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Preparation, characterization and photocatalytic properties of $InVO_4$ nanopowder and $InVO_4$ -TiO₂ nanocomposite toward degradation of azo dyes and formaldehyde under visible light and ultrasonic irradiation

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Abstract In this study, photocatalytic activity of $InVO_4$ and InVO₄-TiO₂ nanoparticles in the degradation of aqueous solutions of industrial textile azo dyes such as Solophenyl Red 3BL, Coperoxon Nevy Blue RL and Black Nilusun 2BC (abbreviated as SR 3BL, CNB RL and BN 2BC, respectively) and also formaldehyde (abbreviated as FAD) under visible light and ultrasonic irradiations has been compared. The effect of various parameters such as pH, temperature, irradiation time, amounts of nanophotocatalyst and nanocomposite, and ultrasonic intensity on degradation rates was investigated. Then based on the Langmuir-Hinshelwood approach, reaction rates and adsorption equilibrium constants were calculated. The nanophotocatalyst and nanocomposite were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Vis spectroscopic methods. It was observed that InVO₄-TiO₂ nanopowder was more reactive than pure InVO₄ in the degradation of azo dyes under both conditions of visible light and ultrasonic irradiations. It was noticeable that degradation percent was more under ultrasonic irradiation rather than under visible light irradiation.

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Introduction

Azo dyes constitute the largest class of dyes used in textile industry. It is estimated that 10-15 % of these dyes is lost during the dyeing process and released as effluent. One of the problems associated with azo dyes is their resistance towards aerobic degradation; however, under anaerobic conditions, the azo bond is reduced and generates aromatic amines that are colorless but can also be toxic and potentially carcinogenic. New developments in advanced oxidation processes (AOPs) are focused on providing a promising and competitive solution for the abatement of numerous hazardous compounds in wastewater. These methods include Fenton or photo-assisted Fenton process, ozone and/or peroxide photolysis, semiconductor photocatalysis process, and ultrasonic cavitation [1-7]. The initial step in the AOPs is the generation of high reactive hydroxyl radicals which are suitable for the complete elimination and full mineralization of various pollutants such as phenols [8], chlorophenols [9], pesticides, [10] and azo dyes [11].

Sonochemical degradation of organic pollutants has been extensively studied in recent years [12–17]. The chemical effects of high-intensity ultrasound primarily result from cavitation phenomena (the formation, growth, and collapse of bubbles in liquids) [18]. These phenomena generate locally high temperatures and pressures for short period of time, which in turn produce radical species (H', HO', HOO') by sonolysis of H₂O. These radicals directly destruct the solute [14, 19, 20].

Heterogeneous photocatalysis by visible light irradiation on a semiconductor surface is an attractive advanced oxidation process [7]. The adsorbed organic molecules in a reaction are mineralized into carbon dioxide and water by hydroxyl radicals or superoxide radical anions. These

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(2)

$$\mathrm{HCHO} + \cdot \mathrm{OH} \rightarrow \cdot \mathrm{CHO} + \mathrm{H}_2\mathrm{O} \tag{1}$$

$$\cdot$$
 CHO + \cdot OH \rightarrow HCOOH

$$\cdot \text{CHO} + \cdot \text{O}_2^- \xrightarrow{+\text{H}^+} \text{HCOOOH} \xrightarrow{+\text{HCHO}} \text{HCOOH}$$
(3)

$$\text{HCOOH} \xrightarrow{\text{OH or } O_2^-} \text{H}_2\text{O} + \text{CO}_2 \tag{4}$$

Scheme 1 Mechanism for decomposition of FAD under visible light and ultrasonic irradiation

active species are produced by the reaction of water with valence band holes, and/or oxygen with conduction band electrons when a photocatalyst absorbs light with greater energy than its band gap. It is known that the photocatalytic process occurs at the surface or within a few monolayers around catalyst particles [21]. Oxides of transition metals are widely applied as photocatalysts, but the activity decline is frequently encountered because the electronhole charge recombination occurs on the oxide surface within nanoseconds [22]. The efficiency of a photocatalytic process can be influenced by many factors. For example, the pH change in an aqueous solution can modify the ionization state of the catalyst surface due to the establishment of acid-base equilibrium [11, 23]. The ionization state change affects not only the adsorption mode of reaction molecules, but also the selectivity of the reaction [24], since redox reactions in the photochemical process are sensitive to variations in the surface potential [25]. Furthermore, addition of a proper electron-acceptor or -donor to the reaction solution inhibits the electron-hole recombination and therefore increases the photocatalysis efficiency [11].

