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Characterization, Photoelectric Properties, Electrochemical Performances and Photocatalytic Activity of the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ Heteronanostructure

Salah Kouass, Hassouna Dhaouadi, Abdelhak Othmani and Fathi Touati

Abstract

The $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite was synthesized on FTO substrate via hydrothermal method. The crystal structure, morphology, band structure of the heterojunction, behaviors of charge carriers and the redox ability were characterized by XRD, HR-TEM, absorption spectra, PL, cyclic voltammetry and transient photocurrent spectra. The as-prepared $\text{Fe}_2\text{O}_3/\text{TiO}_2$ photocatalysts with distinctive structure and great stability was characterized and investigated for the degradation of methylene blue (MB) dye in aqueous solution. The ability of the photocatalyst for generating reactive oxygen species, including O_2^- and $\cdot\text{OH}$ was investigated. It was revealed that the combination of the two oxides (Fe_2O_3 and TiO_2) nano-heterojunction could enhance the visible response and separate photogenerated charge carriers effectively. Therefore, the remarkable photocatalytic activity of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanostructures for MB degradation was ascribed to the enhanced visible light absorption and efficient interfacial transfer of photogenerated electrons from Fe_2O_3 to TiO_2 due to the lower energy gap level of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ hybrid heterojunctions as evidenced by the UV-Vis and photoluminescence studies. The decrease of the energy gap level of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ resulted in the inhibition of electron-hole pair recombination for effective spatial charge separation, thus enhancing the photocatalytic reactions. Based on the obtained results, a possible mechanism for the improved photocatalytic performance associated with $\text{Fe}_2\text{O}_3/\text{TiO}_2$ was proposed. The $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite has a specific capacity of 82 F.g^{-1} and shows a higher capacitance than Fe_2O_3 .

Keywords: $\text{Fe}_2\text{O}_3/\text{TiO}_2$, methylene blue degradation, heterojunction, holes and superoxide radicals, photocatalyst

1. Introduction

The environmental impact caused by the discharge of untreated wastewaters, or even partially treated in sewage stations, is an increasingly worrying problem, considering the damage caused to the environment [1]. In view of this, a great effort

has been made to develop new technologies aiming the treatment of persistent substances in the environment such as heterogeneous photocatalysis, electrochemical techniques and photoelectrochemical processes [2–6]. Among these processes, the heterogeneous photocatalysis that belongs to the class of the advanced oxidation processes has proved very effective as it mineralizes the contaminations existing liquid phases. Over the last few decades, research in the photocatalysis area has been focusing on improving electrochemical and photocatalytic materials [7–10]. So, various photocatalysts such as titanium dioxide (TiO_2) were used. It is one of the most used photocatalysts given its efficiency in pollutant degradation in waste water, because of its inexpensiveness, hard-soluble and long-term photostability. However, there are two defects limiting the use of TiO_2 in the photocatalysis: one, its wide band gap energy that limits its response to visible light and the other is the rapid recombination of photogenerated electron-hole which leads to the decrease of its photocatalytic activity. Therefore, much effort has been devoted to solving these problems. One solution to overcome the defects is to construct heterojunction photocatalysts. In order to construct a heterojunction photocatalyst based on TiO_2 , the adaptation of energy levels between the two components is determining, that is, the conduction band edge of the narrow band gap semiconductor is higher than that of TiO_2 . Fe_2O_3 , as a highly active photocatalyst with a band gap of 2.0 eV [11–13], seems to be a good choice except it has a lower conduction band edge. However, the Fermi level (E_F) of Fe_2O_3 is lower than that of TiO_2 . Indeed, Yanqing Cong and al. proved that Fe_2O_3 nanoparticles present a stronger photo-response under visible light irradiation in the nanostructured $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanotube electrodes [14]. $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposites revealed outstanding photocatalytic activity under visible light and were used as photocatalysts in the degradation of oxytetracycline [15–18]. In this study, we have synthesized by a hydrothermal approach a $\text{TiO}_2/\text{Fe}_2\text{O}_3$ heterojunction photocatalyst that exhibited excellent performance in many fields.

2. Characterization

The XRD analysis of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ indicates the formation of the TiO_2 anatase phase in the presence of the Fe_2O_3 rhombohedral structure. Fe_2O_3 and the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite were recorded using high resolution transmission electron microscope (HR-TEM). As shown in **Figure 1a**, the Fe_2O_3 nanorods are well dispersed with an average diameter of 50 nm.

