

Solar Photocatalytic Degradation of 4-Chlorophenol in Water with Novel Shell-Core P3HT@TiO₂ Nanoparticles

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Abstract

Shell-core poly 3-hexylthiophene (P3HT)@TiO₂ nanoparticles were synthesized by a physical deposition method using tetrahydrofuran (THF) as a solvent of P3HT in a P-25 TiO₂/THF suspension. The P3HT@TiO₂ nanoparticles were characterized by Scanning Electron Microscope (SEM), X-ray Energy Dispersive Spectrometer (EDS), X-ray diffraction (XRD), UV/VIS Diffuse Reflectance Spectroscopy (UV/VIS DRS), and Fourier Transform Infrared Spectroscopy (FTIR). The spectrum of UV/VIS DRS showed that the P3HT@TiO₂ nanoparticles are more responsive to visible light and 1% of the P3HT content of P3HT@TiO₂ nanoparticles could increase the absorption up to 75% in the band of visible light. 4-chlorophenol (4-CP) was used as the target pollutant in aqueous media to assess the solar photocatalytic activities of the P3HT@TiO₂ nanoparticles. Response surface methodology (RSM) with a 3*3 experimental design of Box-Behnken was applied to investigate the effect of critical process parameters ([catalyst], P3HT content, composites catalyst percentage) on treatment performance in terms of 4-CP degradation efficiency. It was found that the optimized reaction conditions were established as a photocatalyst dosage of 1.0 g/L, a P3HT of 0.5% in P3HT@TiO₂ and a 25% P3HT@TiO₂ of total photocatalyst dosage for a 4-CP degradation efficiency of 95%. Under the optimized reaction conditions, the TOC mineralization efficiency of 4-CP wastewater increased 16.3% as compared to that of TiO₂ process for a reaction time of 120 min. As a result, the hybrid of P3HT onto the surface of TiO₂ could extend successfully the visible light photoresponse range of TiO₂ and could effectively enhance TiO₂ solar photoactivity.

Keywords: solar photocatalytic degradation, 4-chlorophenol, P3HT@TiO₂, response surface methodology

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Introduction

Energy conservation and carbon reduction are important issues in the world currently. Solar energy is an essentially unlimited alternative to fossil energy and its utilization is ecologically benign. In the wastewater treatment sector, solar technology can be used as alternative to UV lamps to reduce the operation cost in advanced oxidation processes (AOPs). AOPs are able to produce a highly reactive, nonspecific oxidant, mainly hydroxyl radicals ($\cdot\text{OH}$). The hydroxyl radical possesses inherent properties that enable it to attack refractory organic pollutants in water to achieve a complete mineralization. Among the AOPs, TiO_2 photocatalysis (eq. (1-3)) using solar irradiation has been used as an economically viable process and has attracted great interest in recent years (Malato *et al.*, 2009). However, due to the intrinsic structure characteristics and broad band gap (3.2 eV for anatase) of TiO_2 , TiO_2 can only be excited by ultraviolet light ($<387\text{nm}$) (which is less than 5% in solar light) to produce photoinduced hole–electron pairs and the inherent recombination of photo-generated electron-hole pairs, resulting in a low utilization of solar energy and photocatalytic activity.



To eliminate these drawbacks of TiO_2 , dye-sensitized photocatalytic materials exhibit high efficiency in degradation of organic pollutants and utilization of visible light has been hybridized with TiO_2 . However, the stability of dye with low molecular weight has been suggested as one of the critical factors limiting the long-term performance of the dye-sensitized photocatalytic materials. In recent years, conjugated polymers such as polythiophenes, polypyrroles, polyanilines and their derivatives are extensively applied in photocatalytic area to sensitize TiO_2 and produce polymer/ TiO_2 photocatalytic composite materials. Poly(3-hexylthiophene)(P3HT) has a higher charge carrier mobility, dissolubility and processability, long-term stability and a broad and strong absorption invisible region (with bandgap of 1.9–2.0 eV) (Motaung *et al.*, 2009). Therefore, it should be a good candidate for a sensitizer of TiO_2 . Under UV light irradiation as shown in Figure 1, P3HT promote the separation efficiency of photoinduced electron–hole pairs due to high mobility of photoinduced holes in P3HT conjugated polymer bone (Zhu and Dan, 2010). Under visible light irradiation as shown in Figure 2, P3HT are excited to produce photoinduced electron–hole pairs. And then the photoinduced electrons inject into the conduction band (CB) of TiO_2 . They will react with the electron acceptors such as oxygen adsorbing on the surface of TiO_2 to generate oxidative species, such as hydroxyl radicals and superoxide radicals (Xu *et al.*, 2011).