The semiconductor $InVO_4$ has narrow band gap of 2.0 eV [26, 27], which is able to induce hydrolysis of water molecules under visible light. In this work, the photocatalytic activity of $InVO_4$ nanoparticles and $InVO_4$ -TiO₂ nanocomposite in the degradation of azo dyes under visible light and ultrasonic irradiation is compared.

Experimental

Materials

Indium chloride (InCl₃/Aldrich), sodium metavanadate (NaVO₃/Merck), sodium hydroxide (NaOH/Merck), titanium tetraisopropoxide (TTIP, 98 %, Merck), isopropyl alcohol (Merck), SR 3BL (Ciba-Geigy), CNB RL (Merck), and BN 2BC (Merck) were used as received without further purifications. The pH value of solutions was adjusted with 0.05 mol L^{-1} HCl and 0.2 mol L^{-1} NaOH solutions and doubly distilled water was used for dye solution preparation. Preparation of orthogonal InVO₄ nanoparticles

A solution of NaVO₃ (6.1 ml, 1 M) was added dropwise into a solution of $InCl_3$ (5.5 ml, 1 M) by vigorous stirring. The pH of the solution was adjusted to about 7.9 using NaOH solution (2 M). The solution was stirred for 80 min and transferred into polytetrafluoroethylene reaction vessels and kept at 150 °C for 4 h. After cooling to room temperature, the powders were collected by filtration, washed with deionized water several times and dried at 60 °C [28].

Preparation of InVO₄-TiO₂ nanocomposite

A typical method for the preparation of $InVO_4-TiO_2$ nanocomposites is as follows: titanium tetraisopropoxide (TTIP, 98 %, 20 mmol) was dissolved in isopropyl alcohol (392 mmol). A suspension of $InVO_4$ (0.13 mmol) in water (44 mmol), was added dropwise into the TTIP solution. The pH of the resulting mixture was adjusted to 1–2 using HCl solution (8 M) and stirred at room temperature for 1 h. The mixture was heated to 45 °C until homogeneous $InVO_4-TiO_2$ hydrogel was formed. The hydrogel was transferred into an autoclave, and heated up to 200 °C with a rate of 2 °C min⁻¹. Finally, the temperature was kept at 200 °C for 1 h. The hydrogel was cooled to room temperature and dehydrated slowly at 50 °C in vacuum for 24 h. The dried gel was washed with hot water and dried at room temperature.

Estimation of the point of zero charge (PZC) of $InVO_4$ and $InVO_4\text{--}TiO_2$

PZC of prepared catalyses was estimated according to the pervious literature [29].

Instrumentation

The crystal structures of the catalysts ($InVO_4$ and $InVO_4$ – TiO₂) were investigated by X-ray diffraction (X-ray diffractometer, Bruker, D8ADVANCE, Germany) with Cu K α radiation. Scanning electron micrographs (SEM) were carried out with a Philips XL30 field emission microscope using an acceleration voltage of 20 kV. The specific surface area of catalysts were determined by BET (Brunauer–Emmett–Teller) measurement were carried out at low temperature by adsorption of N_2 gas with an ASAP 2000 micromeritics instrument.

The diffuse reflectance UV–Vis experiments were performed on a Varian Lary 5E diode array spectrometer equipped with a 60-mm Hitachi integrating sphere accessory. The pH values of the solutions were measured using a digital pH-meter (Metrohm 827). The pH-meter was calibrated with standard buffers at 25 °C (pH 4.0 and 7.0). The UV–Vis spectra of the solutions were recorded by a UV–Vis spectrophotometer (160 Shimadzu, Japan). The mineralization percent of azo dyes was estimated by total organic carbon (TOC) analysis. In this regard, TOC curves were obtained with a Beckman 915A analyzer.

