

Application of Enhanced Photocatalytic Activity of Phosphomolybdic Acid upon Hybridization with Hexamine-Cobalt in Fabrication of Visible Light-Driven Titanium Dioxide Nanoparticles

Mehdi Taghdiri^{1,2*}, Ehsan Hassani-Hematabadi¹, Ehsan Mostofi¹, Fatemeh Banifateme¹

¹Department of Chemistry, Payame Noor University, 19395-3697, Tehran, Iran

²Research Center of Environmental Chemistry, Payame Noor University, Tehran, Iran

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Abstract

Phosphomolybdate-hexamine-cobalt (PMA-HMT-Co), a new hybrid prepared by coprecipitation method, was used for coating of titanium dioxide nanoparticles in order to improve photocatalytic activity to visible light. PMA-HMT-Co and TiO₂-PMA-HMT-Co were characterized by Fourier transform infrared spectroscopy, powder X-ray diffraction and scanning electron microscopy. The diffuse reflectance spectroscopy was used to evaluate the band gap variation. The band gap of PMA-HMT-Co decreased and hence, its photocatalytic activity was enhanced under sunlight irradiation. With the incorporation of PMA-HMT-Co, the band gap of titanium dioxide was transferred from UV to visible region successfully. Rhodamine B (RhB) decolorization tests indicated higher photocatalytic activity of TiO₂-PMA-HMT-Co under sunlight irradiation. Photodegradation takes place through the excitation of modified titanium dioxide and the creation of holes (h⁺) and oxidation of dye.

Keywords

Photocatalyst; Titanium Dioxide; Polyoxometalate; Dyes; Organic-Inorganic Hybrid, Solar Light.

1. INTRODUCTION

Until now extensive research has been dedicated to enhancing the photocatalytic performance of TiO₂. However, some of these use valuable and rare metals (e.g. Pt, Pd, Au, Ag, Eu, and Dy) or titanium precursors together with laborious methods (e.g. sol-gel, hydrolysis, and flame spray pyrolysis) [1-3].

There is a possibility of hybridization of TiO₂ with the right components so as to extend its light absorption spectrum and enhance charge carrier separation. There is a great potential for polyoxometalates (POMs), which are inorganic clusters that have unique electronic and redox properties, to be used as co-catalysts [4].

The photocatalytic activity of TiO₂ does not be shifted to visible light through modification with pure POMs but the utilization of organic-inorganic hybrids of POMs can provide this purpose successfully [2]. POMs hybrids show significant properties including (i) low solubility in water and polar solvents, (ii) good adsorption performance [5], (iii) narrower band gaps than pure POMs [6] and hence, (iv) photocatalytic activity in visible

and solar light [1-7] and (v) photo(electro)chemical behavior [8].

POM-based coordination hybrids can be prepared by various transition-metal complexes (TMCs). Ternary photocatalysts containing cobalt have been fabricated with superior visible-light photocatalytic performances [9-10] that used cobalt substituted POMs, organic moieties and TiO₂.

Photocatalysis has been shown to have potential in hybrid materials by integrating cobalt complexes, polyoxometalates (POMs), and TiO₂. Cobalt complexes are good for charge transfer and catalytic activity as they possess redox centres; POM's that act as electron acceptors and electron donors thus enhancing charge separation and stability; and TiO₂ which acts as a wide band gap semiconductor for light absorption and charge formation. The strong oxidation ability of such hybrids can be used to degrade various organic pollutants in water. In addition, it is possible to enhance the rate of degradation and mineralization of pollutants using cobalt complex-POM combinations. Hence, research endeavors must be

* Corresponding author:

continued so as to develop efficient photocatalytic systems that are sustainable based on cobalt complexes-POM-TiO₂ hybrids with multiple applications.

