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Article

Recyclable Sn-TiO₂/polythiophene nanohybrid material for degradation of organic pollutants under visible-light irradiation

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ABSTRACT

A Sn-doped TiO₂/polythiophene nanohybrid (SPNH) was synthesized by a modified sol-gel process at low temperature. The prepared catalyst was characterized by X-ray diffraction (XRD), infrared (IR) spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible (UV-Vis) diffuse reflectance spectrophotometry (UV-DRS), and Brunauer-Emmett-Teller surface area analysis. The XRD results confirmed that polythiophene (PTh) had no effect on the crystal structure of TiO₂. IR spectra and UV-DRS indicated that an interaction occurs between the interface of PTh and metal oxide in SPNH, and doped metal oxide nanoparticles were incorporated into PTh to form a core-shell structure. XPS analysis confirmed the presence of Sn⁴⁺ and respective elements of PTh and TiO₂ in SPNH. SPNH displayed higher adsorption capacities for pollutants than Sn-doped TiO₂ nanoparticles (STN). In addition, SPNH exhibited higher photocatalytic activity and stability than STN towards the degradation of organic pollutants nitrobenzene (NB) and malachite green (MG) under visible-light irradiation. Because of the presence of PTh on STN, there was an increase in the adsorption of NB (24%) and MG (21%) on the surface of SPNH, which led to a higher photocatalytic yield. The recyclability of the photocatalytic activity for the photocatalyst was examined by about five runs and not found any depletion or degradation of PTh under visible light irradiation. The high photocatalytic activity of SPNH makes it an attractive candidate as a photocatalyst for industrial water purification.

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1. Introduction

Inorganic semiconductor photocatalysts such as TiO₂, ZnO and CdS have attracted extensive attention in the field of environmental chemistry for decomposition of organic pollutants in water and air from industries and households [1–3]. TiO₂ is an important technological material that can be used for photocatalytic applications such as self-cleaning and water treatment because it is an effective catalyst that is photostable, reusable, inexpensive, nontoxic, and readily available [4–6]. However, the large band gap of TiO₂ (3.2 eV), which is involved in the

electron-hole recombination process under visible light in photocatalysis, limits its utilization of solar light [7]. To obtain photocatalysts that are active under visible light, many researchers have focused on the modification of the surface or bulk properties of TiO₂ materials by polymer hybridization [8], ion doping [9], and semiconductor coupling [10]. In particular, hybrid structures consisting of a metal oxide and conjugated polymer are an advantageous combination to improve the photo-response of TiO₂ in the visible region. Recently, it has been found that Sn⁴⁺ doped with TiO₂ is stable, and Sn ions can replace Ti ions in the substitutional sites of TiO₂, which alters

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the properties, electronic structure and light absorption properties of the resulting material [11]. Meanwhile, combining conjugated polymers with TiO₂ has resulted in materials with interesting properties and applications like solar cells [12], photocatalysis [13–15], microbial fuel cells [16], and gas sensors [17]. Recently, TiO₂/polymer nanohybrid photocatalysts have become a research focus. Song et al. [14] prepared a visible light-induced H-PVA/TiO₂ composite loaded on glass *via* the sol-gel method and polythiophene (PTh)/TiO₂ composite particles by a photoinduced polymerization process [15]. These catalysts photocatalytically degraded organic pollutants under visible-light irradiation.

Conjugated polymers such as polyaniline, polypyrrole, PTh and their derivatives are promising materials for use as light-absorbing and charge-transporting components because of their suitable properties; for example, narrow, controllable bandgap, easy chemical tailoring, high charge carrier mobility, excellent stability and low cost [18,19]. Moreover, conjugated polymers can also be used in photocatalysis. In recent years, there has been increasing interest in using PTh [20], polyaniline [21], polypyrrole [22], and their derivatives [23] to sensitize TiO₂ by forming photocatalytic TiO₂/polymer hybrid materials. Among conjugated polymers, PTh is a well-known example that has wide-ranging applications in light-emitting diodes, photovoltaics and sensors [24]. PTh exhibits high charge carrier mobility, solubility, processability, long-term stability and strong absorptivity in the visible region [25]. Therefore, it can be considered a good candidate for sensitization of TiO₂.