Photodegradation experiments

The SR 3BL, CNB RL and NB 2BC dyes solutions were prepared by dissolving 0.02, 0.05 and 0.10 g of dyes in 1 L of deionized water, respectively. A photoreactor was designed with a cylindrical quartz cell configuration and an internal light source surrounded by a quartz jacket, where the suspension of the catalyst and aqueous dyes completely surrounded the light source. The temperature of the suspension was maintained at 25 ± 1 °C by water circulation through an external cooling coil. The optical pathlength was ca. 2 cm. The light source was a 400 W Na lamp ($\lambda > 450$ nm).

A general photocatalytic method was carried out as the following: $InVO_4$ or $InVO_4$ -TiO₂ (5 mg) was suspended in fresh aqueous dye solution (10 ml). The suspension was stirred in the dark for 30 min to investigate the amount of dispersion and adsorption in the absence of light. Due to



Fig. 1 XRD patterns of a InVO₄, b InVO₄-TiO₂ and c TiO₂

the amount of photocatalyst used for degradation of dyes (5 mg), no adsorption and/or degradation were observed in the dark. Based on these results, we concluded that the presence of visible light has a significant role in the degradation of dyes. Besides, control experiments involving a solution of azo dyes under visible light or ultrasonicate irradiation in the absence of each photocatalyst were carried out. The results showed that in the absence of photocatalyst, no degradation was observed. The lamp was inserted around the suspension after its intensity became stable. Photodegradation of dye was carried out in an open vessel in the batch photoreactor. After the reaction was over, the photocatalyst was filtered, and the photolyte was analyzed by UV–Vis spectrophotometer at its λ_{max} .

In the case of FAD, 100 mg of catalyst was added to 10 ml of 1,000 ppm solution in a photochemical cell. The mixture then was exposed to visible light for 120 min.

General procedure for degradation of azo dyes under ultrasonic irradiation

A UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe, immersed directly into the reaction mixture, was used for sonication. The operating frequency was 24 kHz and the output power was 0–400 W through manual adjustment. The total volume of the solution was 10 ml.

InVO₄ or InVO₄–TiO₂ (5 mg) was suspended in fresh aqueous dye solution (10 mL). Then, the solution was sonicated by ultrasonic waves. Photodegradation of dye was carried out at atmospheric pressure in a batch photoreactor. The temperature of the suspension was maintained at 25 ± 1 °C by water circulation through an external cooling coil. After the reaction was done, the photocatalyst was filtered, and the photolyte was analyzed by UV–Vis spectrophotometer at λ_{max} for each dye.

The degradation efficiency (%) was calculated by following formula:

Efficiency(%) =
$$(C_0 - C/C_0) \times 100$$
 (1)

where C_0 is the initial dyes concentration and C is the concentration of dyes after irradiation.

Kinetic measurements for degradation of azo dyes

The degradation rate of SR 3BL, CNB RL and NB 2BC at any specified condition was followed by spectrophotometric measurements with the time profile of the absorbance being at their λ_{max} (according to Table 2). All of the measurements were done three times and the mean values of data were reported.

The observed pseudo-first order degradation rate constants, k_{obs} , can be calculated from the slopes of the



Fig. 2 SEM images of a InVO₄, b InVO₄-TiO₂

natural-logarithmic plots of the drug fraction remained versus time in accordance with Eq. (2):

$$\ln(C_t/C_0) = -k_{\rm obs}t\tag{2}$$

where C_0 is the initial concentration and C_t is the remaining concentration of azo dye at time *t*. According to the Beer-Lambert law, the absorption (A) of a dissolved substance is a linear function of its concentration. Therefore, the pseudo-first order rate constants, k_{obs} , were calculated from the slopes of the natural-logarithmic plots of absorption versus time.

