocatalytic performance. It can be seen that doping an appropriate amount of In$_2$O$_3$ in ZnO can significantly improve the photocatalytic activity. The reasons of the improved photoelectrocatalytic performance are that the 5% In$_2$O$_3$-ZnO with flower-like structures possess a higher specific surface area and can provide more active sites in contact with the MB. Moreover, porous flower-like structures allow multiple reflections of visible-light, making more efficient use of the visible-light source.$^{70}$ In addition, doping In$_2$O$_3$ will also reduce the bandgap energy of In$_2$O$_3$-ZnO composites and improves its light energy utilization rate.$^{18,44,71}$ For discussing kinetic information of the photoelectrocatalytic activity of the products, the kinetics process of photoelectrocatalytic degradation of MB was also investigated. The photoelectrocatalytic process of MB can be described using the
Figure 6. UV–Vis absorption spectra of samples (a), and the plot of \((Ahv)^2\) vs. \(hv\) based on the direct transition (b).

pseudo-first-order kinetic model as shown below:\(^{72,73}\)

\[
\ln (C_0 - C_t) = kt \tag{3}
\]

where \(C_0\) and \(C_t\) refer to the concentrations of MB at beginning and time \(t\), \(t\) refers to the light irradiation time and \(k\) is the reaction rate constant, respectively. The curve of pseudo-first-order linear simulation is indicated in the Fig. 9d. The value of apparent rate constant \(k\) is calculated from the corresponding slope and the correlation coefficient \(R^2\) is shown in Table II. Obviously, the \(k\) value of 5% In\(_2\)O\(_3\)-ZnO (0.050 min\(^{-1}\)) is consistent with the conclusions demonstrated in Fig. 9c. The comparison of the preparation method, dosage of catalyst and photocatalytic performance on previous reported In\(_2\)O\(_3\)-ZnO composites is summarized in Table III. In this work the preparation method of In\(_2\)O\(_3\)-ZnO composites not only is simple and time saving, but also can produce a photodegradation with good effect.

The durability of the 5% In\(_2\)O\(_3\)-ZnO was tested in the recycling experiments and the results are shown in Fig. 10. From Fig. 10, 5% In\(_2\)O\(_3\)-ZnO maintained high photodegradation activities (more than 90%) even after 5 cycles, indicates the high stability and reusability of 5% In\(_2\)O\(_3\)-ZnO composites. Moreover, the inset of Fig. 10 shows that the active substances on the as-prepared photoelectrode do not fall off after 5 cycles of experiments. There was no obvious change in the photoelectrode before and after use, indicating that the as-prepared photoelectrode had good physical stability. In addition, loading the active material onto the photoelectrode is convenient to the recovery of the photocatalysis.

Based on the above experimental results the above experimental results, a plausible mechanism was proposed to illustrate the enhanced photodegradation of In\(_2\)O\(_3\)-ZnO composites. The process of photodegradation catalysis is shown in Fig. 11 and the reaction process can be represented in Eqs.\(^{44,74}\)

\[
\begin{align*}
\text{ZnO} & \rightarrow \text{ZnO}(e^- + h^+) \tag{4} \\
\text{In}_2\text{O}_3 & \rightarrow \text{In}_2\text{O}_3(e^- + h^+) \tag{5} \\
\text{ZnO}(e^-) + \text{O}_2 & \rightarrow \text{ZnO} + \cdot\text{O}_2^- \tag{6} \\
\text{In}_2\text{O}_3(e^-) + \text{O}_2 & \rightarrow \text{In}_2\text{O}_3 + \cdot\text{O}_2^- \tag{7} \\
\text{ZnO}(h^+) + \text{H}_2\text{O} & \rightarrow \text{ZnO} + \cdot\text{OH} + \text{H}^+ \tag{8} \\
\text{ZnO}(h^+) + \text{H}_2\text{O} & \rightarrow \text{ZnO} + \cdot\text{OH} + \text{H}^+ \tag{9}
\end{align*}
\]

Table II. The kinetic constant \(k\), correlation coefficient \(R^2\) and linear fitting equation of MB photodegradation affected by different samples.