The magnified high resolution TEM image (**Figure 1a**) illustrates that the Fe_2O_3 nanorods cover the TiO_2 nanoparticles surface. Lattice fringes in the HRTEM image (**Figure 1b**) of the binary hybrid nanocomposite $\text{Fe}_2\text{O}_3/\text{TiO}_2$ could be assigned to a lattice spacing of 2.35 Å nm corresponding to the (103) plane of TiO_2 , while the lattice spacing of 2.52 Å nm could be indexed to the (110) plane of Fe_2O_3 .

The band gap (E_g) for pure Fe_2O_3 , TiO_2 and the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ is determined by extrapolating the absorption edge using the following Equation [19]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

The E_g values are respectively, $E_{g1} = 3.1$ eV, $E_{g2} = 1.93$ eV and $E_{g3} = 2.6$ eV for TiO_2 , Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ junction. It is noted that the presence of Fe_2O_3 in the material increases the intensity of the bands and shifting them to higher wavelengths compared to TiO_2 .

Introducing an appropriate amount of transition metal oxide in the TiO_2 matrix is a promising alternative used to modulate the band gap of the as-obtained

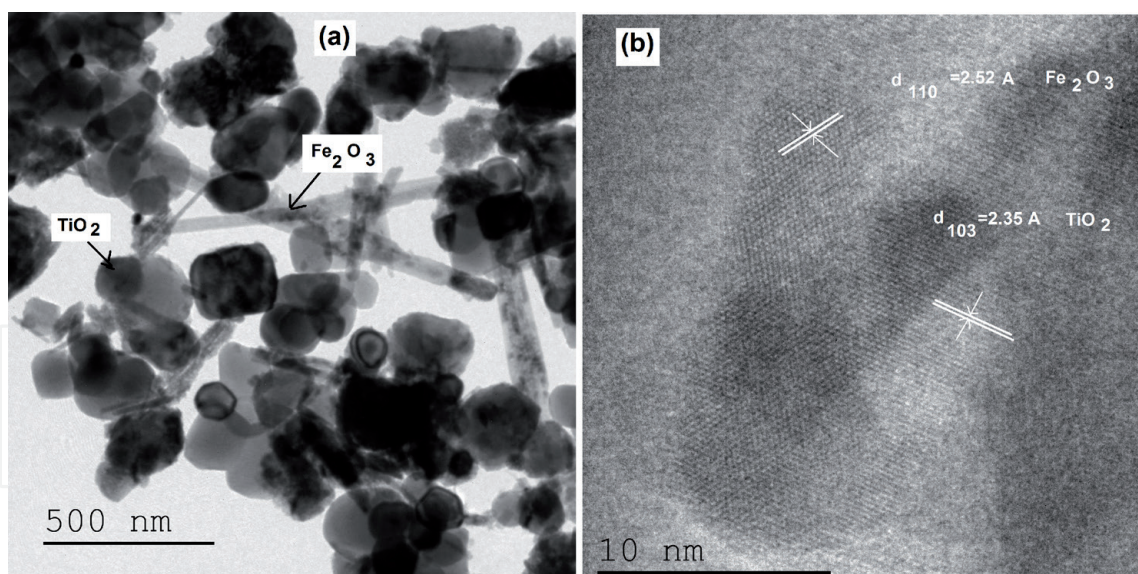


Figure 1.
 HRTEM image of: (a) $\text{Fe}_2\text{O}_3/\text{TiO}_2$, (b) HRTEM lattice fringe image of: $\text{Fe}_2\text{O}_3/\text{TiO}_2$.

nanocomposite. The weakness of band gap due to the electrons excited and injected into the conduction band of TiO_2 leads to the improvement of the electron–hole pair separation. The higher degradation activity of the nanocomposite samples ($\text{Fe}_2\text{O}_3/\text{TiO}_2$, CdO/ZnO , ZnO/TiO_2 , $\text{Bi}_2\text{O}_3/\text{TiO}_2$ and CdS/TiO_2) [19–24] is correlated with its lower band gap and strong adsorption in the visible region. In our case, the synthesized $\text{Fe}_2\text{O}_3/\text{TiO}_2$ heterojunction presents a moderate band gap ($E_g = 2.6 \text{ eV}$) compared to the other nanocomposite samples. Consequently, the separation efficiency of photogenerated electron–hole pairs in the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ heterojunction could be improved, leading to the improvement of the photocatalytic activity.