Chlorophenols (CPs) have been notified as potential toxic compounds by United States Environmental Protection Agency (USEPA) and constitute an important category of organic water pollutants that are not readily biodegradable (Abe and Tanaka, 1997). Consequently, conventional biological treatment is not very effective and activated carbon adsorption is commonly used for removing CPs from chemical effluents. However, the need of frequent carbon reactivation renders this process both inconvenient and costly. Advanced oxidation processes (AOPs) have been previously

described as a promising option to remove persistent pollutants from contaminated water (Al Momani, 2006) when conventional water treatment processes are not efficient enough.

In this study, P3HT@TiO₂ composite nano-particles were prepared and assessed for their solar photocatalytic activities in degrading 4-chlorophenol in water. Response surface methodology (RSM) was employed to obtain the optimal reaction conditions of critical process parameters (including photocatalyst dosage, g/L; P3HT@TiO₂, %; P3HT@TiO₂/(P3HT@TiO₂+TiO₂), %) to reach a 4-CP degradation efficiency of 95%.

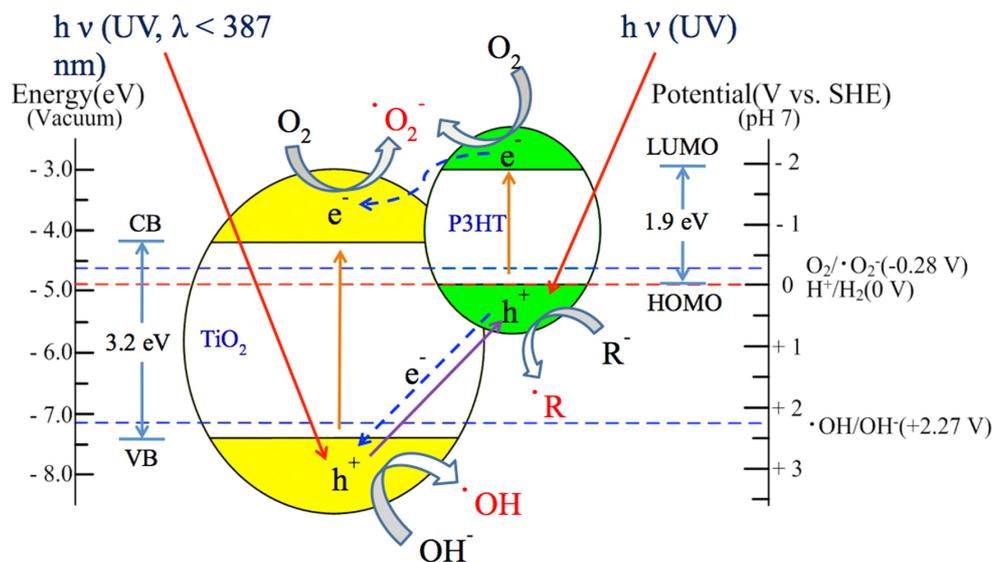


Figure 1: Electron transfer pathway on P3HT@TiO₂ composite under UV irradiation (Zhang, 2014)