Results and discussion

Catalysts characterization

The XRD technique was used to investigate the phase structures of the samples. The XRD pattern of the as-prepared $InVO_4$, $InVO_4$ -TiO₂ and TiO₂ samples are shown in Fig. 1. The XRD peaks in Fig. 1a correspond to the orthorhombic phase of $InVO_4$. The peak at 32.9° was used for calculation of the mean crystallites size. In Fig. 1b, five distinctive TiO₂ peaks are found at 25.3°, 37.9°, 48.0°, 54.6° and 62.8°, which correspond to anatase (101), (103, 004 and 112), (200), (105 and 211), (204) crystal planes, respectively. This XRD pattern is the same as XRD pattern of pure TiO₂ (Fig. 1c), which indicates that the TiO₂ has retained its crystallinity upon mixing with InVO₄ and no change in its crystallinity was observed during the preparation of nanocomposite. According to XRF results, the amount of InVO₄ is low (<5 %) and obviously it does not present in the XRD pattern of InVO₄–TiO₂.

The crystal size of the InVO₄ and InVO₄–TiO₂ species were calculated by Scherer equation. The particle sizes were about 39–45 nm and 12–15 nm for InVO₄ and InVO₄–TiO₂, respectively, which demonstrate that these compounds are nanoparticles. The BET specific surface area (92 m²/g) of the InVO₄–TiO₂ is larger than those of the pure TiO₂ (64 m²/g) and pure InVO₄ (18.3 m²/g).

Figure 2 presents the SEM images of both pristine $InVO_4$ and $InVO_4$ coated with TiO_2 . As shown in Fig. 2a, b, both photocatalysts have the sizes in nanometer range. The size of the $InVO_4$ particles treated with TiO_2 is similar to that of the pristine $InVO_4$. However, the surface of the TiO_2 -coated $InVO_4$ was smoother compared with that of pristine $InVO_4$.

Figure 3 shows the UV–Vis diffusion reflectance spectra of $InVO_4$ and $InVO_4$ –TiO₂ photocatalysts. In comparison with $InVO_4$ –TiO₂ whose absorption edge is about 520 nm, the $InVO_4$ showed an obvious absorption in visible light region at 650 nm. The band gap of the compound, which was estimated from the absorption edge, is about 2.0 eV. This value is much narrower than observed values for the 4d (4th row transition metals) compounds such as $InNbO_4$ (2.5 eV) and 5d (5th row transition metals) compounds such as $InTaO_4$ (2.6 eV) [30]. In addition, the absorption



Fig. 3 UV-vis diffusion reflectance spectra of $InVO_4$ (solid line) and $InVO_4$ -TiO₂ (dash line)

Name	Structure	MW (g mol ⁻¹)	$\lambda_{max}(nm)$	Dye concentration $(mg L^{-1})$
SR 3BL	NaSO3-N=N-N=N-NCOH NaSO3-2	1,373	530	20
CNB RL	NH ₂ OH NH ₂ OH N N SO ₃ Na N N COONa 2	1,110	570	50
NB 2BC	N=N-N=N-N=N-N-N-N-N-N-N-N-N-N-N-N-N-N-N	731.26	570	100

edge of $InVO_4$ -TiO₂ is more than pristine TiO₂ (absorption edge ~400 nm), that demonstrates coating $InVO_4$ with TiO₂ cause to improve TiO₂ band gap.

Degradation of azo dyes

Table 1 summarized the structure, characteristics and concentration of the azo dyes.

First, the reaction parameters (i.e., pH, irradiation time, temperature, amount of catalyst, and ultrasonic intensity) were optimized and their optimum values are presented in Table 2.

Effect of pH

In Fig. 4, the degradation efficiency of CNB RL in the presence of $InVO_4$ and $InVO_4$ -TiO_2 under visible light and ultrasonic irradiation at different pH values is shown. Similar patterns were obtained for other azo dyes that due to brevity are not shown here. It was found that the degradation of these dyes by $InVO_4$ and $InVO_4$ -TiO_2 are pH dependent and increased by decreasing pH. This can be explained by the point of zero charge (PZC) of $InVO_4$ and $InVO_4$ -TiO_2 nanopowders and a difference in the adsorption ability of $InVO_4$ and $InVO_4$ -TiO_2 nanopowders are almost at pH 4.9 and 7.8, respectively. While above these pH values, the surface of these catalysts is negatively

Table 2 The optimum values of different factors for degradation ofSR 3BL, CNB RL and BN 2BC at different conditions