To evaluate the photocatalytic activity of a nanohybrid under visible-light irradiation, nitrobenzene (NB) and malachite green (MG) are often used as target organic pollutants. Nitroaromatic compounds are widely used as pesticides, explosives, solvents, and intermediates in the synthesis of dyes, plastics and other chemicals [26]. Most of these compounds are of global toxicological concern. Exposure of the skin or eyes to very small amounts of NB can cause mild irritation, vomiting, and headache, while continuous exposure may cause liver damage. Relatively high levels of MG are harmful to humans and other organisms because of its genotoxic and carcinogenic properties [27]. MG accumulates in fat tissue, which further increases its toxicity. Therefore, it is necessary to remove NB and MG when they are present as pollutants.

In the present work, we add PTh as a surface photosensitizer and Sn as a dopant to TiO₂ through an in-situ oxidative polymerization technique at low temperature. The photocatalytic performance of the resulting hybrids in the degradation of toxic pollutants NB and MG in aqueous media is assessed. The role of the PTh layer on the Sn-doped TiO₂ nanoparticles in the nanohybrid is investigated. Recycling experiments are performed to evaluate the photostability of the nanohybrid under visible-light irradiation.

2. Experimental

2.1. Materials

Titanium tetra-*n*-butoxide and SnCl₄ were used as titanium

and tin sources, respectively, to prepare the nanohybrid catalyst. Thiophene monomer (99%), Milli-Q water, (NH₄)₂S₂O₈, and HCl were used without further purification to prepare solutions. NB and MG were used as organic pollutants in photo-degradation experiments. All chemicals were reagent grade and obtained from Aldrich. Distilled water was used for all catalyst syntheses and to prepare NB and MG solutions.

2.2. Catalyst preparation

The Sn-doped TiO₂/PTh nanohybrid (SPNH) was prepared by a modified sol-gel process at low temperature. In a round-bottomed flask, SnCl₄ (0.85 g, 0.75 wt%) was stirred with 2-propanol (12.5 mL) for 20 min followed by addition of titanium tetra-*n*-butoxide (12.5 mL). A suitable weight percentage (1.0 wt%) of distilled monomer thiophene determined from our previous work [28] was added to the above solution. The resulting mixture was stirred for 20 min and then added Milli-Q water (60 mL). A white precipitate formed immediately, which was then peptized with concentrated HCl at 60 °C for 8 h in a reflux system. To polymerize the thiophene, aqueous (NH₄)₂S₂O₈ solution (30 mL) containing 1.0 mol/L of HCl was added to the reaction mixture, which was subsequently stirred at room temperature for 3 h. The resulting brown solid was separated by centrifugation and then washed five times with distilled water. The resulting hybrid material denoted SPNH was dried at 40 °C for a week and stored in desiccator in the dark until further characterization. Sn-doped TiO₂ nanoparticles (STN) were formed using the same experimental procedure without adding thiophene and (NH₄)₂S₂O₈.

2.3. Characterization

X-ray diffraction (XRD) patterns of the SPNH and STN catalysts were acquired by a Panalytical X-Ray diffractometer using Cu K α radiation at 45 kV and 40 mA with a scan rate of 0.2°. Fourier transform infrared (FT-IR) spectra of the samples in KBr pellets were recorded on a Shimadzu spectrometer in the range of 400 to 4000 cm⁻¹. Band gap energies *E* and absorption edges of the samples were determined using UV-Vis diffuse reflectance spectroscopy (UV-DRS) (S-3100, Scinco Co., Ltd.) with BaSO₄ as a reference. Spectra were recorded at room temperature in the wavelength range of 200–800 nm. The band gap energies (*E*) of the synthesized samples were calculated according to Eq. (1):

$$E = hc/\lambda \quad (1)$$

where *h* is Planck's constant, *c* is the velocity of light (m/s), and λ is the wavelength (nm). Brunauer-Emmett-Teller (BET) surface areas were determined from N₂ adsorption-desorption isotherms measured at -196 °C using a Quantachrome Nova 2200 E system. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI quantum ESCA microprobe system using the Al K α line of a 250-W X-ray tube as a radiation source with an energy of 1253.6 eV, current of 16 mA, and voltage of 12.5 kV. Transmission electron microscopy (TEM) measurements were conducted on a JEOL 120 kV instrument using a copper grid support. Photoluminescence (PL) spectra

were measured at room temperature on a fluorescence spectrophotometer (F-7000, Hitachi, Japan) with an excitation wavelength of 315 nm, scan rate of 1200 nm/min, and PMT voltage of 700 V. The excitation and emission slits both had a width of 5.0 nm.