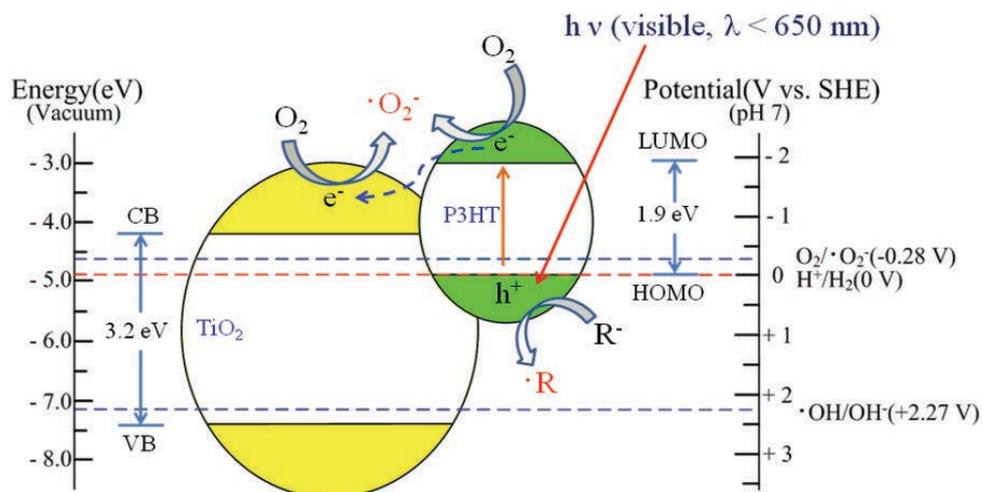


Figure 2: Electron transfer pathway on P3HT@TiO₂ composite under VIS irradiation (Zhang, 2014)

Material and Methods

Materials and Sample Preparation

4-CP with a purity of 99% were purchased from Acros Co., USA and used without further purification. An initial 4-CP concentration of 50 mg/L was prepared for all experimental runs. TiO₂ powder - P25 (mainly anatase form, with a mean particle size of 30 nm and a BET surface area of 50±15 m²/g) from Degussa Co. (Frankfurt, Germany) were used in this study. HPLC grade methanol (J.T. Baker Co., USA) was employed as eluent. P3HT (MW: 40,000 - 80,000) with a purity of 99.9% were purchased from Uni-Ward Co., Taiwan and used without further purification. All other chemicals used in this study were analytical grade and used as received. The shell-core P3HT@TiO₂ composite particles were synthesized by a physical deposition method using tetrahydrofuran (THF) as a solvent of P3HT in a TiO₂/THF suspension. The composites are labeled as P3HT(X %)/TiO₂, where X corresponds to the P3HT content in the composites.

Characteristic Analysis of P3HT@TiO₂ Composites

The shell-core P3HT@TiO₂ composites were characterized by a JEOL JSM-6700F Scanning Electron Microscope (SEM)/ X-ray Energy Dispersive Spectrometer (EDS), a Rigaku TTRAX III X-ray diffraction (XRD), a Hitachi U-3900 UV/VIS Diffuse Reflectance Spectroscopy (UV/VIS DRS), and a Microtrac S3500 Laser diffraction particle size analyzer.

Experimental Procedures

All experiments were carried out in a batch mode and performed under artificial solar light irradiation. A 0.7-L stainless steel beaker containing 200 mL of 4-CP solution was used. In this study, a 3 factors * 3 levels experimental design with three replicates at center point according to the methodology of response surface (Box *et al.*, 1978) as shown in Table 1 was applied to investigate the influence of three factors (namely, photocatalyst dosage, g/L; P3HT@TiO₂, %; P3HT@TiO₂/(P3HT@TiO₂+TiO₂), %) for 4-CP and TOC degradation efficiency. In the RSM runs, the prepared 4-CP solution was placed into the photoreactor and irradiated by a 1500 W Xe lamp in an ATLAS Suntest CPS+ solar simulator (ATLAS Co., USA) emitting artificial solar light with a spectral distribution resembling the solar spectrum (300 – 800 nm) in which the UV_{280-400nm} intensity is around 55±1.0 W/m² as showed in Figure 3. In addition, the 4-CP solution was maintained at 25±0.5 °C in a water bath. During the experiments, the pH of the solution was monitored using a pH meter (SP-701LI 120, Suntex Co., Taiwan) equipped with a glass electrode. Samples were withdrawn from the reactor at preset time intervals and then stored at 4 °C for the following 4-CP, TOC and IC analysis.