Conditions	Azo dye	Visible light		Ultrasonic irradiation	
		InVO ₄	InVO ₄ – TiO ₂	InVO ₄	InVO ₄ – TiO ₂
рН	SR 3BL	3.0	7.2	3.1	7.2
	CNB RL	3.5	7.4	3.8	7.4
	BN 2BC	3.1	7.4	3.3	7.4
Irradiation	SR 3BL	15	15	1	1
time (min)	CNB RL	15	15	1	1
	BN 2BC	15	15	1	1
Temperature	SR 3BL	25	25	25	25
(°C)	CNB RL	25	25	25	25
	BN 2BC	25	25	25	25
Catalyst amount	SR 3BL	5	5	5	5
(mg)	CNB RL	5	5	5	5
	BN 2BC	5	5	5	5
Ultrasonic	SR 3BL	-	-	100	100
intensity (%)	CNB RL	-	-	100	100
	BN 2BC	_	_	100	100

charged, below these, it is positively charged. The ionic compounds like SR 3BL, CNB RL and BN 2BC bearing negative charge can easily be adsorbed on the surface of $InVO_4$ and $InVO_4$ -TiO₂ below pH 4.9 and 7.8,



Fig. 4 Influence of the initial pH on the degradation percent of CNB RL (50 mg L^{-1}) solution in various conditions

respectively. Moreover, the degradation of SR 3BL, CNB RL and BN 2BC in acidic medium is favorable and due to the electrostatic repulsion, the adsorption ability of $InVO_4$ and $InVO_4$ -TiO₂ nanoparticles rapidly decreases in basic medium.

Effect of the time

The degradation percent of 50 mg L^{-1} CNB at optimum pH values by InVO₄ and InVO₄-TiO₂ under visible light and ultrasonic irradiations is shown in Fig. 5a, b, respectively. The degradation percent under visible light in the presence of InVO₄ powder increased by increasing the irradiation time and after 5 min, the degradation yield of CNB RL was about 42 %. While due to the synergistic effect between the two phases, the degradation percent in the presence of InVO₄-TiO₂ powder was 98 % at the same time. In addition, there was an increase in the photocatalytic activity of InVO₄ and InVO₄-TiO₂ under ultrasonic irradiation than visible light irradiation. The chemical effect of high intensity ultrasound primarily results from acoustic cavitation: the formation, growth, and impulsive collapse of bubbles in liquids. Ultrasound affected the degradation rate of organic dyes from three different phenomena. First of all, ultrasound may induce the deaggregation of the photocatalyst, leading to an increase in its surface and thus in its catalytic performance. Then, it induces mass transport acceleration of chemical species between the solution phase and the photocatalyst surface and vice versa. The main effect of ultrasound is to contribute through cavitation to scissor the H_2O_2 produced by this method. Thus, ultrasonic irradiation promotes the generation of radicals in the reaction media. On the other hand, collapse of the produced bubbles results in generation of high temperature and pressure. Therefore, the reaction can be accelerated under ultrasonic irradiation [31].



Fig. 5 Influence of irradiation time on degradation percent of CNB RL (50 mg L^{-1}) solution under **a** visible light and **b** ultrasonic irradiation



Fig. 6 Initial degradation of CNB RL (50 mg L^{-1}) solution at 25 °C in the presence of InVO₄ and InVO₄–TiO₂ at λ max (570 nm)

Table 3 Pseudo-first order degradation rate constants (*k*) for the photodegradation of different azo dyes under visible light and ultrasonic irradiation in presence of $InVO_4$ and $InVO_4$ -TiO₂

Azo dye	Visible ligh	nt	Ultrasonic irradiation	
	$\frac{\text{InVO}_4}{k \text{ (min}^{-1})}$	$InVO_4-TiO_2 k (min^{-1})$	$\frac{\text{InVO}_4}{k \ (\text{s}^{-1})}$	$InVO_4-TiO_2 k (s^{-1})$
$\frac{\text{SR 3BL}}{(20 \text{ mg } \text{L}^{-1})}$	0.0969	0.164	0.035	0.011
$\begin{array}{c} \text{CNB RL} \\ (50 \text{ mg } \text{L}^{-1}) \end{array}$	0.0582	0.055	0.011	0.002
BN 2BC (100 mg L ⁻¹)	0.0506	0.067	0.006	0.002