2.4. Adsorption study

To evaluate the adsorption capacity of the synthesized catalysts, a solution of NB or MG (10 mg/L, 250 mL) was combined with the SPNH or STN (100 mg) under continuous stirring at 25 °C in a 1000-mL conical flask covered with aluminum foil to avoid light. Aliquots (5 mL) were withdrawn every 15 min and centrifuged to separate the catalyst from the supernatant. The concentration of NB and MG in the solution was then determined using UV-Vis spectrophotometry. The adsorption ratio (R) of NB and MG was calculated as follows:

$$R = (C_0 - C)/C_0 \times 100\% \quad (2)$$

where C is the concentration of the NB or MG solution at adsorption time t , and C_0 is the concentration of the initial NB or MG solution.

2.5. Evolution of photocatalysis

The photocatalytic activities of the samples were evaluated by the decomposition of NB and MG under visible light ($\lambda > 450$ nm). Visible light was obtained by a high-pressure 400-W mercury vapor lamp with a 450-nm cutoff filter to ensure the desired irradiation light [29]. SPNH or STN photocatalyst (0.1 g) was added to an aqueous suspension of NB or MG (150 mL, 10 mg/L). To ensure establishment of an adsorption-desorption equilibrium of dye on the catalyst surface, each solution was stirred for 45 min in the dark. The suspensions

were kept under constant air-equilibrated conditions before and during illumination. To determine the change in NB and MG concentration in each solution during irradiation, aliquots (5 mL) of the solution were withdrawn using a Millipore syringe (0.45 μ m) at certain time intervals, and the absorbance of NB or MG remaining in the solution was measured on a UV-Vis spectrophotometer at 269 or 617 nm, respectively. The concentration of dye solutions during degradation was calculated using ratio C/C_0 , where C is the absorbance at time t and C_0 is the initial dye concentration before degradation.

2.6. Analysis of hydroxyl radicals ($\cdot$ OH)

The production of hydroxyl radicals ($\cdot$ OH) on the surface of the samples was detected by a PL method using coumarin as a probe molecule. Coumarin readily reacts with $\cdot$ OH to produce the highly fluorescent product 7-hydroxycoumarin (7HC) [30]. The experimental procedure was similar to the measurement of photocatalytic activity except that the dye solution was replaced by aqueous coumarin solution (150 mL, 10 mg/L). The PL spectra of generated 7HC were measured on a Hitachi F-7000 fluorescence spectrophotometer. After visible-light irradiation for 1 h, the reaction solution was filtered and the increase in the PL intensity around 456 nm excited by 332-nm light was measured.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD patterns of the SPNH and STN are shown in Fig. 1(a). Rutile phase (JCPDS: 01-088-1172) with preferred (110)

Fig. 1. XRD patterns (a), FT-IR spectra (b and c), and UV-DRS (d) spectra for STN (1), SPNH (2), and PTh (3).

orientation along with (101), (111), (211), (002) and (301) reflections were mainly detected in the prepared samples; no anatase phase was observed. The XRD data reveals that there was no change in the structure of the TiO_2 diffraction pattern caused by the addition of PTh and Sn because there was no decrease in the intensity of the peak corresponding to the rutile phase at $2\theta = 27.3^\circ$ for SPNH compared with that for STN. This indicates that PTh is not incorporated in the TiO_2 lattice. In addition, the broad XRD peaks of STN and SPNH indicate small crystallite sizes of about 18 and 14 nm, respectively (Table 1). The crystallite size is smaller for SPNH than STN possibly because of the presence of thiophene residue, which can control the growth and nucleation of metal oxide.

3.1.2. FT-IR results

Figure 1(b) depicts the FT-IR spectra of STN, SPNH and PTh. The pure TiO_2 has one major band at 585 cm^{-1} associated with the Ti–O–Ti stretching mode of TiO_2 [28]. Two peaks at ~ 3404 and 1635 cm^{-1} , which are characteristic of stretching and bending vibrations of water molecules, reveal that there is molecularly adsorbed water on the dried samples. After polymerization of thiophene, the characteristic peaks of PTh are observed, confirming the formation of PTh on the surface of STN. The bands at 1458 and 1543 cm^{-1} are attributed to the symmetric C–C stretching modes of the thiophene ring. The bands at 1450 , 1440 , 1135 , and 1052 cm^{-1} correspond to symmetric C=C stretching, C–H stretching in the thiophene ring, C–H bending, and C–S stretching in the thiophene ring, respectively [31]. The band at 985 cm^{-1} is consistent with the symmetric

