光诱导聚合制备聚噻吩/二氧化钛复合粒子的结构及光催化性能

徐守斌, 江 龙, 杨海刚, 宋远卿, 淡 宜*

四川大学高分子研究所, 高分子材料工程国家重点实验室, 四川成都 610065

摘要: 通过光诱导噻吩在 TiO_2 的氯仿悬浮液中聚合反应, 制备了聚噻吩/二氧化钛 (PTh/ TiO_2) 复合粒子, 并采用比表面积分析仪、扫描电子显微镜、粒径分析仪、X 射线光电子能谱、紫外-可见漫反射光谱和红外光谱对复合粒子进行了表征。结果表明, PTh/ TiO_2 复合粒子上的聚噻吩骨架中 S 原子与 TiO_2 粒子间存在强相互作用, 该复合粒子对可见光具有响应。以罗丹明 B 为模型污染物, 研究了该复合粒子在紫外光和可见光照射下的光催化活性。分别以乙二胺四乙酸二钠和呋喃甲醇为空穴捕捉剂和自由基捕捉剂研究了 PTh/ TiO_2 复合粒子在紫外光和可见光照射下的光催化反应机理。结果表明, 空穴和自由基是主要的光催化反应中的氧化性物质。在紫外光照射下, 空穴起主要作用; 在可见光照射下, 自由基起主要作用。

关键词: 光诱导聚合; 聚噻吩; 二氧化钛; 复合粒子; 光催化; 罗丹明 B

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*通讯联系人. Tel: (028)85407286; Fax: (028)85402465; E-mail: danyichenweiwei@163.com

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Structure and Photocatalytic Activity of Polythiophene/ TiO_2 Composite Particles Prepared by Photoinduced Polymerization

XU Shoubin, JIANG Long, YANG Haigang, SONG Yuanqing, DAN Yi*

State Key Laboratory of Polymer Materials Engineering of China, Polymer Research Institute of Sichuan University,
Chengdu 610065, Sichuan, China

Abstract: Polythiophene/titanium dioxide (PTh/ TiO_2) composite particles were synthesized via the photoinduced polymerization of thiophene in a TiO_2 -chloroform suspension. The resultant composite particles were characterized by BET analysis, scanning electron microscopy, laser particle size analysis, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS). The XPS spectra indicated that a strong interaction exists between the S sites of the polymer backbone and the TiO_2 particles. The UV-Vis DRS spectra showed that the resultant composite particles are responsive to visible light. The photocatalytic activities of the PTh/ TiO_2 composite particles were examined through the degradation processes of a rhodamine B (RhB) solution under UV irradiation and visible light irradiation. The degradation ratios of the RhB solution were found to be 76% and 98% after UV irradiation (180 min) and visible light irradiation (10 h), respectively. The photocatalysis reactive mechanisms under UV irradiation and visible light irradiation were investigated using disodium ethylenediamine tetraacetate (EDTA-2Na, hole scavenger) and furfuryl alcohol (radical scavenger). The oxidant from the holes and the radicals are competitive. Under UV irradiation, photogenerated holes are the main active species while under visible light irradiation the radicals are the main oxidant for the degradation of RhB.

Key words: photoinduced polymerization; polythiophene; titanium dioxide; composite particle; photocatalysis; rhodamine B

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*Corresponding author. Tel: +86-28-85407286; Fax: +86-28-85402465; E-mail: danyichenweiwei@163.com

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自 1976 年 Carey 等^[1]首次报道采用 TiO_2 在紫外光辐照下降解联苯以来, TiO_2 光催化剂广泛应用于环境治理中。然而, TiO_2 的禁带宽度为 3.2 eV, 只能被仅占太阳光能量 5% 左右的紫外光激发^[2,3], 因而严重限制了 TiO_2 的实际应用。因此, 人们尝试聚合物杂化^[4-6]、离子掺杂^[7,8]、半导体耦合^[9,10]和其它方法^[11-16]来拓宽 TiO_2 的光响应范围。共轭聚合物/ TiO_2 杂化材料在紫外光和可见光辐照下表现出优良的光催化降解有机污染物活性^[4,5,17,18]。目前制备共轭聚合物/ TiO_2 复合光催化材料的方法有原位聚合^[4]、共混^[19]和电化学聚合^[20]。其中在原位氧化聚合过程中引入的 Fe^{3+} 很难完全去除, 而 Fe^{3+} 的存在将降低共轭聚合物中载流子的迁移率^[21]。另外, 共混法得到的复合粒子中共轭聚合物只是简单地沉积在 TiO_2 表面, 使得两者接触不充分而导致稳定性较低, 而杂化材料中稳定的界面结构对光生电荷或电激发电荷的注入是必须的^[22]。