In continuation of our studies on organic-inorganic hybrids of POMs [1, 7], we introduce a new hybrid material prepared by coprecipitation method containing phosphomolybdic acid (PMA, H₃PMo₁₂O₄₀), hexamine or hexamethylenetetramine (HMT), and Co²⁺ as the transition metal linker. In this study, we explore a novel approach to enhance the visible light photocatalytic activity of TiO₂ by hybridizing phosphomolybdic acid (PMA) with hexamine-cobalt (HMT-Co) through a simple coprecipitation method. The resulting PMA-HMT-Co hybrid not only extends the light absorption of TiO₂ into the visible region but also improves the separation efficiency of photogenerated charge carriers. This work aims to demonstrate the synergistic effect of the PMA-HMT-Co hybrid in boosting the photocatalytic performance of TiO₂ under solar irradiation for the degradation of Rhodamine B dye, offering a sustainable and cost-effective solution for environmental remediation. In the pursuit of sustainable and environmentally friendly technologies, the development of photocatalysts that utilize solar energy is of paramount importance. This study investigates the fabrication of a visible light-driven titanium dioxide photocatalyst modified with aforementioned hybrid. By harnessing the power of sunlight, this material offers a promising avenue for the degradation of organic pollutants, contributing to a cleaner and more sustainable future.

2. EXPERIMENTAL

2.1. Chemicals and reagents

The TiO₂ was from Plasma Chem GmbH (Berlin, Germany) with nominal 21±10 nm particle size. Phosphomolybdic acid, NaOH (99%), HCl (aqueous solution, 37 wt. %), Co(NO₃)₂·6H₂O, isopropyl alcohol (99%), benzoquinone and KI were purchased from Merck. The HMT (C₆H₁₂N₄, 99.5%) was from Sina Chemical Industries Co. (Shiraz, Iran). Other reagents were purchased from commercial sources, and used without further purification.

2.2. Apparatus

An analytical balance model Sartorius MCBA 100 (±0.0001 g) was used for weighing of materials. Stirring of solutions was performed using an ISOLAB magnetic stirrer model 613-03. The solutions pH was measured by a HACK HQ-40d pH-meter. For spectrophotometric measurements, a HACK UV-Vis spectrophotometer model DR6000 was used. A Shimadzu 8400s

spectrometer was used for recording FTIR spectra of samples after dilution in KBr. Powder X-ray diffraction patterns were collected on a Bruker D8 advance X-ray diffractometer using Cu target at room temperature. C, H and N elemental analyses were conducted on Perkin-Elmer 2400 CHN elemental analyzer. Solid state diffuse reflectance spectrum (DRS) was tested on an Avantes spectrometer (AvaSpec-2048-TEC) and BaSO₄ as the reference material. Scanning electron microscopy (SEM) was performed using scanning electron microscope SEM PHENOM and TESCAN VEGA Model.

2.3. Preparation of organic-inorganic hybrid

PMA-HMT-Co was prepared as following: 5 mL ethanolic solution of HMT (2.0 % w/w) was added to 5 mL aqueous solution of Co(NO₃)₂·6H₂O (4.0 % w/w). Then, 5 mL ethanolic solution of PMA (13.0 % w/w) was added to the mixture of HMT and Co²⁺. A yellow suspension solution was produced immediately. The mixture was stirred at 500 rpm using a hot plate magnetic stirrer at ambient temperature for 3 h. The suspension was centrifuged and washed with distilled water and then dried in an oven at 100 °C.

2.4. Preparation of TiO₂-PMA-HMT-Co

TiO₂-PMA-HMT-Co was obtained by adding 0.195 g PMA-HMT-Co to 50 mL MB solution (134 mg L⁻¹) and the pH of the mixture reached 2.5 by adding dilute HCl solution. Then, 0.195 g TiO₂ was added to it and the solution was stirred for 6 h. At the end, the precipitate was filtered and dried in an oven for 3 h, at 100 °C.