S–O stretching vibration [32]. The FT-IR spectrum of SPNH showed absorption peaks attributed to $\text{C}_\alpha\text{--C}_\alpha$ conjugation at 1450 , 1135 , and 1052 cm^{-1} , which confirms that the thiophene monomer was successfully polymerized to PTh. Comparison of the spectrum of PTh with those of STN and SPNH (Fig. 1(c)) indicated that the nanoparticles were incorporated into PTh to form a core-shell structure, and, interaction exist between PTh and metal oxide in SPNH.

3.1.3. UV-DRS measurements

The UV-DRS of STN and SPNH are shown in Fig. 1(d). STN and SPNH both exhibit an apparent absorption in the visible region between 400 and 500 nm . Interestingly, a monotonic increase in the UV-DRS spectra of STN and SPNH was detected; there are evident red shifts in the absorbance peak edges of these samples, which should be caused by the presence of Sn and PTh. The extension of the absorption edge to longer wavelength for SPNH indicates there is a strong interaction between the metal oxide and PTh in the hybrid material. This interaction may accelerate photoinduced charge transfer from PTh to STN in SPNH. These results indicate that the nanohybrid can be excited by visible light. The band gap energies of the samples were calculated from the reflectance spectra using equation (1) and are presented in Table 1.

3.1.4. XPS results

XPS analysis of the SPNH sample was performed; the survey spectrum and high-resolution scans are provided in Fig. 2. The elements Ti, Sn, O, C, and S were detected on the surface of the

Fig. 2. XPS spectra of samples: (a) survey spectrum of SPNH, (b) high resolution spectrum of Ti $2p_{3/2}$, (c) high resolution spectrum of C 1s, (d) high resolution spectrum of O 1s, (e) high resolution spectrum of Sn 3d, and (f) high resolution spectrum of S 2p.

Fig. 3. EDX spectra of STN (a) and SPNH (b).

nanohybrid. Ti, Sn and O can be assigned to metal oxide in the hybrid, while C and S originate from PTh. The Ti 2*p* peaks are narrow with slight asymmetry and have binding energies of 459.408 and 465.123 eV, attributable to Ti 2*p*_{3/2} and Ti 2*p*_{1/2}, respectively. These values are consistent with those reported for TiO₂ [33]. The doublet peaks at 487.84 and 496.768 eV in the Sn 3*d* spectrum are ascribed to Sn 3*d*_{5/2} and Sn 3*d*_{3/2} of the substitutional Sn⁴⁺ dopants in the lattice, respectively (Fig. 2(e)). The radii of Sn⁴⁺ and Ti⁴⁺ ions are 0.071 and 0.068 nm, respectively. These values are so close that it is easy for Sn⁴⁺ to replace Ti⁴⁺ in the lattice of TiO₂ [34]. These observations confirm the formation of Ti–O–Sn structure in the Sn-doped TiO₂ induced by the substitution of Ti with Sn. The presence of an S 2*p* signal located at a binding energy of 168.617 eV (Fig. 2(f)) is associated with the formation of positively charged sulfur (S⁺) [35]. This positive charge is consistent with the formation and transport of polarons and bipolarons in the conjugated chains, which indicates that presence of polymer in the sample. These results are consistent with the energy-dispersive X-ray spectroscopy (EDX) data and the elemental composition of STN and SPNH shown in Fig. 3. The XPS analysis confirmed the presence of all of the intended elements and respective compositions of the nanohybrid.

3.1.5. SEM

SEM images of the samples are presented in Fig. 4. The SEM image of STN showed an uneven distribution of agglomerated spherical particles, while SPNH possessed a well-dispersed uniform spherical structure with micro- and mesopores at the interface of the particles. The spheres in SPNH were more uniform and smaller than those in STN. The smaller particle size is consistent with an increase of surface area, which correlates with the BET surface areas of SPNH and STN (Table 1). These results show that the polymer produced uniform particles with

Fig. 4. SEM images of STN (a, b) and SPNH (c, d).

Table 1

Properties and photocatalytic activities of samples.

Catalyst	Crystallite size (nm)	BET surface area (m ² /g)	Degradation of NB after 105 min (%)	Degradation of MG after 120 min (%)
STN	18	86	72.5	70.5
SPNH	14	136	99.4	98.6

controlled size and morphology.