紫外光能够激发 TiO_2 价带的电子到导带, 并在导带留下空穴^[2]。最近的研究表明, 光激发的 TiO_2 纳米粒子能够引发烯烃(如甲基丙烯酸甲酯^[23]和丙烯酸^[24])的自由基聚合。由于该聚合反应是由无机半导体向单体进行电子转移引发, 这使得聚合物与无机半导体间存在着良好的电化学接触^[18,25]。该方法还可用于吡咯/ TiO_2 复合粒子的合成^[25]。我们曾采用光引发聚合法在 TiO_2 氯仿悬浮体系中合成了聚噻吩 (PTh)/ TiO_2 复合粒子。

本文考察了 PTh/ TiO_2 复合粒子的结构及光催化活性, 并分别以乙二胺四乙酸二钠 (EDTA-2Na) 和咪唑甲醇为空穴捕捉剂和自由基捕捉剂, 研究了 PTh/ TiO_2 复合粒子在紫外光和可见光照射下的光催化反应机理。

1 实验部分

1.1 催化剂的制备

将 1 g TiO_2 (99%, 舟山明日纳米材料有限公司) 置于经提纯的 200 ml 氯仿中超声分散 30 min 后, 加入 1 g 噻吩单体 (99%, 成都科龙试剂公司), 再将混合液倒入烧杯, 并用聚乙烯薄膜将烧杯口封闭以避免氯仿和噻吩挥发。所用紫外光源为 10 W 杀菌灯 (TUV 10W, Philips), 中心波长为 253.7 nm。经紫外辐照 24 h 后, 将悬浮液离心分离, 用甲醇 (CP, 成都

科龙试剂公司) 将所得固体进行洗涤, 最后真空干燥 24 h, 即得 PTh/ TiO_2 复合粒子。

1.2 催化剂的表征

采用全自动比表面积和孔隙分析仪 (Micromeritics Tristar 3000) 在 77 K 测定比表面积及孔结构。使用激光粒径分析仪 (Malvern 2000) 测量 TiO_2 和 PTh/ TiO_2 复合粒子的平均粒径。采用 JEOL 公司的 JSM-5900LV 型扫描电镜 (SEM) 观察样品的形貌。使用傅里叶变换红外光谱 (FT-IR) 研究 TiO_2 和 PTh/ TiO_2 复合粒子的基团组成。采用 X 射线光电电子能谱 (XPS) 仪 (XSAM-800 型, KRATOS 公司) 研究 PTh/ TiO_2 复合粒子的表面元素组成和碳元素与钛元素的精细 XPS 谱。在德国 Analutikjena 型紫外可见漫反射光谱 (UV-Vis) 仪上测定 TiO_2 、PTh 和 PTh/ TiO_2 复合粒子的光响应性能。

1.3 催化剂的评价

1.3.1 吸附实验

以罗丹明 B (CP, 成都科龙试剂公司) 为模型污染物, 考察光催化剂的吸附性能和光催化活性。将 300 mg 催化剂加入到装有 300 ml 罗丹明 B 溶液 (40 mg/L) 的烧杯中, 在避光条件下进行吸附实验。一定时间后取等量的样品进行离心分离。

取上层清液, 去离子水稀释 3 倍后, 用紫外-可见分光光度计测量 $\lambda = 553 \text{ nm}$ 处的吸光度 A , 在本文中, 它与罗丹明 B 浓度 C 的关系为: $A = 0.186 C$ 。PTh/ TiO_2 复合粒子对罗丹明 B 的吸附率 (R_1): $R_1 = (C_0 - C_t)/C_0$, 式中, C_0 和 C_t 分别表示初始浓度和 t 时刻浓度。

1.3.2 紫外光和可见光辐照下的光催化反应

光催化反应的实验装置及过程参见文献^[4,19]。紫外光源为上文所用杀菌灯; 以经过 0.01 mol/L 铬酸钾溶液过滤紫外线的卤钨灯 (ENX 82 V 320 W, Fujifilm 公司) 作为可见光源^[19], $\lambda > 425 \text{ nm}$, 辐照强度为 $34 \mu\text{W}/\text{cm}^2$ 。以达吸附平衡时作为光催化反应的起始, 按照上述方法测量反应过程中罗丹明 B 的浓度变化。罗丹明 B 的降解率 $R_2 = (C_0' - C_t')/C_0'$ 。式中, C_0' 和 C_t' 分别为反应开始和 t 时刻的罗丹明 B 溶液浓度。

使用 EDTA-2Na (空穴捕捉剂)^[26] 和咪唑甲醇 (自由基捕捉剂)^[27] 研究光催化过程中的主要氧化性物种。EDTA-2Na 和咪唑甲醇的浓度均为 40 mg/L。

2 结果与讨论

2.1 催化剂的物化性质

TiO₂ 和 PTh/TiO₂ 复合粒子的比表面积和平均孔径见表 1. 可以看出, 两个样品的比表面积和平均孔径差别不大. 这表明 PTh/TiO₂ 复合粒子的合成过程对 TiO₂ 粒子粒径的影响很小.