Table 1: Experimental range and levels of the process independent variables

Independent variable	Factor	Range and level		
		-1	0	+1
Photocatalyst dosage, g/L	X ₁	0.5	1.0	1.5
P3HT@TiO ₂ , %	X ₂	0.1	0.5	1.0
P3HT@TiO ₂ /(P3HT@TiO ₂ +TiO ₂), %	X ₃	25	50	75
Y (Response) – 4-CP degradation, %				

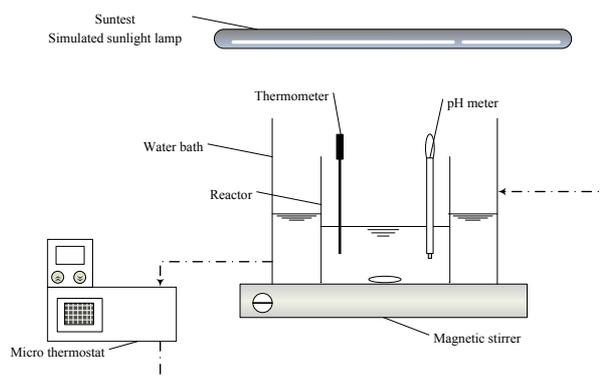


Figure 3: Schematic diagram of the solar photocatalytic reactor

Analysis

Analytical Measurement of 4-CP

Residual 4-CP in solution was analyzed by HPLC using a Jasco system (Japan). This system was equipped with two PU1580 of pumps and a MD-2010 of PDA detector setting at a wavelength of 280 nm for 4-CP analysis. A Supelco C-18 reversed phase column (L: 25 cm, ID: 4.6 mm, particle size: 5 μ m) was used. The mobile phase was a mixture of methanol (50%) and deionized water (50%). The flow rate of mobile phase was set at 1 mL/min. Under the analytical conditions, the retention time of 4-CP was 19.3 ± 0.1 min.

Total Organic Carbon (TOC) Measurement

TOC of solution was measured by using a Shimadzu VCPH analyzer (Shimadzu Co., Japan) in order to know the amount of 4-CP molecules degraded to CO₂ during oxidation.

Results and discussion

Characteristics of the P3HT@TiO₂ Photocatalysts

Fig. 4 shows the appearance of TiO₂ and P3HT(X%)@TiO₂ powder. As showed in Fig. 4, the more the P3HT content on TiO₂, the more purple the color of the composite. Fig. 5 shows the UV-VIS diffuse reflectance spectra of TiO₂ and P3HT(X%)@TiO₂ and P3HT powder. It found that TiO₂ powder could only absorb UV light with wavelength lower than 390 nm while the pure P3HT powder can absorb

UV and VIS light with wavelength lower than 650 nm because of its narrow band gap (1.9 – 2.0 eV). P3HT@TiO₂ composites can absorb both UV light (200 – 400 nm) and visible light (400 – 700 nm). This may be due to the characteristic absorption of TiO₂ and the P3HT absorption band in the UV light region. Also, it is attributed to the electron transition from the valence bond to the antibonding polar on state (π - π^* type) of P3HT in the VIS band (Zhu and Dan, 2010). With an increase of P3HT content, the absorbance for P3HT@TiO₂ composites increases in the visible light region. This result was similar to that showed in the study of Zhu and Dan (2010). In this study, P3HT(1%)@TiO₂ composites could increase the absorption up to 75% in the band of visible light.

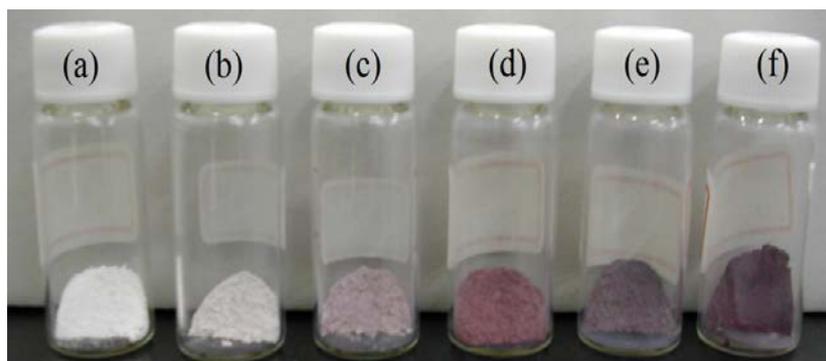


Figure 4: Photograph of the powders - (a) P-25 TiO₂; (b) P3HT(0.1%)@TiO₂; (c) P3HT(0.5%)@TiO₂; (d) P3HT(1%)@TiO₂; (e) P3HT(2%)@TiO₂; (f) P3HT(4%)@TiO₂