3.1.6. TEM

The morphology and size of STN and SPNH were further studied by TEM and high-resolution (HR) TEM (Fig. 5). The TEM images in Fig. 5(a, c) reveal that both SPNH and STN were spherical with diameters of 14±2 and 20±2 nm, respectively. These values are consistent with the XRD results. Compared

Fig. 5. TEM images of STN (a) and SPNH (b, c); (d) HRTEM images of PTh layer present on Sn-TiO₂ particles in SPNH; (e) Selected area diffraction pattern of SPNH.

Fig. 6. Adsorption ratios of NB (a) and MG (b) on prepared catalysts over time.

with STN, SPNH possessed smaller crystallites that were better dispersed. This indicates that polymerization of thiophene on the surface of metal oxide may allow the growth and nucleation of metal oxide to be controlled by the polymer residue. Figure 5(d) shows that SPNH consisted of particles with a core-shell structure coated with a polymer layer with a thickness of approximately 3 nm. In these images, the dark areas are the metal oxide and lighter regions are the polymer. The lattice spacing between adjacent lattice planes of metal oxide particles in SPNH is about 0.325 Å (Fig. 5(e)), corresponding to the distance between (110) crystal planes of the rutile phase of TiO₂.

3.2. NB and MG adsorption study

The adsorption of dye molecules on STN and SPNH was determined spectrophotometrically. To determine the surface adsorption of dye by the catalysts, the NB/MG concentration and catalyst loadings used were the same as those in the photocatalysis experiments. The catalysts were dried for 24 h at 60 °C to remove adsorbed water, then the dried catalyst was added to NB solution (10 mg/L, 250 mL) and kept in the dark for 2 h. Aliquots were removed every 15 min, centrifuged, and analyzed by UV-Vis spectrophotometry to determine the NB concentration. STN and SPNH adsorbed 14% and 24% NB, respectively, and 13% and 21% MG, respectively (Fig. 6). SPNH adsorbed more dye than STN, which may be caused by its higher surface area than that of STN. These results confirmed that adsorption of NB and MG on the catalyst surface was increased by the presence of PTh on the metal oxide. Similar enhancement in the adsorption capability of another photocatalyst for methyl orange was reported by Xu et al. However, although it is well known that the ability of a catalyst to adsorb organic compounds does not affect its photocatalytic activity, it does help to bring the organic molecule close to the photoactive site.

3.3. Photocatalytic activities of catalysts

The photocatalytic activity of the samples was evaluated by their ability to degrade NB and MG in aqueous suspensions

under visible-light irradiation at room temperature. Figure 7 shows the evolution of UV-Vis spectra of NB degradation by STN and SPNH during simulated visible-light irradiation over time. In both spectra, the intensity of the absorption peak from NB decreased gradually. The decrease in absorbance is consistent with the efficient decomposition of NB by both catalysts. This indicates that the degradation of NB proceeded under oxidative reaction conditions and electrophilic •OH are the predominant reactive species. •OH can produce isomeric nitrophenols, isomeric diphenols by denitration of nitrophenol isomers, and phenol, and these by-products can be oxidized to CO [36]. Compared with SPNH, STN exhibited a lower degradation capacity (Fig. 7(b)), probably because of the low adsorption capacity of STN caused by its small surface area (Table 1). When more NB molecules are adsorbed on the photocatalyst surface, the degradation of NB occurs more quickly. Figure 7(c) illustrates the degradation of NB over the catalyst samples under visible-light irradiation. When the photocatalyst was absent (blank in Fig. 7(c)), the photodegradation of NB under visible-light irradiation was very slow, with only 8.9% of NB removed after 105 min. In contrast, after 105 min of visible-light irradiation, 99.4% and 72.5% of NB was degraded in the presence of SPNH and STN, respectively. These results suggest that SPNH exhibited higher photocatalytic activity than STN under visible-light irradiation.