表 1 TiO₂ 和 PTh/TiO₂ 复合粒子的比表面积和平均孔径

Table 1 BET surface area and average pore size of TiO₂ and the PTh/TiO₂ composites

Catalyst	BET surface area (m ² /g)	Pore size diameter (nm)
TiO ₂	220	8.5
PTh/TiO ₂	193	8.7

PTh—Polythiophene.

图 1 为 TiO₂ 和 PTh/TiO₂ 复合粒子的 SEM 照片. 由图可见, TiO₂ 纳米粒子的粒径为 20~30 nm, 但严重团聚, 尽管 PTh/TiO₂ 复合粒子的粒径也为 20~30 nm, 但其分散性更好. 激光粒度分析也证明了这一点: TiO₂ 在水悬浮液中的平均粒径为 1.9 μm, 而 PTh/TiO₂ 复合粒子为 1.5 μm.

图 1 TiO₂ 和 PTh/TiO₂ 复合粒子的 SEM 照片

Fig. 1. SEM images of TiO₂ (a) and the PTh/TiO₂ composites (b).

为了比较聚噻吩和 PTh/TiO₂ 复合粒子的 FT-IR 谱, 本文采用典型的化学氧化聚合法制备了聚噻吩^[4]. 图 2 为聚噻吩、纯 TiO₂ 和 PTh/TiO₂ 复合粒子的 FT-IR 谱. 可以看出, 聚噻吩在 2800~3100 cm⁻¹ 出现一组弱峰, 归属于噻吩环上碳氢键的伸缩振动; 600~1500 cm⁻¹ 的弱峰是噻吩环的指纹区; 695 和 784 cm⁻¹ 处吸收峰是碳氢键的面外弯曲振动. 在 1406 cm⁻¹ 处吸收峰为 2,5 位取代噻吩环碳碳双键对称或不对称伸缩振动. 而 TiO₂ 中钛氧键吸收峰出现在 436~495 cm⁻¹. PTh/TiO₂ 复合粒子中均出现了 TiO₂ 和聚噻吩吸收峰, 说明所制备样品由聚噻吩和 TiO₂ 组成.

图 2 PTh, TiO₂ 和 PTh/TiO₂ 复合粒子的 FT-IR 谱

Fig. 2. FT-IR spectra of PTh (1), TiO₂ (2), and the PTh/TiO₂ composites (3).

表 2 为聚噻吩、TiO₂ 和 PTh/TiO₂ 复合粒子的表面元素相对含量. 由 XPS 光谱可知, PTh/TiO₂ 复合粒子表面含有 Ti, O, C 和 S 元素; 而纯 TiO₂ 粒子表面只有 Ti, O 和 C (C 由测试环境引入), 没有探测到 S 元素. 这说明 PTh/TiO₂ 复合粒子中 S 元素由聚噻吩引入. 此外, PTh/TiO₂ 复合粒子表面的 Ti/O 比低

表 2 PTh, TiO₂ 和 PTh/TiO₂ 复合粒子的表面元素组成

Table 2 Surface element composition of PTh, TiO₂, and the PTh/TiO₂ composites

Catalyst	Surface element composition (%)			
	Ti	O	C	S
PTh ^[4]	not detected	11.6	74.7	10.5
TiO ₂ ^[4]	25.4	44.0	30.6	not detected
PTh/TiO ₂	12.8	30.2	56.6	0.4

于 TiO_2 表面. 这是由于 PTh/ TiO_2 复合粒子表面包覆了聚噻吩造成的.

图 3 为 PTh/ TiO_2 复合粒子中 S 2*p* 和 Ti 2*p* 的高分辨 XPS 谱. 由图可见, PTh/ TiO_2 复合粒子中 S 2*p* 电子的结合能为 169.11 eV, 这与聚噻吩中 S 原子带的正电荷 ($\text{S}^{\delta+}$) 有关^[28], 与包覆 TiO_2 的聚噻吩中极化子和双极化子传输相一致. 结果表明, PTh/ TiO_2 复合粒子中聚噻吩与 TiO_2 间以电荷转移或硫钛成键的方式存在着强相互作用. 还可以看出, PTh/ TiO_2 复合粒子的 Ti 2*p* 电子结合能可以分为以 458.92 和 464.52 eV 峰值的两个峰, 分别代表 Ti 2*p*_{3/2} 电子和 Ti 2*p*_{1/2} 电子^[28]. PTh/ TiO_2 复合粒子中 Ti 2*p*_{3/2} 电子结合能 (458.9 eV) 较纯 TiO_2 (459.5 eV^[28]) 有所降低. 这也表明聚噻吩骨架中硫原子与 Ti 存在着强相互作用.

图 4 为 PTh, TiO_2 和 PTh/ TiO_2 复合粒子的 UV-Vis 谱. 由图可见, PTh/ TiO_2 复合粒子在 $\lambda = 350\sim 700$ nm 的吸收明显高于纯 TiO_2 . 这是由聚噻吩中 π 电子的 $\pi-\pi^*$ (HOMO-LUMO) 跃迁造成的吸收所致.