3. Photocatalytic activity

The study of the photocatalytic activity of $\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{FTO}$ heterojunction is realized by following the degradation of MB in an aqueous solution under visible light irradiation. The absorption spectrum of MB without a catalyst is characterized by a broad peak centered at 670 nm. The MB absorbance at around 650 nm decreases and there is almost no shift in the peak maximum. This shows that MB was degraded via the destruction of the conjugated structure. This demonstrates that $\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{FTO}$ exhibits outstanding photocatalytic activity compared to pure TiO_2 . The obtained results confirm that TiO_2 alone is unable to absorb under visible irradiation. This could be attributed to the scaling down of the distance between the valence band (VB) and the conduction band (CB) after the addition of Fe_2O_3 which boosts the transfer of electrons between bands after excitation. In comparison, the $\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{FTO}$ exhibits better photocatalytic degradation than the TiO_2 film. Photocatalytic activity is controlled by many factors, such as the phase structure, particle size, light absorption capacity and electron/hole recombination rate [25].

The heterogeneous photocatalysis mechanism has been discussed extensively in the literature [26, 27]. The photo-activity mechanism presented in this study of the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ thin film is described as follows: when the system is irradiated with visible light, the Fe_2O_3 electrons at the valence band are excited and hop to the conduction band, leaving a hole (h^+). As a result, electron (e^-)/hole (h^+) pairs are forming. Then, the excited-state electrons produced by Fe_2O_3 can be transferred to the conduction band (CB) of the coupled TiO_2 due to the existence of electric fields

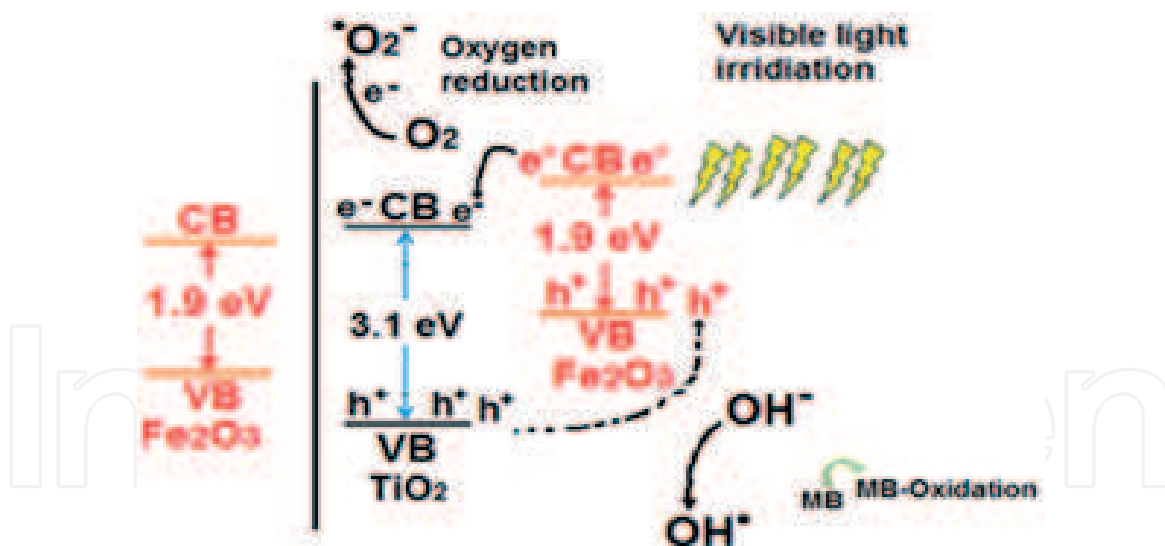


Figure 2.

Schematic illustration of the MB degradation mechanism, under visible light irradiation on the surface of the $\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{FTO}$ heterojunction.

between the two materials. At the same time, the photo-generated holes (h^+) of TiO_2 can quickly transfer to the VB of Fe_2O_3 . The transferred electrons into the conduction band of TiO_2 react with dissolved (O_2) to form ($\cdot\text{O}_2^-$) and further produce $\cdot\text{OH}$. On the other hand, the holes generated on the valence band of Fe_2O_3 can easily transfer to that of TiO_2 inducing an effective charge separation and transfer. Then the positive charge hole (h^+) on Fe_2O_3 surfaces reacts with H_2O to generate OH .