2.5. Photocatalytic degradation of RhB

RhB solutions with defined concentrations were prepared. The pH of the solutions was adjusted on the desired values by adding dilute HCl and NaOH solutions. The specific amount of photocatalysts were added to the dye solutions in a beaker, capped by cellophane and exposed to sunlight irradiation in consecutive sunny days in September between 11 a.m. and 3 p.m. (GPS coordinates: N = 31° 58', E=55° 40'). It should be noted, the solutions were not stirred during solar irradiation. The decolorization values of dye solutions were calculated by the following formula:

$$D = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

Where D is decolorization percent; C₀, A₀ and C, A are the concentration and absorbance of dye solution at maximum wavelength before and after irradiation, respectively. The pseudo-first-order kinetic (Equation 2) was used for the kinetic analysis of decolorization.

$$\ln \frac{C_0}{C_t} = \ln \frac{A_0}{A_t} = kt \quad (2)$$

Where A_0 and C_0 is the initial absorbance and concentration of dye solution; A_t and C_t is the absorbance and concentration of dye solution at time t , and the slope k is the kinetic constant in min^{-1} . All C_0/C_t values were evaluated through the maximum absorption in order to plot $\ln(C_0/C_t)$ vs. t .

3. RESULTS AND DISCUSSION

3.1. Characterizations of compounds

The stoichiometric formula of $\text{Co}_7[\text{C}_6\text{H}_{12}\text{N}_4]_{15}[\text{PMo}_{12}\text{O}_{40}]_4(\text{NO}_3)_2 \cdot 40\text{H}_2\text{O}$ was suggested for PMA-HMT-Co from the carbon, hydrogen and nitrogen elemental analyses (C, 10.18%; H, 2.45%; N, 8.16%). On the basis of this composition, the calculated elemental analyses (C, 10.15%; H, 2.46%; N, 8.16%) are in good agreement with the proposed formula.

The FTIR spectra of HMT, PMA, PMA-HMT-Co, TiO_2 and TiO_2 -PMA-HMT-Co are shown in Fig. 1. The IR spectrum of PMA-HMT-Co exhibits the characteristic bands of the HMT organic moieties and of PMA inorganic moieties [11, 12]. The strong absorption peaks at $1100\text{-}750\text{ cm}^{-1}$ show the presence of $\text{PMo}_{12}\text{O}_{40}^{3-}$ anions with α -Keggin structure. The band of about 880 cm^{-1} is related to the Mo-O_b-Mo stretching mode of PMA while the band of about 970 cm^{-1} corresponds to its Mo-O_a scissoring mode [12]. The band at 1392 cm^{-1} has been assigned to uncoordinated NO_3^- ion [13]. The main bands of PMA-HMT-Co are observed in TiO_2 -PMA-HMT-Co spectrum, confirming the incorporation of hybrid into TiO_2 .

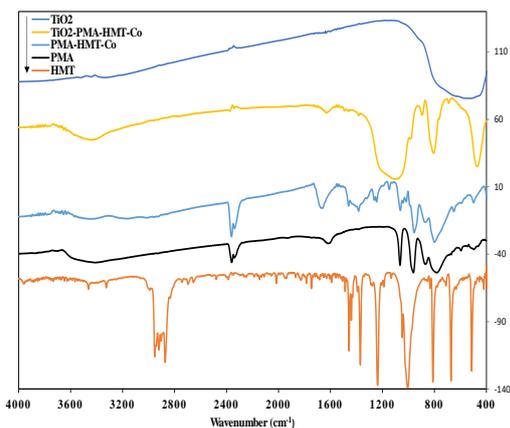


Fig. 1. FTIR spectra of HMT, PMA, PMA-HMT-Co, TiO_2 and TiO_2 -PMA-HMT-Co.

The XRD patterns of PMA, TiO_2 (asntase) and TiO_2 -PMA-HMT-Co are depicted in Fig. 2. The presence of typical peaks of TiO_2 , $\text{PMo}_{12}\text{O}_{40}^{4-}$, HMT and Co is evident from XRD patterns [12, 14-15]. The characteristic diffraction peaks of TiO_2 -PMA-HMT-Co resembled to TiO_2 (asntase) (Reference code: 96-900-9087) and Co (Reference code: 96-901-2939).