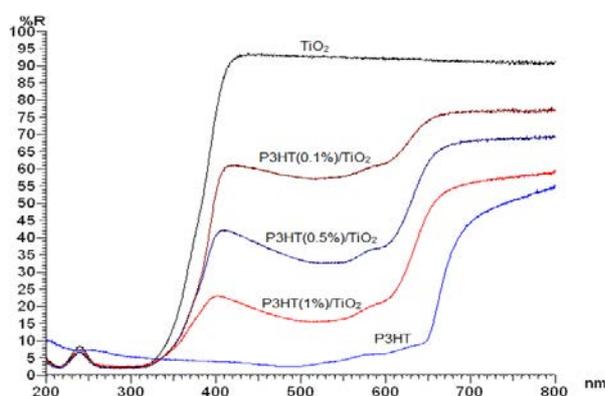


Figure 5: UV-VIS diffuse reflectance spectra of TiO₂, P3HT(X%)@TiO₂ and P3HT powders

Powder XRD analysis confirmed the presence of TiO₂ mainly with anatase phase in the composites as showed in Fig. 6 (a). Also, the representative peak (5.3°) of P3HT appeared in Fig. 6 (c), illustrating the existence of P3HT in P3HT@TiO₂ composite. In addition, Fig. 7 showed the SEM images of TiO₂ and P3HT@TiO₂ composites. As shown in Fig. 7, P3HT polymers were homogeneously dispersed onto the surface of TiO₂. The particle size of TiO₂ and P3HT@TiO₂ were estimated to be in the same range. The results of laser particle size analysis (Fig. 8) showed that the mean size of these two photocatalysts as be dispersed in water during experiments were to be in the range of 3.0 – 3.2 μ m.

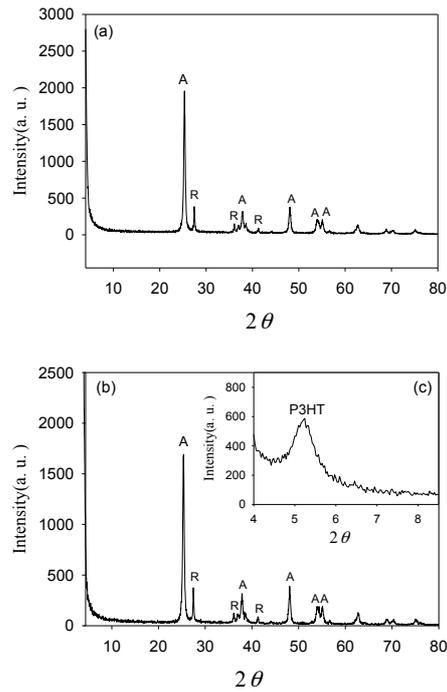


Figure 6: XRD patterns of the powder of ((a) TiO_2 ; (b) $\text{P3HT}(1\%)\text{@TiO}_2$; (c) $\text{P3HT}(4\%)\text{@TiO}_2$)