2.2 PTh/ TiO_2 催化剂的光催化活性

2.2.1 罗丹明 B 的避光吸附

图 5 为 PTh/ TiO_2 复合粒子上罗丹明 B 吸附率随时间的变化. 由图可见, 罗丹明 B 吸附率约为 18%, 并在 1 h 内达到平衡, 吸附主要在前 10 min 内完成. 这表明 PTh/ TiO_2 复合粒子对阳离子染料罗丹明 B 的吸附源于 PTh/ TiO_2 复合粒子的负电荷.

2.2.2 紫外光辐照下的活性

图 6 为紫外光辐照下 PTh/ TiO_2 复合粒子光催化降解罗丹明 B 的降解率随时间的变化曲线和动

图 4 PTh, TiO_2 和 PTh/ TiO_2 复合粒子的 UV-Vis 谱

Fig. 4. UV-Vis diffuse reflectance spectra of PTh (1), TiO_2 (2), and the PTh/ TiO_2 composite particles (3).

图 5 PTh/ TiO_2 复合粒子对罗丹明 B 的吸附率随时间的变化曲线

Fig. 5. Variation in the adsorption ratio of a RhB solution with experimental time.

力学拟合曲线. 由图可见, 在光照过程中罗丹明 B 降解率逐渐增加, 在前 180 min 即达到 75.6%. 可见 PTh/ TiO_2 复合粒子表现出了较高的光催化活性. 拟合后的动力学曲线的线性相关系数为 0.989. 这表明该反应级数为 1.

图 3 PTh/ TiO_2 复合粒子中 S 2*p* 和 Ti 2*p* 的高分辨率 XPS 谱

Fig. 3. High resolution XPS spectra of S 2*p* (a) and Ti 2*p* (b) in the PTh/ TiO_2 composite particles.

图 6 PTh/TiO₂ 复合粒子紫外光催化过程中罗丹明 B 降解率变化及反应动力学拟合曲线

Fig. 6. Variation in the degradation ratio of the RhB solution with experimental time under UV irradiation (a), and apparent first-order linear transform $\ln(C_0/C_t) = K_{app}t$ of the RhB degradation kinetic plots for the PTh/TiO₂ composites under UV irradiation (b).

2.2.3 可见光辐照下的活性

图 7(a) 为可见光辐照下 PTh/TiO₂ 复合粒子光催化降解罗丹明 B 降解率随时间变化曲线。可以看出, 随着反应的进行, 罗丹明 B 降解率持续升高, 至 10 h 时达 98%, 表明在可见光辐照下 PTh/TiO₂ 复合粒子具有很高的光催化活性。图 7(b) 为拟合后的该反应的动力学曲线, 其线性相关系数为 0.97。这表明该反应为一级动力学反应。

2.3 氧化性物质和光催化机理

2.3.1 紫外光辐照下光催化反应机理

为了研究 PTh/TiO₂ 复合粒子光催化反应机理, 本文分别采用 EDTA-2Na 和呋喃甲醇为空穴捕捉剂和自由基捕捉剂研究了光催化反应过程中主要的氧化性物质。表 3 为各光催化反应过程的速率常数。由表 3 可见, 添加呋喃甲醇或 EDTA-2Na 后, 罗丹明 B 降解反应的速率常数均降低。尤以 EDTA-2Na

为甚。这表明光生空穴是该体系中主要氧化性物质。由于 PTh/TiO₂ 复合粒子表面的聚噻吩能够促使激子分离成空穴和光生电子^[29], 故在紫外光辐照下 PTh/TiO₂ 复合粒子光催化降解罗丹明 B 的速率常数大于纯 TiO₂。图 8(a) 为该过程机理的示意图^[17]。

2.3.2 可见光辐照下光催化反应机理

众所周知, 纯 TiO₂ 粒子不能被可见光激发, 而

表 3 不同条件下 TiO₂ 和 PTh/TiO₂ 复合粒子光催化降解罗丹明 B 的速率常数

Table 3 Apparent rate constants for the degradation of RhB by TiO₂ and PTh/TiO₂ composites.

Experimental condition	Apparent rate constants (h ⁻¹)	
	UV irradiation	Visible light irradiation
TiO ₂	0.307	0.004
PTh/TiO ₂	0.406	0.429
PTh/TiO ₂ + EDTA-2Na	0.059	0.166
PTh/TiO ₂ + furfuryl alcohol	0.168	0.122

图 7 PTh/TiO₂ 复合粒子可见光催化过程中罗丹明 B 降解率变化及反应动力学拟合曲线

Fig. 7. Variation of the degradation ratio of a RhB solution with experimental time under visible light irradiation (a), and apparent first-order linear transform $\ln(C_0/C_t) = K_{app}t$ of the RhB degradation kinetic plots for the PTh/TiO₂ composites under visible light irradiation (b).