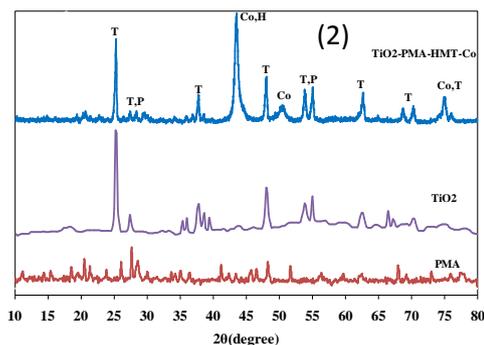


Fig. 2. X-ray diffraction patterns of PMA, TiO_2 and TiO_2 -PMA-HMT-Co.

The band gaps of PMA, PMA-HMT, PMA-HMT-Co and TiO_2 -PMA-HMT-Co were determined from the diffuse reflectance spectra (Fig. 3a) using the Tauc's plot (Fig. 3b). The band gap of PMA decreased due to hybridization (Table 1). The calculated band gap of PMA (2.86 eV) is compatible with the values reported in the literature [16-18]. With the adding of HMT into the PMA structure, the band gap decreased to 2.45 eV in PMA-HMT. With the incorporation of Co into the PMA-HMT, the band gap decreased further down to 2.22 eV in PMA-HMT-Co. The band gap has been shifted from preliminary visible region (433 nm) into middle visible region (558 nm). The band gap of TiO_2 (asntase) was transferred from 3.20 eV (387 nm) to 2.60 eV (477 nm) due to the incorporation of PMA-HMT-Co. SEM images of TiO_2 -PMA-HMT-Co are shown in Fig. 4 that exhibits TiO_2 nanoparticles.

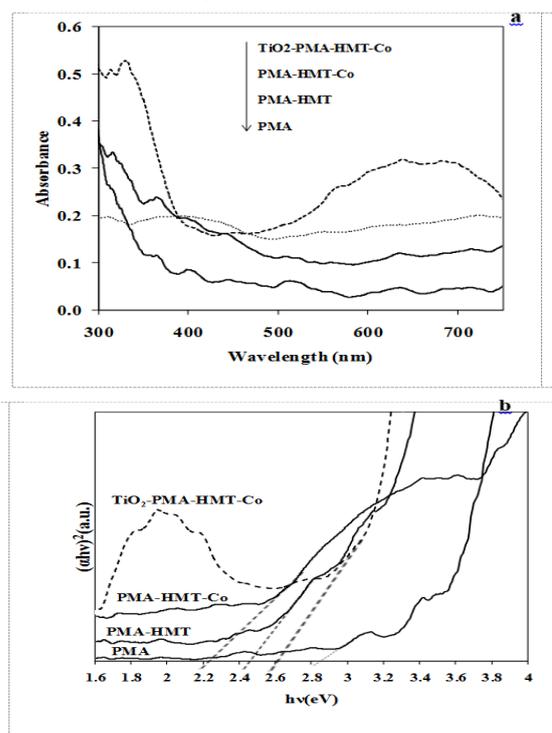
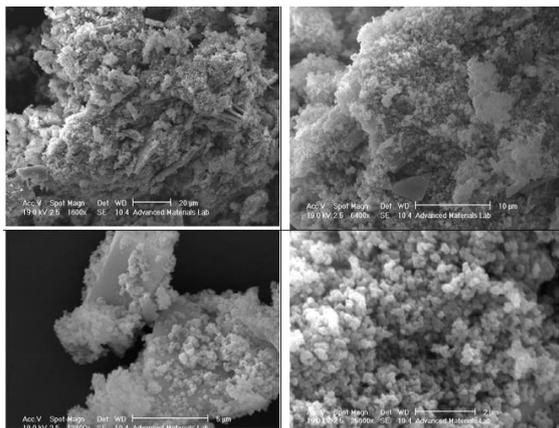


Fig. 3. DRS spectra (a) and Tauc's plots (b) of PMA, PMA-HMT, PMA-HMT-Co and TiO_2 -PMA-HMT-Co.