Fig. 8 Influence of ultrasonic power on degradation percent of CNB RL (50 mg L^{-1}) solution

was investigated in the range of 25-80 °C. The results

showed that temperature effect on degradation yield is negligible. Thus, the 25 °C was introduced as optimum

temperature. The influence of temperature on degradation

percent of CNB RL under different conditions is shown in

Kinetics study Figure 6 shows the variations of $\ln(C_0/C_t)$ at λ_{max} versus time for CNB RL (50 mg L⁻¹) solution at 25 °C in the presence InVO₄ and InVO₄–TiO₂ under visible light. The high correlation coefficient of lines can be taken as pronounced evidence for pseudo-first order degradation kinetics. Similar plots have been obtained for SR 3BL (20 mg L⁻¹), and BN 2BC (100 mg L⁻¹). The values of observed pseudo-first order rate constants, k_{obs} , for these azo dyes under visible light and ultrasonic irradiations were collected in Table 3.

Effect of temperature

The prepared SR 3BL (20 mg L⁻¹), CNB RL (50 mg L⁻¹), and BN 2BC (100 mg L⁻¹) at optimum pH values were treated with $InVO_4$ and $InVO_4$ -TiO₂ (5 mg) nanopowders and exposed to visible light and ultrasonic irradiations for 15 and 1 min, respectively. The effect of temperature on the degradation percent of SR 3BL, CNB RL and BN 2BC







Fig. 7.



Fig. 9 TOC reduction during the degradation of BN 2BC at pH 3.3 mediated by combined heterogeneous photocatalysis under visible light, induced by InVO₄

Table 4 Degradation and mineralization efficiency of BN 2BC (100 mg L^{-1} , pH 3.3) by InVO₄ under visible light after prolonged time of irradiation

Time of irradiation (min)	Absorbance	$\begin{array}{c} \text{TOC} \\ (\text{mg } \text{L}^{-1}) \end{array}$	Degradation (%)	Mineralization (%)
0	0.525	39.1	_	_
30	0.016	17.3	96.9	55.7
60	0.015	13.1	97.1	66.5
120	0.010	9.2	98.1	76.5
240	0.005	5.1	99.0	87.0

which in turn enhanced the degradation percent. In addition, the degradation percent increased slightly under ultrasonic irradiation and in the presence of $InVO_4$ -TiO₂ nanopowder by increasing the amount of catalyst.

Effect of ultrasonic intensity

An ultrasonic horn (24 kHz) with different power from 20 to 100 Wcm⁻³ were used to study the effect of US intensity on the degradation of SR 3BL (20 mg L⁻¹), CNB RL (50 mg L⁻¹), and BN 2BC (100 mg L⁻¹) at optimum pH values by InVO₄ and InVO₄–TiO₂. As shown in Fig. 8, the effect of US intensity on the degradation of CNB RL is negligible. For two other azo dyes similar results were obtained.

Mineralization

The total organic carbon (TOC) of BN 2BC solution was monitored during 4 h irradiation with visible light with $InVO_4$. It was observed that the total mineralization

Table 5 Degradation percent of FAD $(1,000 \text{ mg } \text{L}^{-1})$ by InVO₄ and InVO₄–TiO₂ nanopowders under visible light for 120 min

Catalyst	Degradation (
InVO ₄	64.25		
InVO ₄ -TiO ₂	83.17		

increased by increasing the irradiation time (Fig. 9 and Table 4). The absorbance and TOC measurements indicated that degradation of the dye molecule is a relatively fast process but overall degradation is not.