图 8 PTh/TiO₂ 复合粒子紫外光和可见光辐照下光催化反应过程的示意图

Fig. 8. Schematic diagram illustrating the photocatalysis process of the PTh/TiO₂ composites under UV light (a) and visible light (b). LUMO: Lowest unoccupied molecular orbital; HOMO: Highest occupied molecular orbital; P: Rhodamine B; VB: Valence band; CB: Conduction band.

将聚合物与 TiO₂ 进行杂化则可使 PTh/TiO₂ 复合粒子吸收可见光. 由表 3 可见, 添加 EDTA-2Na 或吡喃甲醇后, 罗丹明 B 降解反应的速率常数分别降至 0.166 和 0.122 h⁻¹. 这表明自由基是可见光辐照下罗丹明 B 降解过程中的主要氧化物. 根据以上反应结果, 可见光辐照下 PTh/TiO₂ 复合粒子光催化降解罗丹明 B 的机理如图 8(b) 所示. 由于 TiO₂ 的导带电位低于聚噻吩的最低空轨道电位, 聚噻吩最高占用轨道的电子被可见光激发到最低空轨道后向 TiO₂ 导带跃迁, 并处于 PTh/TiO₂ 复合粒子表面^[30]. 这些电子与水反应生成能够氧化罗丹明 B 的羟基自由基和超氧基自由基^[31]. 综上所述, 空穴和自由基都是氧化性物质, 两者存在竞争关系, 在特定条件下其中一种起主要作用.

3 结论

采用光诱导聚合法制备的 PTh/TiO₂ 复合粒子中聚噻吩骨架上 S 原子与 TiO₂ 之间存在强相互作用. 该复合粒子在紫外光或可见光辐照下可有效地降解罗丹明 B. 空穴和自由基是主要的氧化性物质, 且两者存在竞争关系. 在紫外光辐照条件下, 光生空穴是主要的氧化性物质; 在可见光辐照下, 自由基是主要的氧化性物质.

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英 译 文

English Text

Since Carey et al. [1] first reported the results of the photocatalytic degradation of biphenyl by titanium dioxide (TiO₂) with ultraviolet (UV) light irradiation in 1976, there has been an increase in the amount of interest in the environmental application of the TiO₂ photocatalyst. However, the bandgap of TiO₂ (anatase) is 3.2 eV so it can only absorb and be excited by UV light with a wavelength below 387 nm [2]. UV light accounts for < 5% of sunlight [3]. This intrinsic characteristic of anatase restricts its practical application.

To overcome this shortfall, polymer hybridizing [4–6], ion doping [7,8], semiconductor coupling [9,10], and some other measures [11–16] were introduced. Conjugated polymer/TiO₂ hybrid materials exhibit high efficiency in degrading organic pollutants under both UV light and visible light [4,5,17,18]. Several groups have reported in situ polymerization [4], a blend method [19] and electro-polymerization [20] for the preparation of conjugated polymer/TiO₂ composites. The ferric ion that was added during in situ polymerization using FeCl₃ was difficult to eliminate completely. The carrier mobility in the conjugated polymers of the polymers decreases with an increase in the levels of impurities because of scattering by ionized impurities [21]. Using the blend method, it was found to be difficult to obtain electric contact between the metal oxide particles and the conjugated polymer film since the polymer chain may interfere with the connection formed within the metal oxide. Complete hybridization may not be obtained using the penetration method as the polymer may not be filled because of the limited penetration depth of the conducting polymer layer. Because the conjugated polymers simply deposit onto the TiO₂ nanoparticles, the interface between the TiO₂ semiconductor and the conjugated polymer film does not stabilize. A stabilized interface for the heterojunction composite is highly desirable because it favors the rate of charge

injection when imposed by light excitation or electrical stimulation [22].

UV excitation of TiO₂ generates conduction band electrons (e⁻) and valence band holes (h⁺) in pairs giving surface-mediated redox behavior [2]. Recently, it has been shown that photoexcited TiO₂ nanoparticles are capable of catalyzing the free radical polymerization of alkenes such as in methyl methacrylate [23] and acrylic acid [24]. This polymerization method leads to good adhesion for the contact between the polymeric materials and the inorganic materials. The polymers prepared by this technique have good electronic contact with the inorganic semiconductor phase because the polymerization reaction is locally initiated by charge transfer across the inorganic semiconductor-monomer interface [18,25]. This polymerization method has been used to synthesize polypyrrole/TiO₂ composite particles [25]. We thus synthesized polythiophene/titanium dioxide (PTh/TiO₂) composite particles by the photoinduced polymerization of thiophene in a TiO₂-chloroform (CHCl₃) suspension.

In this work, we investigated the oxidative polymerization of thiophene using TiO₂ nanoparticles in chloroform suspensions under irradiation by UV light. The oxidative species generated in the photocatalytic process under UV light irradiation and visible light irradiation was studied by adding disodium ethylenediamine tetraacetate (EDTA-2Na, hole scavenger) and furfuryl alcohol (radical scavenger).