Table 1. Optical band gap and exciting wavelength of PMA, PMA-HMT and PMA-HMT-Co

Sample	Band gap (eV)	λ (nm)
PMA	2.86	433
PMA-HMT	2.45	506
PMA-HMT-Co	2.22	558
TiO ₂ (asntase)	3.20	387
TiO ₂ -PMA-HMT-Co	2.60	477

**Fig. 4.** SEM images of TiO₂-PMA-HMT-Co.

3.2 Photocatalytic experiments

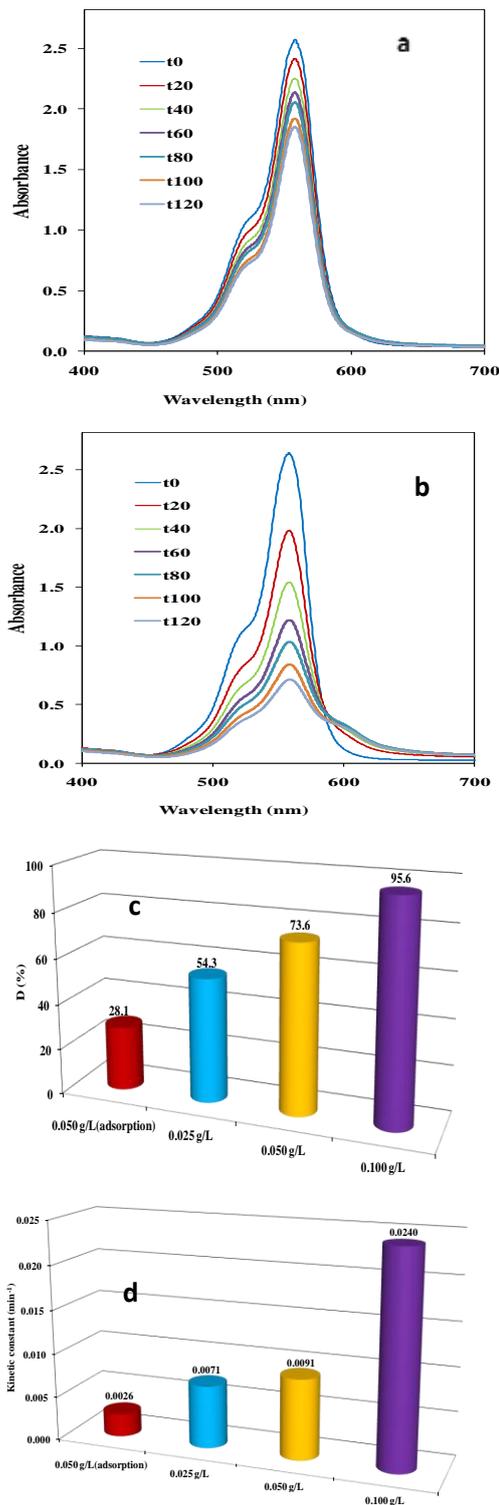
3.2.1. Photocatalytic activity of PMA-HMT-Co

At first, the efficiency of PMA-HMT-Co hybrid was evaluated by removal and degradation of RhB. Before the photocatalytic degradation, adsorption of RhB on the hybrid was evaluated. The hybrid was then tested as catalyst for the photocatalytic degradation of RhB. Results (Fig. 5) show that photocatalytic degradation displays higher kinetic and removal efficiency than adsorption. Moreover, the higher kinetic and removal efficiency was obtained with increase dosage of hybrid. It should be noted, the kinetic and removal efficiency of RhB in the solar photocatalytic process with PMA-HMT-Co are 0.0091 min⁻¹ and 73.6 % respectively, whilst these are 0.0035 min⁻¹ and 32.8 % with PMA-HMT hybrid (Fig. S1).