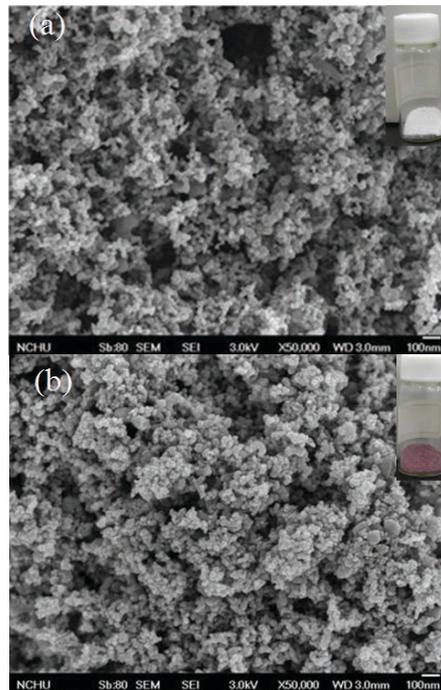


Figure 7: SEM images of (a) TiO_2 and (b) $\text{P3HT}(1\%)\text{@TiO}_2$

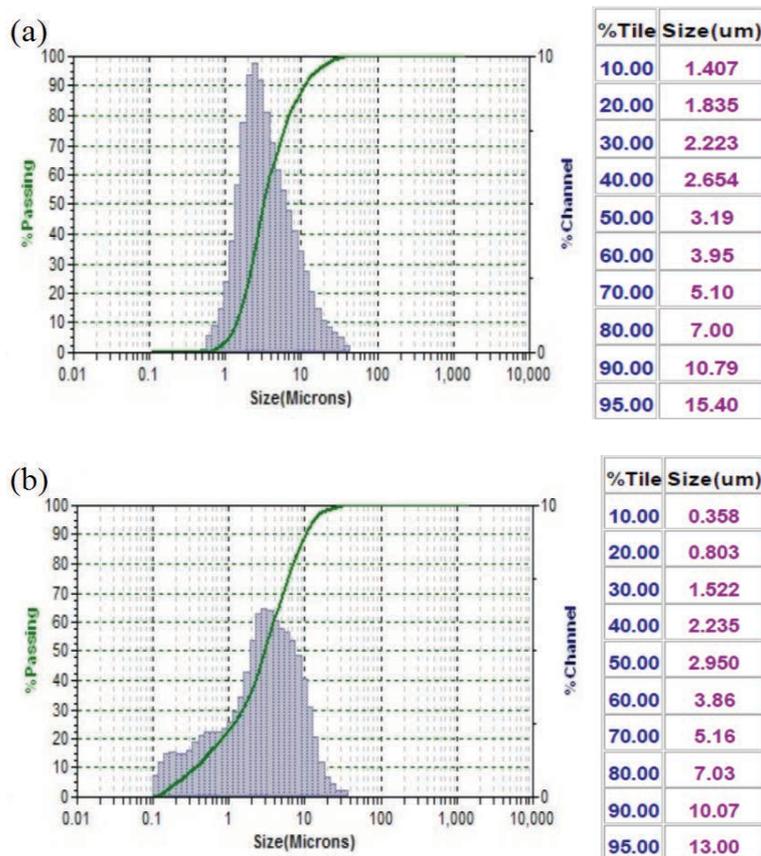


Figure 8: Laser particle size analysis of (a) TiO₂; (b) P3HT(1%)@TiO₂

Photocatalytic Degradation of 4-CP Wastewater

Table 2 lists the 4-CP degradation efficiency at a reaction time of 90 min for each run with a 3*3 Box-Behnken experimental design. Based on the results, a regression model (eq. (4)) could be established with a high coefficient of determination (r^2 : 0.962). Therefore, this regression model was used to develop 3 D response surface plots for 4-CP degradation efficiency and to predict the required experimental conditions for a preset of 4-CP degradation efficiency using Minitab R16 software. Fig. 9 displays the three dimensional response surface plots for percent 4-CP degradation efficiencies as a function of P3HT@TiO₂ (%) and P3HT@TiO₂/(P3HT@TiO₂+TiO₂) (%). As shown in Fig. 9, with an increase in the P3HT content of P3HT@TiO₂ composites, the 4-CP degradation efficiency first increases and then decreases. This could be due to P3HT with π -conjugated structure which has high electron mobility, leading to facilitate the separation of the electron-hole pairs generated under UV-irradiation, a certain content of P3HT can improve the photocatalytic activities of P3HT@TiO₂ composites (Zhu and Dan, 2010). With the content of P3HT increasing, P3HT gradually exhibits its contribution on charger transfer, and the adsorption capacities of composites was enhanced, P3HT(0.5%)/TiO₂ composites exhibit the highest 4-CP degradation efficiency. With a further increase in P3HT content, the decrease in activity of P3HT/TiO₂ composites is considered to be related to the increased absorbing and scattering of photons by a large amount of P3HT adsorbed on the surface of TiO₂.