1 Experimental

1.1 Sample preparation

TiO₂ (1 g, 99 %, Zhoushan Mingri Nanometre Material Co., Ltd, China) was dispersed in purified chloroform (200 ml, Chengdu Kelong Chemical Reagents, China) using ultrasonic dispersion (SC-I, Chengdu Jiuzhou Ultrasonic Technology Co., China) for 30 min at room temperature. Thiophene monomer (1 g, 99%, Chengdu Kelong Chemical Reagents, China) was added to the suspension. The mixture was added to a beaker that was equipped with a magnetic stirrer. The beaker was sealed with a polyethylene film (one layer) to prevent a reaction with air and to prevent the evaporation of thiophene and chloroform. UV irradiation was carried out using a germicidal lamp (TUV 10W, 10 W, Philips) with a maximum wavelength of 253.7 nm. After 24 h the suspension was centrifuged. The reacted mixture was washed with methyl alcohol (CP, Chengdu Kelong Chemical Reagents, China), and then dried under vacuum for 24 h.

1.2 Characterization of samples

The BET surface area of TiO₂ and the TiO₂/PTh compos-

ites was determined by the N_2 adsorption method at 77 K using a BET analyzer (Micromeritics Tristar 3000). The mean particle size of TiO_2 and the PTh/ TiO_2 composites was determined using a laser particle size analyzer (Malvern 2000, England). The morphology of TiO_2 and PTh/ TiO_2 was characterized by scanning electron microscopy (SEM, JEOL JSM-5900LV, Japan, operating at 20 kV). The Fourier transform infrared (FT-IR) transmission spectra of the samples were measured on a Nicolet 560 FT-IR spectrometer. KBr pellets were prepared using dried samples and the spectra were collected from 4000 to 400 cm^{-1} . The X-ray photoelectron spectra (XPS) were obtained using a spectrometer (XSAM-800, KRATOS Co., America) with a Mg K_{α} anticathode at 12 kV, 11 mA, and in FAT mode. Ultraviolet-visible (UV-Vis) diffuse reflectance spectra of the TiO_2 , PTh, and PTh/ TiO_2 powders were recorded on a Specord 200 spectrophotometer (Analutikjena, Germany).

1.3 Evaluation of photocatalysis

1.3.1 Adsorption experiments

An aqueous solution of rhodamine B (RhB, CP, Chengdu Kelong Chemical Reagents, China) was used to investigate the adsorption performance and photocatalytic activities of the prepared photocatalysts. The initial RhB concentration (C_0) was 40 mg/L. The adsorption experiments were performed by adding 300 ml of a RhB solution and 300 mg of photocatalyst to a beaker wrapped tightly in a black rubberized fabric, which prevented the suspension from being irradiated by light. The beaker was sealed and the suspension was magnetically stirred throughout the experiments. A portion of a sample was then withdrawn regularly from the reactor and immediately centrifuged at 5000 r/min for 10 min (TDL-5-A centrifuge, Shanghai Anting Scientific Instrument Factory, China) to separate any suspended solid. The change in the concentration of RhB was monitored by measuring the absorbance at $\lambda_{\max}$ (553 nm) with a UV-2300 UV-Vis spectrophotometer (Shanghai Tianmei Scientific Instrument Factory, China). Before the tests, the RhB solution was diluted three times with deionized water.

The adsorption ratio (R_1) of RhB on the PTh/ TiO_2 composite particles can be calculated using $R_1 = (C_0 - C_t)/C_0$, where C_0 is the initial RhB solution concentration and C_t is the RhB concentration at adsorption time t .

1.3.2 Experiments under UV and visible light irradiation

Photocatalysis experiments under UV and visible light irradiation were carried out in two different self-regulating instruments. The instruments and the experimental methods

have been described in detail elsewhere [4,19]. The source of UV was the germicidal lamp mentioned in section 1.1. The source of visible light was a halogen lamp (ENX 82 V 320 W, Fujifilm Co., Japan) that was fitted with a glass bottle, which was filled with a 0.01 mol/L potassium chromate solution [19]. The wavelength of the visible light was $\geq 425\text{ nm}$. The irradiation intensity was $34\text{ }\mu\text{W}/\text{cm}^2$. The change in the concentration of RhB was monitored by the same method described in the adsorption experiments section. The first sample was taken out at the end of the dark adsorption period, just before the lamps were turned on, to determine the RhB concentration in solution, which was hereafter considered to be the initial concentration (C_0') after dark adsorption.

The degradation ratio (R_2) of RhB can be calculated using $R_2 = (C_0' - C_t')/C_0'$, where C_0' is the concentration of the RhB solution when the photocatalytic reaction is initiated and C_t' is the RhB concentration at degradation time t .

Detection of the main oxidant was carried out through radical and hole trapping experiments using EDTA-2Na (CP, Chengdu Kelong Chemical Reagents, China) [26] or furfuryl alcohol (CP, Chengdu Kelong Chemical Reagents, Chengdu China) [27], respectively. The concentration of both EDTA-2Na and furfuryl alcohol were 40 mg/L.