In the degradation of MG using STN and SPNH as photocatalysts, the color of MG solution decreased gradually (Fig. 8). The photocatalytic removal of MG differed from that of NB. While the intensity of the absorption peak of NB decreased, that of MG exhibited a hypsochromic shift. Because MG is a cationic triphenylmethane dye, the conjugated system made up of aryl rings is the main chromophore of MG. Thus, the complete photodegradation of MG involves five processes: cleavage of the central carbon reaction, *N*-demethylation, adduct reaction of •OH on MG, removal of benzene, and opening of phenyl rings [37,38]. In the spectra, the absorbance of MG solution decreased over time. The main absorption peak almost disappeared after irradiation for 2 h (Fig. 8(a)), indicating the complete degradation of MG. SPNH removed 98.6% of MG after 120

Fig. 7. UV-Vis spectra of NB samples collected at different intervals during photodegradation in the presence of SPNH (a) and STN (b); (c) NB photodegradation over different catalysts under visible-light irradiation; (d) Recycling test results of SPNH in the photocatalytic reaction.

min of irradiation, while STN removed 70.5%. When the photocatalyst was absent, with only 6.4% of MG was removed after 2 h of irradiation (blank in Fig. 8(c)).

PL measurements were carried out to examine the production of $\cdot\text{OH}$ on the surface of the samples using coumarin as a probe molecule, as shown in Fig. 9. $\cdot\text{OH}$ is an important reactive species in photocatalytic reactions and is responsible for oxidative decomposition of pollutants. The results confirmed that the SPNH and STN enhanced the formation of $\cdot\text{OH}$ in 1 h. SPNH induced a higher PL intensity than STN, which confirms that the rate of formation of $\cdot\text{OH}$ was higher for SPNH than STN. Overall, SPNH exhibited higher photocatalytic activity under visible-light irradiation than STN.

The morphology and surface area of a photocatalyst greatly influence its photocatalytic activity for the degradation of dyes under visible-light irradiation [39]. The presence of PTH in SPNH controlled the growth and nucleation of metal oxide, sensitized the rutile Sn-TiO_2 surface to visible light, and improved the adsorption capacity of the photocatalyst. SPNH has a larger surface area than STN (Table 1), which resulted in an extremely high adsorption capacity. This is beneficial to the collection of organic pollutant molecules like NB and MG, be-

cause it leads to strong adsorption of organic contaminants, which contributes to high photodegradation efficiency. In SPNH, the polymer bound to Sn-TiO_2 can actively harvest the visible light matching the semiconductor energy levels, and then inject electrons into the conduction band (CB) of TiO_2 [40]. A schematic diagram of the charge transfer processes of PTH and Sn-TiO_2 is illustrated in Fig. 10. When the conjugated PTH harvests visible light, an absorbed photon promotes an electron from the ground state of the polymer located in the semiconductor energy gap to an excited state that is in resonance with the CB of TiO_2 . The polymer p -orbital becomes the highest occupied molecular orbital (HOMO) in the combined system. Because the lowest unoccupied molecular orbital (LUMO) levels of the polymer are energetically higher than the CB edge of TiO_2 [41,42], the electron-transfer pathways in Fig. 10 are energetically feasible [43]. Meanwhile, the ejected electrons from the valence band of TiO_2 get trapped by the Sn^{4+} ions doped in TiO_2 . The trapped electrons can move immediately to the HOMO of PTH, preventing electron-hole recombination. To achieve photosensitization, interfacial charge transfer between the photosensitizer and doped semiconductor needs to occur to make the catalyst capable of responding to visible light. However,

Fig. 8. UV-Vis spectra of MG collected at different intervals during photodegradation in the presence of SPNH (a) and STN (b); (c) MG photodegradation over different catalysts under visible-light irradiation; (d) Recycling test results of SPNH during photocatalytic reaction.

there are few reports on the photocatalysis of TiO_2 sensitized by such a polymer under visible-light irradiation.

3.4. Recyclability of photocatalyst

The recyclability of a photocatalyst is a very important parameter to assess its practicability. Photocatalysts should maintain high photocatalytic activity during long-term use for their practical application. Moreover, the catalyst should be

easily separated from solution to facilitate recycling [42]. SPNH can be easily recovered and separated from the reaction system simply through sedimentation or centrifugation.

Recycling experiments were carried out to evaluate the photostability of SPNH under visible-light irradiation. After

Fig. 9. PL spectra of prepared catalysts indicating the formation of $\cdot\text{OH}$.

Fig. 10. Schematic diagram outlining the photocatalytic degradation of NB and MG on SPNH.