Figure 2 shows the band gap structure and the possible charge carrier transfer between Fe_2O_3 and TiO_2 under visible light radiation. Before the contact between the two materials, the conduction band (CB) of TiO_2 lies above the CB of $\alpha\text{-Fe}_2\text{O}_3$. The energy values of VB (Fe_2O_3) and CB (TiO_2) were obtained by the two formulas: $E_{\text{VB}} = \chi - E_e + 0.5E_g$ and $E_{\text{CB}} = E_{\text{VB}} - E_g$. [28–30], where E_g , E_e and χ represent the band gap energy of the semiconductor, the energy of free electrons (about 4.5 eV) and the electronegativity of the semiconductor, respectively. The χ values for TiO_2 and Fe_2O_3 are 5.83 eV and 5.88 eV, respectively [19]. After substituting χ into the equation, the E_{VB} of TiO_2 and Fe_2O_3 are found to be 2.93 eV and 2.35 eV, respectively. Therefore, the CB potentials of TiO_2 and Fe_2O_3 were calculated to be (−0.27 eV) and (0.4 eV), respectively. After coupling TiO_2 with Fe_2O_3 to form the p-n heterojunction, the Fermi level of Fe_2O_3 was dragged upwards, while the Fermi level of TiO_2 was dragged downwards, until they were at the same level and reached equilibrium [31, 32].

4. Photoelectric properties

The PL spectrum is one of efficient approaches to depict the recombination efficiency of photogenerated electron–hole pairs through their different intensities [33]. When the photo-induced electrons and holes are easier to recombine and the lifetime of the photogenerated electrons is shorter, and correspondingly the fluorescence intensity is higher. It is obvious that the PL emission intensity of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ is lower than that of TiO_2 , implying that the coupling of TiO_2 and Fe_2O_3 can effectively inhibit the recombination of the photo-generated electron–hole pairs. The decrease recombination rate would be more beneficial for many photocatalyst performance enhancement than TiO_2 [34].

Figure 3 shows the transient photocurrent spectra for TiO_2 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples. As shown in **Figure 3**, the maximum photocurrent density of the $\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{FTO}$

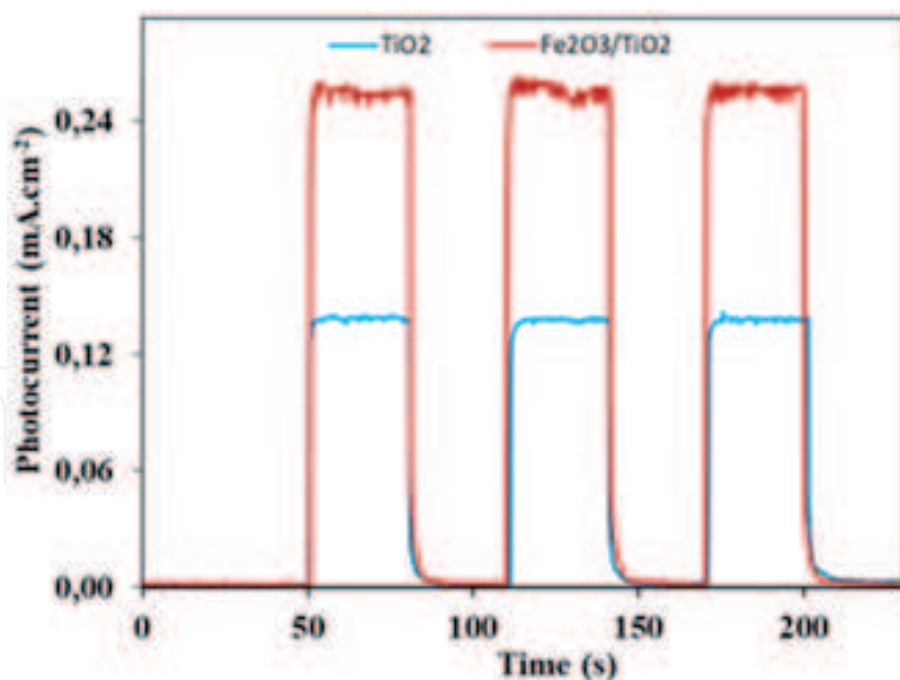


Figure 3.
 Transient photocurrent vs. irradiation time for pure TiO_2 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ heterojunction samples in 0.1 M NaOH solution under visible light irradiation.

heterojunction electrode reached 0.25 mA.cm^{-2} which is almost the twice of the pure TiO_2 electrode. This indicates more charge carriers are generated and transferred from conduction band of the photocatalysts to the electrodes. It could be seen that the photocurrent density produced instantly and increased sharply when exposed to visible light, but promptly reduced to zero as soon as the light source is turned off. Those results confirm that $\text{Fe}_2\text{O}_3/\text{TiO}_2$ heterojunction is more effective in generating and separating the photogenerated charge carriers than TiO_2 , and much faster interfacial charge transfer, benefitting photocatalytic activity.