2 Results and discussion

2.1 Characterization results

The specific surface area and average pore size of TiO_2 and the PTh/ TiO_2 composites are listed in Table 1. From Table 1, we can see that the specific surface area and the average pore size did not change greatly. This result indicates that the synthesis process does not change the diameter of the particles.

SEM micrographs of TiO_2 and the PTh/ TiO_2 composites are shown in Fig. 1. From Fig. 1(a), we determined that the diameter of the TiO_2 composites is 20–30 nm. However, these particles are seriously aggregated. The diameter of the PTh/ TiO_2 composites is 20–30 nm too, as shown in Fig. 1(b). The dispersion property of the PTh/ TiO_2 composites is better than that of TiO_2 , as shown by the data obtained using the laser particle size analyzer. The mean particle size of TiO_2 was found to be 1.9 μm . However, the mean particle size of the PTh/ TiO_2 composites decreased to 1.5 μm .

To compare the FT-IR spectra of polythiophene (PTh) and the synthesized composite particles, PTh was prepared using a typical chemical oxidative polymerization of thiophene [4]. The FT-IR transmission spectra of PTh, naked TiO_2 , and the PTh/ TiO_2 composites are shown in Fig. 2. Several low-intensity peaks are present in the FT-IR spectrum of PTh between $2800\text{--}3100\text{ cm}^{-1}$ and this can be attributed to aromatic C–H stretching vibrations. The

600–1500 cm^{-1} region is the fingerprint region of PTh. The peaks at 695 and 784 cm^{-1} are usually attributed to the C–H out-of-plane deformation mode. The peak at 1406 cm^{-1} is a combination of C=C asymmetric and symmetric stretching vibrations of the 2,5-thiophenylene units. From Fig. 2, the FT-IR spectrum of the TiO_2 particles has a characteristic Ti–O–Ti absorption band at 436–495 cm^{-1} . Bands from both TiO_2 and PTh are present in the spectrum of the PTh/ TiO_2 composites. The results show that the composites are composed of PTh and TiO_2 .

The relative ratios of the elements on the surface of PTh, TiO_2 , and the PTh/ TiO_2 composites are shown in Table 2. According to the XPS spectra for the surface of the PTh/ TiO_2 composites, Ti, O, C, and S are present on the surface of the PTh/ TiO_2 composites. From this table, it is apparent that only Ti, O, and C (C from the testing environment) were detected on the surface of the TiO_2 particles while S was not detected. However, S was detected in PTh and the PTh/ TiO_2 composites. The S present is attributed to originating from PTh. The relative content of Ti and O on the surface of the PTh/ TiO_2 composites decreases by comparison with that of the TiO_2 particles because of the coverage of PTh on the surface of the TiO_2 particles.

High resolution XPS analyses of S 2*p* and Ti 2*p* were determined using a Mg K_{α} anticathode with a voltage of 12 kV, an electric current of 11 mA, and in FRR analyzer mode, as shown in Fig. 3. The binding energy of S 2*p* for PTh/ TiO_2 was found to be 169.11 eV, as shown in Fig. 3(a). It is associated with the formation of positively charged sulfur ($\text{S}^{\delta+}$) [28]. This positive charge is consistent with the transport of polarons and bipolarons in the conductive polythiophene chains that cover the TiO_2 particles. This indicates a strong interaction between polythiophene and TiO_2 because of electron transfer from polythiophene to titania, or the formation of bonds between sulfur and oxygen.

As shown in Fig. 3(b), the binding energy of Ti 2*p* in PTh/ TiO_2 can be deconvoluted into two peaks centered at 458.92 eV and 464.52 eV. These two peaks are assigned to Ti 2*p*_{3/2} and Ti 2*p*_{1/2} [28]. A small shift to the lower value of the Ti 2*p* binding energy (458.9 eV) of PTh/ TiO_2 is apparent compared to the naked TiO_2 (459.5 eV [28]). This also reflects the strong interaction between the S sites of the polymer backbone and the TiO_2 nanoparticles, in which electron transfer from polythiophene to titania takes place.

The optical properties of the prepared samples were studied by measuring their UV-Vis DRS. The UV-Vis DRS spectra of TiO_2 , PTh, and the PTh/ TiO_2 composites are shown in Fig. 4. The spectrum of PTh/ TiO_2 shows a higher absorption than that of TiO_2 from 350 to 700 nm, which is attributed to the π - π^* (HOMO-LUMO) transition of the polythiophene backbone.

2.2 Photocatalytic degradation of RhB

2.2.1 Adsorption of RhB on the surface of the PTh/ TiO_2 composites in the dark

The adsorption ratio of RhB over different periods during darkness adsorption is shown in Fig. 5. From Fig. 5, a negligible decoloration (only about 18% adsorption ratio) of RhB was observed within 1 h in the presence of the PTh/ TiO_2 composites, and the main adsorption process was complete during the first 10 min. This indicates that the cation dye RhB is adsorbed by the PTh/ TiO_2 composite particles that contain a negative charge.