3.2.2. Photocatalytic activity of TiO₂-PMA-HMT-Co

The TiO₂-PMA-HMT-Co was applied for photodecomposition of RhB under sunlight irradiation. UV-Vis absorption spectra of RhB during the photodegradation under sunlight in the presence of the TiO₂-PMA-HMT-Co have been shown in Fig. 6a. The TiO₂-PMA-HMT-Co is more active than pure TiO₂ toward RhB degradation under solar light (Fig. 6b, c). The effect of photocatalyst dosage was studied using varying quantities of the composite (0.1-0.3 g/L) under solar light. The percent and rate of RhB

decolorization increased with increase of the TiO₂-PMA-HMT-Co concentration (Fig. 6b, c).

**Fig. 5.** UV-Vis absorption spectra of the RhB solution (15 mg/L, pH=1.5) during the adsorption in the dark on 0.05 g/L PMA-HMT-Co (a), during the photodegradation under sunlight in the presence of 0.05 g/L PMA-HMT-Co (b), the degradation percent (c), and the kinetic constants (d).

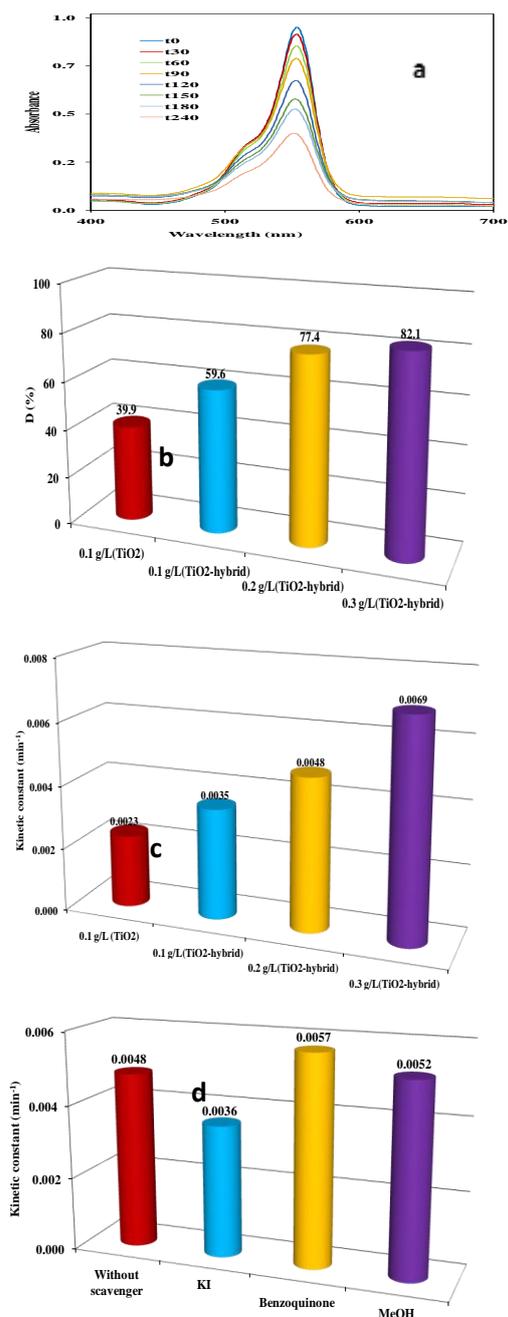


Fig. 6. UV-Vis absorption spectra of the RhB solution (5 mg/L, pH=9) during the photodegradation under sunlight in the presence of 0.4 g/L TiO₂-PMA-HMT-Co (a), the degradation percent for TiO₂ and TiO₂-PMA-HMT-Co (b), the kinetic constants for TiO₂ and TiO₂-PMA-HMT-Co (c), and the kinetic constants in the presence of scavengers for TiO₂-PMA-HMT-Co (d).