| Samples | \(k\) | \(R^2\) | Fitting equation |
|---------|-------|---------|-----------------|
| ZnO particles | 0.011 | 0.99 | \(y = 0.011x + 0.019\) |
| In\(_2\)O\(_3\) particles | 0.024 | 0.99 | \(y = 0.024x - 0.028\) |
| 3% In\(_2\)O\(_3\)-ZnO | 0.031 | 0.99 | \(y = 0.031x - 0.887\) |
| 5% In\(_2\)O\(_3\)-ZnO | 0.050 | 0.97 | \(y = 0.050x - 0.211\) |
| 7% In\(_2\)O\(_3\)-ZnO | 0.042 | 0.98 | \(y = 0.042x - 0.143\) |

Table III. Comparison of the photodegradation activity of several In\(_2\)O\(_3\)-ZnO composites.

| Preparation method | Dosage | Reaction time | Dye | Catalytic efficiency | Ref. |
|--------------------|--------|---------------|-----|---------------------|-----|
| one-step hydrothermal | In\(_2\)O\(_3\)-ZnO particles 50 mg | 2h | MB (10 mg/L, 100 ml) | photocatalytic, 98% after 6h | 44 |
| chemical coprecipitation | In\(_2\)O\(_3\)-ZnO particles 50 mg | 24h | MB (20 mg/L, 100 ml) | photocatalytic, 97% after 2h | 40 |
| layered precursor | MgO/ZnO/In\(_2\)O\(_3\) mixed-metal oxide 50 mg | 6h | MB (10 mg/L, 100 ml) | photocatalytic, 95% after 5h | 71 |
| microwave hydrothermal | In\(_2\)O\(_3\)-ZnO particles 12 mg | 30min | MB (20 mg/L, 100 ml) | photoelectrocatalytic 95% after 60 min | this work |
Figure 7. Nitrogen adsorption-desorption isotherms (a) and the pore size distributions (b) of samples.
Figure 8. The electrode fabrication process (a), transient photocurrent (b), current density versus potential (I–V) curves (c), EIS Nyquist plots of the samples (d).

Figure 9. Photocatalytic degradation of MB using samples under visible-light irradiation (a), photoelectrocatalytic degradation performance of 5% In$_2$O$_3$-ZnO on MB at different voltages (b), the photoelectrocatalytic degradation efficiency of different samples to MB at 0.2V applied voltages and under visible-light irradiation (c) and the photodegradation kinetic curves of samples (d).
Due to the doping of In$_2$O$_3$, the photoresponse range of In$_2$O$_3$-ZnO composites is raised to the visible region. The In$_2$O$_3$-ZnO electrode generates photo-generated electrons ($e^{-}$) and holes ($h^{+}$) in their conduction band (CB) and valence band (VB) under the visible light (Eqs. 4 and 5). However, electron-hole pairs are easy to recombine after separation, charge recombination will greatly reduce the photoelectrocatalytic efficiency. When In$_2$O$_3$ was doped into ZnO to form a composite material, a small number of electrons can be excited in the CB of In$_2$O$_3$, and be drifted to the CB of ZnO. At the same time, the hole ($h^{+}$) from ZnO is trapped in the VB of In$_2$O$_3$. The electron drift and hole capture will suppress the recombination of electron-hole pairs. Meanwhile, the applied voltage will rapidly prompt the photo-generated electrons to move to the external circuit rapidly, which tremendously reduces the recombination of electron-hole pairs. These photogenerated electrons ($e^{-}$) and holes ($h^{+}$) can convert O$_2$ and -OH in solution into •O$_2$ and •OH (Eqs. 6 ~ 11). Finally, due to the strong oxidizing properties of these substances, the MB molecules can be oxidatively decomposed into CO$_2$, H$_2$O and other nontoxic substances (Eq. 12).

**Conclusions**

In$_2$O$_3$-ZnO composites with prominent photoelectrocatalytic properties were successfully synthesized through microwave hydrothermal method. The as-prepared 5% In$_2$O$_3$-ZnO composites exhibited higher photoelectrocatalytic activities than that of ZnO particles and In$_2$O$_3$ particles. Under the 60 min visible-light irradiation and bias voltage of 0.2 V, 95.3% of MB was degraded using 5% In$_2$O$_3$-ZnO composites and the dye degradation followed pseudo-first-order kinetic process. The results of recycling experiments indicate that the MB photoelectrocatalytic degradation rate of 5% In$_2$O$_3$-ZnO photoelectrode is over 90% after recycling 5 times. In addition, the convenience of recycling photocatalysts makes it possible to be widely used in practical industries, especially in harsh environments like strong acids where metals will be dissolved or high temperature where carbon, polymer or its composites will be burned.

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