2.2.2 Photocatalytic degradation of RhB by the PTh/ TiO_2 composites under UV irradiation

The degradation ratio of RhB over different periods during UV irradiation is shown in Fig. 6(a). A continuous increase in the degradation ratio of RhB is apparent. The degradation ratio of RhB after 180 min of UV irradiation in the presence of the PTh/ TiO_2 composites was 75.6%, which indicates that the PTh/ TiO_2 composites are effective photocatalysts for the degradation of RhB under UV irradiation. The linear fitting curve (Fig. 6(b)) between $\ln(C_0/C_t)$ and the irradiation time is consistent with first-order kinetics, $\ln(C_0/C_t) = K_{\text{app}}t$. The correlation constant (R^2) of the fitted line is 0.989, which indicates that the photocatalytic degradation of RhB can be described by a first-order kinetic model.

2.2.3 Photocatalytic degradation of RhB by PTh/ TiO_2 composites under visible light irradiation

The degradation ratio of RhB over different periods during visible light irradiation is shown in Fig. 7(a). A continuous increase in the degradation ratio was observed for the PTh/ TiO_2 composites under visible light irradiation. The degradation ratio of RhB after 10 h of visible light irradiation in the presence of the PTh/ TiO_2 composites is 98%, which indicates that the PTh/ TiO_2 composites also have photocatalytic activity during the degradation of RhB under visible light irradiation. The linear fitting curve (Fig. 7(b)) between $\ln(C_0/C_t)$ and the irradiation time is consistent with first-order kinetics. The correlation constant (R^2) of the fitted line is 0.97. Therefore, the photocatalytic degradation of RhB under visible light irradiation also can be described by a first-order kinetic model.

2.3 Oxidative species and photocatalytic mechanisms

2.3.1 Mechanism of photocatalysis under UV

irradiation

To investigate the photocatalytic mechanism, EDTA-2Na (hole scavenger) and furfuryl alcohol (radical scavenger) were used to determine the main oxidant in the photocatalytic process. The apparent rate constants of the photocatalysis reaction are shown in Table 3. Table 3 reveals that the apparent rate constants of the degradation of RhB decreases when either furfuryl alcohol or EDTA-2Na is added. The apparent rate constant of degradation decreased more when EDTA-2Na was added. EDTA-2Na is a hole scavenger. It can capture almost all the holes that are produced as shown by photos of the PTh/TiO₂ composites. Photogenerated holes are, therefore, the main active species in this system. The PTh in the PTh/TiO₂ composites promotes the charge separation in TiO₂ [29]. Therefore, the PTh/TiO₂ composites can degrade RhB more quickly than naked TiO₂. As shown in Fig. 8(a), the PTh/TiO₂ composites induce the generation of electron-hole pairs under UV light irradiation, which yields radical and hole oxidants [17].

2.3.2 Mechanism of the photocatalysis under visible light irradiation

It is well known that TiO₂ particles are not excited by visible light. The surface hybridization of the PTh/TiO₂ composite particles will induce visible light photon absorption. The apparent rate constants of the degradation of RhB decreases when either furfuryl alcohol or EDTA-2Na is added (Table 3). The apparent rate constant of the degradation of RhB decreases to 0.166 h⁻¹ after the addition of EDTA-2Na. However, after adding furfuryl alcohol this constant decreases to 0.122 h⁻¹. This phenomenon indicates

that radicals are the main oxidant for the degradation of RhB under visible light irradiation. On the basis of the results from the photocatalytic and photogenerated carrier trapping tests, the mechanism of charge separation and photocatalytic activity of the PTh/TiO₂ photocatalysts under visible light is shown in Fig. 8(b). The conduction band (CB) position of TiO₂ is lower than that of the LUMO of PTh and, therefore, TiO₂ particles could trap photogenerated electrons in the PTh/TiO₂ composite particles. The PTh layer absorbs visible light, which induces excited-state electrons and these photoexcited electrons are readily injected into the CB of TiO₂ and subsequently transferred to the photocatalyst's surface [30]. These electrons react with water and oxygen to generate hydroxyl radicals and superoxide radicals [31], which are able to oxidize RhB. From these results, we find that the hole and the radical oxidants compete although only one of these is the main element.

3 Conclusions

PTh/TiO₂ composite particles were prepared by the photoinduced polymerization of thiophene. A strong interaction exists between the S sites of the polymer backbone and the TiO₂ particles. The PTh/TiO₂ composite particles can degrade a RhB solution effectively under UV irradiation or visible light irradiation. The oxidants that derive from the holes and the radicals are competitive. Under UV irradiation, photogenerated holes are the main active species while under visible light irradiation, radicals are the main oxidant for the degradation of RhB.

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