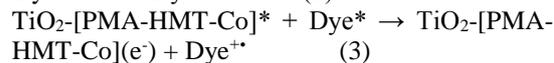
3.3. Mechanism of photodegradation

The decrease of the decolorization rate in the presence of KI, as scavenger of h⁺, indicates the existence of the radical cations of dye (Dye^{•+}) in photodegradation process unlike benzoquinone and methanol (Fig. 6d). A photodegradation

mechanism can be proposed according to following steps:

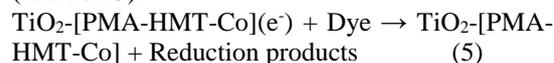
1) Photoexcitation: irradiation of the TiO₂-PMA-HMT-Co with light ($h\nu$) results in the formation of the excited state ([PMA-HMT-Co]^{*}) without significant change on its molecular structure [19]:
 $\text{TiO}_2\text{-PMA-HMT-Co} + h\nu \rightarrow \text{TiO}_2\text{-[PMA-HMT-Co]}^*$ (1)

2) Oxidation of organic compound: the [PMA-HMT-Co]^{*} is a strong oxidant able to oxidize and, most often, mineralize organic dyes [20]. The excited hybrid is reduced with excited organic dye in aqueous solution through reactions 2-4,



Dye^{•+} → ... → decomposition into colorless products (4)

3) Reoxidation of reduced hybrid: The reduced hybrid can be re-oxidized by reduction of dye [21] (reaction 5):



3.4. Comparison with doped TiO₂ photocatalysts

Comparison of TiO₂-PMA-HMT-Co's photocatalytic activity was done with doped TiO₂ photocatalysts in the literature (Table 2). The doping process improved TiO₂ effectiveness by introducing various metals as well as nonmetals. This is shown by the fact that the RhB decolorization efficiency of TiO₂-PMA-HMT-Co is comparable to those of doped TiO₂ photocatalysts. This outcome is realized without use of precious and uncommon metals such as Pt, Ag, Ce, Sm, La and Gd and without using complicated methods like sol-gel, hydrothermal and solvothermal techniques.

4. CONCLUSIONS

This study provides a foundation for understanding the potential of TiO₂-PMA-HMT-Co hybrid. The incorporation of amine organic ligand (HMT) and transition metal linker (Co²⁺) are an effective strategy for solidification and photocatalytic activity improvement of phosphomolybdic acid. The PMA-HMT-Co hybrid indicated narrower band gap than PMA-HMT and PMA. The integration of PMA-HMT-Co into titanium dioxide nanoparticles shifts the band gap of TiO₂ toward visible region, thereby facilitating the solar light driven photocatalysis. The ability to degrade organic pollutants highlights the versatility of this photocatalyst. This modified TiO₂ can compete with doped TiO₂ photocatalysts without using expensive materials and complex methods in their preparation.

Table 2. Comparison of photodegradation of RhB by using doped TiO₂ photocatalysts reported in the literature and TiO₂-PMA-HMT-Co