It was found that the optimized reaction conditions were established as a photocatalyst dosage of 1.0 g/L, a P3HT of 0.5% in P3HT@TiO₂ and a 25% P3HT@TiO₂ of total photocatalyst dosage for a 4-CP degradation efficiency of 95%. Under the optimized reaction conditions, the TOC mineralization efficiency of 4-CP wastewater increased 16.3% as compared to that of TiO₂ process for a reaction time of 120 min (Fig. 10). As a result, the introduction P3HT onto the surface of TiO₂ could extend successfully the visible light photoresponse range of TiO₂ and could effectively enhance TiO₂ solar photoactivity.

Table 2: Box-Behnken design matrix and the 4-CP degradation efficiency at each run

Run	X ₁	X ₂	X ₃	4-CP degradation (%)
				@ 90 min
1	1	-1	0	99.00
2	0	-1	-1	92.00
3	0	0	0	95.33
4	-1	1	0	95.88
5	0	1	1	90.47
6	1	0	-1	91.78
7	0	0	0	95.09
8	-1	0	1	94.20
9	0	0	0	97.06
10	-1	0	-1	97.40
11	-1	-1	0	95.79
12	1	0	1	98.63
13	0	1	-1	88.82
14	0	-1	1	90.46
15	1	1	0	94.30

$$Y_{\text{degradation}(\%)} = 95.83 + 0.06X_1 - 0.97X_2 + 0.47X_3 + 2.74X_1^2 - 2.32X_2^2 - 3.06X_3^2 - 1.20X_1X_2 + 2.51X_1X_3 + 0.80X_2X_3, \quad r^2 = 0.962 \quad (4)$$

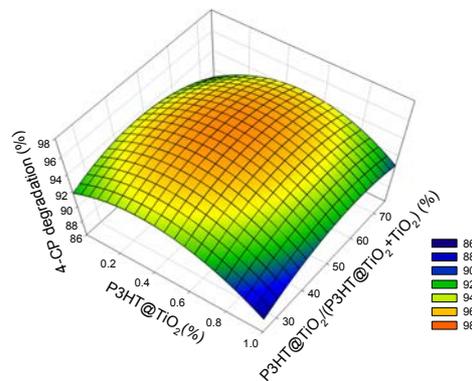


Figure 9: Response surface for the degradation efficiency of 4-CP wastewater (photocatalyst dosage: 1 g/L; photocatalytic reaction time: 90 min)

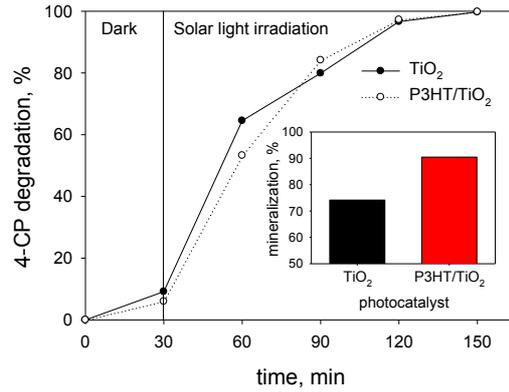


Figure 10: Comparisons of the 4-CP degradation efficiency with dosing pure TiO₂ and 25% P3HT(0.5%)@TiO₂ + 75% TiO₂ (total photocatalyst dosage: 1 g/L)

Conclusion

Based on the results of this study, the shell-core P3HT@TiO₂ composites are promising materials which can be excited by solar light and could be used effectively to enhance TiO₂ solar photoactivity. Also, it was suggested that the RSM technique was an efficient approach to predict the optimum operation conditions for solar photocatalytic process. The optimized reaction conditions based on the application of a 3*3 RSM regression model were established as a photocatalyst dosage of 1.0 g/L, a P3HT of 0.5% in P3HT@TiO₂ and a 25% P3HT@TiO₂ of total photocatalyst dosage for a 4-CP degradation efficiency of 95% for a reaction time 90 min. Under the optimized reaction conditions, the TOC mineralization efficiency of 4-CP wastewater increased 16.3% as compared to that of TiO₂ process for a reaction time of 120 min.

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