105/120 min of photocatalytic reaction with NB/MG, the photocatalyst was separated from the reaction solution and then washed with distilled water. The concentrations of NB or MG and photocatalyst were maintained as constant. As illustrated in Fig. 7(d) and 8(d), after five cycles, the catalytic activity of the catalyst towards the two pollutants decreased slightly but it was still high, revealing the good repeatability of the photocatalytic activity of the nanohybrid. The slight decrease in activity may be attributed to the coverage of the photocatalyst surface by NB or MG molecules. The photocatalyst surface is very difficult to clean thoroughly, so it influences the surface properties and photocatalytic efficiency of SPNH. Finally, the washed catalyst was examined by FT-IR spectroscopy (Fig. 11). All corresponding C=C, C–C, C–H and C–S stretching peaks of PTh in SPNH were observed in the spectrum, which indicates that there was no depletion or degradation of PTh by $\cdot\text{OH}$ generated in solution during visible-light irradiation. Moreover, PTh and its derivatives are not degraded under UV radiation in the presence of TiO_2 . The organic and inorganic components of SPNH before and after the recycling tests were examined by EDX analysis. All of the respective elements and the composition of SPNH remained unchanged after the recycling test (Fig. 12). This indicates that both the organic and the inorganic components of SPNH did not degrade during photocatalytic recycling. The good stability, reusability and high photocatalytic activity of SPNH make it an attractive candidate as a photocatalyst for industrial water purification.

4. Conclusions

In this study, a reusable Sn-doped TiO_2 /PTh nanohybrid was synthesized by a modified sol-gel method at low temperature without alteration of the crystalline structure of TiO_2 . The structural and physical studies of the resulting SPNH indicated that there was efficient interaction between PTh and Sn-doped TiO_2 nanoparticles. In photocatalytic experiments, 99.4% and 72.5% of NB was removed in 105 min by SPNH and STN, respectively, under visible-light irradiation. Meanwhile, 98.6% and 70.5% of MG was removed after 120 min by SPNH and STN, respectively, under visible-light irradiation. The results

Fig. 11. FTIR spectra of SPNH after five runs in NB solution (1), SPNH after five runs in MG solution (2), and prepared SPNH catalyst (3).

Fig. 12. EDX spectra of (a) before used pure SPNH and (b) after used SPNH in recyclable process.

show that PTh increased the photocatalytic activity of Sn-doped TiO_2 nanoparticles under visible light. The catalyst showed no marked decrease in photocatalytic activity after five cycles, indicating good reusability. Based on its remarkable photocatalytic performance and reusability, SPNH shows promise in the field of photocatalysis and environmental remediation for industrial applications.

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Graphical Abstract

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Recyclable Sn-TiO₂/polythiophene nanohybrid material for degradation of organic pollutants under visible-light irradiation

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The presence of polythiophene on the surface of rutile Sn-doped TiO₂ nanoparticles can extend their photoresponse and adsorption capacity, so they exhibit higher photocatalytic activity than bare Sn-doped TiO₂ nanoparticles under visible-light irradiation.

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可循环使用的Sn-TiO₂/聚噻吩纳米杂化材料用于可见光下降解有机污染物

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摘要: 采用改进的溶胶-凝胶法在低温制备了Sn-TiO₂/聚噻吩纳米杂化材料(SPNH), 运用X射线衍射(XRD)、扫描电镜、X射线光电子能谱(XPS)、红外光谱(IR)、紫外-可见光漫反射光谱(UV-DRS)和BET比表面积分析对所制样品进行了表征. XRD结果证实聚噻吩(PTh)对TiO₂晶相结构没有影响. IR和UV-DRS结果表明, 在掺杂的金属氧化物与PTh的纳米杂化和结合过程中, PTh表面与金属氧化物之间存在相互作用(类似核壳结构). XPS结果显示, 纳米杂化材料中存在Sn⁴⁺以及PTh与TiO₂各自所含的元素. 催化剂表面吸附污染物结果发现, SPNH的吸附容量高于Sn-TiO₂纳米粒子(STN). 在可见光下降解有机污染物硝基苯(NB)和孔雀绿(MG)的反应中, SPNH表现出比单纯STN更高的光催化活性和稳定性. 由于STN上存在聚噻吩, 使得样品表面吸附NB(24%)和MG(21%)的能力增加, 从而导致更高的光催化收率. 考察了该光催化剂在可见光下重复使用5次时的光催化活性, 未见PTh的消耗和降解. 这些高光催化活性的SPNH材料有望在工业水净化中用作光催化剂.

关键词: 锡; 二氧化钛; 聚噻吩; 纳米杂化材料; 硝基苯; 孔雀绿; 可见光; 光催化; 可循环使用性

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