The improved photocurrent shows the effective interfacial charge transfer between Fe_2O_3 and TiO_2 . Thus, the stable and enhanced photocurrent of the obtained heterojunction is more favorable for photocatalytic dye degradation; furthermore, it is more efficient for water splitting [18].

From the resulting Mott-Schottky plot (C^{-2} versus the applied potential E) [35], the flat band potential E_{FB} could be obtained as the intercept with the x -axis and from the slope of the linear part. The value of the flat band potential determined from capacitance measurements is reported to be -0.45 V and -0.55 V vs. Ag/AgCl for TiO_2 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ respectively. It should be noted that the E_{FB} of the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ photoanode exhibits a positive shift in comparison to that of the pure TiO_2 electrode. Combined with the E_g calculated from the DRS spectra, the optical band gaps of TiO_2 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ are 3.1 and 2.6 eV, respectively. According to the formula $E_g = E_{\text{VB}} - E_{\text{CB}}$, the valence band positions (E_{VB}) of TiO_2 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ are 2.65 and 2.05 V vs. Ag/AgCl, respectively.

5. Electrochemical performances

Transition metal oxides such as oxides of Fe, Cu, Ni, Mn, Cu, and TiO_2 for electrode materials offer rich redox reactions such as in electrochemical cells providing high specific capacitance values for supercapacitors [36, 37]. Among these metal oxides, Fe_2O_3 , TiO_2 , metal doped TiO_2 and composite $\text{Fe}_2\text{O}_3/\text{TiO}_2$ are very promising electrodes materials, due to their acceptable charge/discharge

capacities [38–40]. Cycling stability and specific capacitance are critical factors in evaluating the electrochemical properties, influenced by synthesis method, morphology and grains size.

The specific capacitance of the electrode calculated from the CV curves, according to the following Equation [40–42]:

$$C = \frac{\int I(V)d(V)}{mv\Delta V} \quad (2)$$

α -Fe₂O₃ with rod-like structure is synthesized to evaluate as electrode material comparing with Cu foil and Ni foam, the as-prepared electrodes with Ni-foam exhibited higher capacity of 415 mAh g⁻¹ and more stable cycle performance [43]. Fe-based materials, Fe₂O₃, Fe₃O₄, and FeOOH, were synthesized via the microwave-hydrothermal process by Young Dong Noh and al, the results showed that FeOOH had better anode capacity as lithium-ion batteries than those of Fe₂O₃ and Fe₃O₄ [44]. Yudai Huang and al prepared -Fe₂O₃/MWCNTs composites by a simple hydrothermal process and show that initial discharge capacity of Fe₂O₃ is 992.3 mAh g⁻¹ and the discharge capacity is 146.6 mAh g⁻¹ after 100 cycles [45].

5.1 TiO₂

Anantha Kumar and al demonstrated that synthesis of a grapheme-TiO₂ using a microwave technique exhibited a high specific capacitance of 165 F g⁻¹ at a scan rate of 5 mV s⁻¹ [46]. G. Wang and al fabricate TiO₂-B nanotubes via a mixed solvothermal technical and subsequent heat treatment and found that specific capacitance is equal to 17.7 F/g [47]. The same, capacitances of the CNTs, CNTs/TiO₂ composite and UVlight irradiated CNTs/TiO₂ composite materials were 4.1F/g; 6.4F/g and 9.8F/g, respectively [48].