Degradation of FAD

To a solution of FAD (1,000 mg L⁻¹) with the acidic pH, catalyst (100 mg of $InVO_4$ or $InVO_4$ -TiO₂) was added and exposed to visible light for 120 min. The data are listed in Table 5. It was observed that $InVO_4$ -TiO₂ was more efficient in comparison with $InVO_4$ nanopowder. The higher photocatalytic activity of $InVO_4$ -TiO₂ can be illustrated by synergistic effect. Scheme 1 has been proposed for FAD degradation under visible light and ultrasonic irradiation [32].

$$\text{HCHO} + \cdot \text{OH} \to \cdot \text{CHO} + \text{H}_2\text{O} \tag{1}$$

$$\cdot CHO + \cdot OH \to HCOOH \tag{2}$$

$$CHO + \cdot O_2^- \longrightarrow +H^+HCOOOH \longrightarrow +HCHOHCOOH$$

$$\text{HCOOH} \longrightarrow \text{OH or } O_2^- H_2 + CO_2. \tag{4}$$

Relation between phase composition and photocatalytic activity

Considering the consistency of photocatalytic activities and phase compositions, higher photocatalytic activities of mixed-phase TiO₂ can be ascribed to the synergistic effect. On one hand, as confirmed in Fig. 2, the stronger photoabsorption of InVO₄ in the range of wavelengths 650 nm provides more probabilities to promote electrons from valence band into conductive band, which is favorable to produce more electron-hole pairs and hence to form more active hydroxyl and oxygen anion free radicals. On the other hand, in InVO₄-TiO₂, the electron transfer from InVO₄ to TiO₂ phase can reduce the recombination of photogenerated charges. As shown in Fig. 10a, this is because the conductive band of TiO₂ locates at a higher energy position than that of InVO₄. Since InVO₄ has a stronger photoabsorption than TiO₂, there will be more photogenerated carriers in it. For the photocatalysis following free radical mechanism, hydroxyl free radicals are formed by oxidating hydroxyl groups with photogenerated holes. According to the mechanism of photodecomposing FAD and azo dyes (in Fig. 10b, c), more hydroxyl free **Fig. 10** Representation of the drive electron transfer and relative photocatalysis reactions. **a** Bands positions of InVO₄ and TiO₂, **b** the surface bands bending of InVO₄ and TiO₂ during degradation of azo dyes and FAD, **c** mineralization of azo dyes and FAD by oxygen anion free radicals on the surface of TiO₂



radicals are consumed during the formation of formic acid and dye_{OX} , suggesting that more photogenerated holes are consumed. Combined with its faster rate of forming formic acid than TiO_2 , more photogenerated electrons will temporarily accumulate in $InVO_4$. As presented in Fig. 8b, this accumulation of electrons leads to a bigger bending

(upward shift) of conductive band in $InVO_4$ than that in TiO_2 and makes the electron transfer from $InVO_4$ to TiO_2 feasible as expected. After the electron transfer from $InVO_4$ to TiO_2 , oxygen anion free radicals are formed on the surface of TiO_2 phase (Fig. 10c). Due to their strong Lewis base characteristics, formic acid molecule and dye_{OX} can be adsorbed more easily on TiO_2 phase. The electron transfer not only inhibits the recombination of photogenerated charges, but is also favorable for adsorbed compounds to be further oxidized. This can be considered as the activation effect by TiO_2 . Therefore, the relation between phase composition and photocatalytic activity can be ascribed to maximizing the synergistic effect in $InVO_4$ –TiO₂.

Conclusion

Heterogeneous photocatalytic oxidation process using visible light and ultrasonic irradiations can be efficiently applied for the degradation of non-biodegradable azo dyes such as SR 3BL (20 mg L^{-1}), CNB RL (50 mg L^{-1}) and BN 2BC (100 mg L^{-1}). The results clearly delineate the important role of the reaction conditions in achieving the highest degradation efficiency. Photodegradation rate was found to reach maximum value at acidic and neutral medium with 5 mg amount of InVO₄ and InVO₄-TiO₂. The comparison of photocatalytic activity of InVO₄ and InVO₄-TiO₂ clearly indicated that InVO₄-TiO₂ is more efficient for degradation of these azo dyes. Moreover, the photocatalytic activity of InVO₄-TiO₂ is greater in the presence of ultrasonic irradiation compared to visible light irradiation. The photocatalytic degradation shows pseudo-first order kinetics. The TOC analysis revealed that complete mineralization of dyes can be achieved in longer irradiation times.

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