Catalysts	Light	C _{dye} (mg/L)	Catalyst dosage (g/L)	Time (min)	Decolorization (%)	Ref.
Ag-TiO ₂	UV	RhB (20)	0.15	50	98.7	[22]
La-N-TiO ₂	UV	RhB (10)	0.05	120	80	[23]
Pure-TiO ₂	UV-Vis.	RhB (10)	0.3	180	39	[24]
Pt-TiO ₂	UV-Vis.	RhB (10)	0.3	180	63	[24]
Pt-TiO ₂	UV-Vis.	RhB (10)	1.0	90	99.5	[25]
Ni-TiO ₂	UV-Vis.	RhB (10)	0.3	180	57	[24]
Ni-Pt-TiO ₂	UV-Vis.	RhB (10)	0.3	180	54	[24]
Fe-TiO ₂	Vis. (420 nm)	RhB (10)	1.0	30	90	[26]
Zr-TiO ₂	Vis. (420 nm)	RhB (5)	1.0	90	65	[27]
C-S-N-Fe-TiO ₂	Vis.	RhB (4.8)	0.3	150	36	[28]
Ce-Sm-TiO ₂	Vis.	RhB (10)	-	30	98	[29]
N-TiO ₂	Vis.	RhB (20)	0.3	60	98	[30]
Gd-N-TiO ₂	Vis.	RhB (25)	1.0	120	81.4	[31]
Mn-N-TiO ₂	Vis.	RhB (-)	1.0	180	95.3	[32]
Cu-N-TiO ₂	Vis.	RhB (10)	0.2	240	70	[33]
Mo-C-TiO ₂	Vis.	RhB (20)	1.0	360	94	[34]
Pure-TiO ₂	Sunlight	RhB (50)	0.5	240	30	[35]
Bi-TiO ₂	Sunlight	RhB (50)	0.5	240	43	[35]
Ce-TiO ₂	Sunlight	RhB (20)	0.5	240	77	[36]
Sm-TiO ₂	Sunlight	RhB (30)	-	120	89	[37]
TiO ₂ -PMA-HMT-Co	Sunlight	RhB (5)	0.3	240	82.1	This work

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استفاده از افزایش فعالیت فوتوکاتالیستی فسفومولیبدیک اسید پس از هیبریداسیون با هگزامین-کبالت به منظور ساخت نانوذرات تیتانیوم دی اکسید فعال در نور مرئی

مهدی تقدیری^{۱،۲*}، احسان حسنی همت آبادی^۱، احسان مستوفی^۱، فاطمه بنی فاطمه^۱

^۱ گروه شیمی، دانشگاه پیام نور، صندوق پستی ۳۶۹۷-۱۹۳۹۵، تهران، ایران

^۲ مرکز پژوهشی شیمی محیط زیست، دانشگاه پیام نور، تهران، ایران

* E-mail: taghdiri@pnu.ac.ir, mehditaghdiri@yahoo.com

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چکیده

فسفومولیبدات-هگزامین-کبالت (PMA-HMT-Co)، یک هیبرید جدید تهیه شده به روش هم رسوبی، برای پوشش نانوذرات تیتانیوم دی اکسید به منظور بهبود فعالیت فوتوکاتالیستی در برابر نور مرئی استفاده شد. PMA-HMT-Co و TiO₂-PMA-HMT-Co با طیفسنجی زیرقرمز تبدیل فوری، پراش پودر اشعه ایکس و میکروسکوپ الکترونی روبشی شناسایی شدند. طیفسنجی بازتاب پخشی برای محاسبه شکاف نواری استفاده شد. شکاف نواری PMA-HMT-Co کاهش یافت و از این رو، فعالیت فوتوکاتالیستی آن تحت تابش نور خورشید افزایش یافت. در اثر پوشش تیتانیوم دی اکسید با فسفومولیبدات-هگزامین-کبالت، شکاف نواری تیتانیوم دی اکسید با موفقیت از ناحیه فرابنفش به مرئی منتقل شد. آزمایش‌های رنگ‌زدایی رودامین بی (RhB) فعالیت فوتوکاتالیستی بالاتر TiO₂-PMA-HMT-Co را تحت تابش نور خورشید نشان داد. تخریب نوری از طریق تحریک تیتانیوم دی اکسید اصلاح شده و ایجاد حفره (h⁺) و اکسیداسیون رنگ صورت می‌گیرد.

کلید واژه‌ها

فوتوکاتالیست؛ تیتانیوم دی اکسید؛ پلی اکسومتالات؛ رنگ‌ها؛ هیبرید آلی-معدنی؛ نور خورشید.