5.2 TiO₂-Fe₂O₃ composite

The performances of TiO₂-Fe₂O₃ composite prepared using abundant ilmenite via a heat treatment are improved compared with that of P25, with the increased iron oxide content, the capacity gets higher [49]. Again, the α -Fe₂O₃/TiO₂/C composite fibers prepared by Luis Zuniga and al, via centrifugal spinning and subsequent thermal processing, showed a superior specific capacity of 340 mAh g⁻¹ after 100 cycles, compared to 61 mAh g⁻¹ and 121 mAh g⁻¹ for TiO₂/C and α -Fe₂O₃/C materials, respectively [50]. So, TiO₂/FeTiO₃@C porous materials, synthesized by carbonizing the mixture of pyrrole with lab-made TiO₂/Fe₂O₃, have a superior capacity of 441.5 mAh g⁻¹ after 300 cycles, Comparing with TiO₂, TiO₂@C, and TiO₂/Fe₂O₃ [51]. Also, TiO₂, Fe₂O₃ NPs and TiO₂-Fe₂O₃ are synthesized via green combustion method with *Aloe Vera* gel as a fuel. Compared to pure TiO₂ and Fe₂O₃ materials, the composite showed stable electrochemical performance after 1000 cycles, which can be beneficial for rechargeable supercapacitor [52].

Based on the synergy between the two metallic oxides, TiO₂ and Fe₂O₃, we have produced Fe₂O₃/TiO₂ nanocomposite and heterojunction film via the hydrothermal process. The electrochemical performance of the Fe₂O₃ and Fe₂O₃/TiO₂ nanostructures as potential electrode material for supercapacitors, cyclic voltammetry (CV) tests were performed in a three-electrode cell with Na₂SO₄ aqueous electrolyte. The current response as a function of the potential applied to the working electrode, recorded at 100 mV/s in a potential range between -0.8 V and -0.4 V with 1000 cycles of the Fe₂O₃/TiO₂ nanocomposite in the

Na⁺-system. Therefore, the Fe₂O₃/TiO₂ nanocomposite shows electrochemical and structural stability during redox cycling.

The excellent pseudocapacitive performance of the Fe₂O₃/TiO₂ nanocomposite electrode is probably attributed to the positive synergistic effects between the Fe₂O₃ and TiO₂.

First, This combination can not only inhibit the agglomerating of TiO₂ nanoparticles but also reduce the aggregation of the nanoparticles made the nearly every Fe₂O₃ nanoparticle access to the electronic and ionic transport pathways resulting in high double-layer capacitance, and importantly, enhancing the utilization of active materials [28]. Second, the large distance between neighboring graphene nanosheets provide enough void spaces to buffer volume change during the redox reaction, and endow good electrical contact with the nanoparticles upon cycling [32, 37]. Third, the unique structure can facilitate the diffusion and migration of the electrolyte ions that can increase the specific capacitance value and improve the high rate charge-discharge performance [38, 39]. Finally, graphene also provides a highly conductive network for electron transport during the charge and discharge processes, thus reducing the polarization of the electrodes [44–46].

6. Conclusion

TiO₂, Fe₂O₃ hematite nanoparticles and Fe₂O₃/TiO₂ nanocomposites were synthesized via a simple hydrothermal process. The photocatalytic activity of the Fe₂O₃/TiO₂ nanocomposite was evaluated using the degradation of methylene blue (MB) under sunlight irradiation for pollution prevention. The results proved that the Fe₂O₃/TiO₂ heterojunction has a higher removal efficiency of MB and stronger photo-response under visible light irradiation. Compared to both pure TiO₂ and Fe₂O₃, the Fe₂O₃/TiO₂ photocatalyst have enhanced photocatalytic activity. This improved activity of the heterojunction between the TiO₂ and Fe₂O₃ nanoparticles results from the improved charge transfer and suppressed electron-hole recombination. We have also compared the photoelectric properties of Fe₂O₃/TiO₂ heterogeneous photocatalysts with that of pure TiO₂. The obtained result demonstrated that the formation of heterojunction between Fe₂O₃ and TiO₂ was pivotal for improving the separation and thus restraining the recombination of photogenerated electrons and holes, which accounts for the enhancement of photocatalytic activity. The study of the role of the active species on Fe₂O₃/TiO₂ confirmed that the crucial active species were both holes and superoxide radicals. The Fe₂O₃/TiO₂ sample also showed good stability and reusability, suggesting its potential for water purification applications. Likewise, the visible photogenerated electrons in the obtained heterojunction would provide a feasible route to improve solar water splitting, which will be investigated in further studies. The electrochemical properties of the as-synthesized nanocomposite materials (α -Fe₂O₃/TiO₂) were evaluated by cyclic voltammetry for 1000 cycles. The α -Fe₂O₃/TiO₂ nanocomposite materials exhibited an enhanced specific discharge capacity compared to Fe₂O₃ nanomaterials. The as-fabricated hybrid electrodes show an impressive performance as a high-capacity anode for Na⁺-ion batteries.

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