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HYDROTHERMAL SYNTHESIS OF Co AND Pd DOPED TIN OXIDE NANORODS AND THEIR PHOTOCATALYTIC DEGRADATION OF POLYPROPYLENE

(Sintesis Hidroterma Nanorod Stanum Oksida Terdop Co dan Pd dan Degradasi Fotokatalitik Polipropilena)

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Abstract

It has been reported that the wastewater treatment processes are unable to remove microplastics (MPs) from wastewater completely and often bypass the treatment plants into water resources. Hence, this study tested cobalt (Co) and palladium (Pd) doped tin oxide SnO_2 nanorods as photocatalysts to degrade the MPs. Co and Pd were selected as dopants due to their high oxidation catalytic characteristics. A dosage of 10 mol% dopants was used to prepare the doped SnO_2 nanorods. The SnO_2 was synthesized using a facile hydrothermal route at a relatively lower temperature, 180 °C. To study the photocatalytic performance of MPs, the reaction was executed on polypropylene (PP) for 72 hours under visible light irradiation. While, the effect of pH was tested at different pH conditions (5,7, and 9). The SnO_2 nanorods were analyzed using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), Fourier transforms infrared (FTIR) spectrometer, and UV-Vis spectrometer. The broadening of XRD peaks in Pd and Co-doped SnO_2 nanorods signifies a decrease in crystalline size, which is supported by FESEM images with ~15 nm diameter. The performance of the photodegradation of PP is verified by using FTIR analysis. The strong vibration peaks of the carbonyl and hydroxyl bands confirmed that the polymer chain broke down via a photo-oxidation reaction. Cracks and cavities have been found on the surface of PP after the photocatalytic reaction. Overall, 10% Pd-doped and Co-doped SnO_2 have exhibited good performance after 72 hours of photocatalytic reaction at pH 9, and it has a high potential as a photocatalyst for the degradation of MPs.

Keywords: tin oxide, palladium doped, cobalt doped, microplastics, photodegradation

Abstrak

Laporan menunjukkan bahawa proses rawatan air sisa tidak dapat membuang mikroplastik (MP) sepenuhnya yang terkandung dalam air sisa malah sering memintas loji rawatan ke sumber air. Oleh yang demikian, dalam kajian ini kobalt (Co) dan paladium (Pd) terdop stanum oksida (SnO_2) telah diselidik sebagai fotokatalis untuk mendegradasi MP. Co dan Pd telah dipilih sebagai logam dopan disebabkan kedua-dua logam tersebut mempunyai ciri-ciri pemangkin oksida yang tinggi. Sukatan sebanyak 10 mol% dopan telah digunakan untuk menyediakan nanorod SnO_2 terdop. SnO_2 telah disintesis menggunakan laluan hidroterma yang mudah pada suhu yang agak rendah, 180 °C. Untuk mengkaji prestasi fotodegradasi MP, proses fotokatalisis telah dijalankan pada polipropilena (PP) selama 72 jam, di bawah penyinaran cahaya nampak. Manakala, kesan pH pada telah dikaji pada pH yang berlainan (5,7 dan 9). Nanorod SnO_2 yang terhasil telah dianalisis menggunakan pembelauan sinar-X (XRD), mikroskop elektron pengimbasan pancaran medan (FESEM), spektrometer Fourier inframerah transfomasi (FTIR) dan spektrometer UV-Vis. Pelebaran puncak XRD bagi sampel nanorod SnO_2 terdop menunjukkan penurunan dalam saiz kristal, yang disokong oleh imej FESEM dengan diameter ~ 15 nm. Prestasi fotodegradasi PP telah disahkan melalui analisis FTIR. Kehadiran puncak getaran kuat karbonil dan hidroksil mengesahkan rantai polimer terputus melalui tindak balas pengoksidaan foto. Keretakan dan rongga telah ditemui pada permukaan PP yang telah dirawat dengan fotokatalisis. Secara keseluruhan, SnO_2 terdop dengan 10 mol% Co and Pd telah menunjukkan prestasi yang baik selepas 72 jam tindak balas fotokatalitik pada pH 9 dan ia mempunyai potensi tinggi sebagai fotomangkin untuk degradasi mikroplastik.

Kata kunci: stanum oksida, dop palladium, dop kobalt, mikroplastik, penguraian foto.

Introduction

The contamination of water by microplastics (MPs) has emerged as a global environmental and public health issue. In contrast to large plastic waste, the removal of MPs is more difficult due to the microscale size, which is often less than 5 mm and hard to detect with the naked eye [1]. Scientists suspect that wastewater treatment plants are the primary source of MPs in rivers and oceans, despite the fact that MPs break down from larger plastics into smaller pieces and eventually enter the water resources. As MPs' concentration in the environment rises, so does the likelihood of ecosystem exposure. Consequently, there is an increased risk of interaction, ingestion, and adverse effects across food webs [2].

Therefore, in recent years, extensive effort has thus been focused on developing ways to minimize the volume of MPs entering the natural aquatic system using various technologies such as electrocoagulation, magnetic extraction, and photodegradation. Electrocoagulation is a method that utilizes metal electrodes to create coagulation for the removal of MPs. Although this method has a higher MP removal efficiency, the characteristics of the electrode and wastewater, such as density, conductivity, and pH, have a significant impact on the process, making consistency difficult to achieve [3]. On the other hand, in magnetic extraction, MPs bind with iron-based nanoparticles before being separated by external magnetic attraction from the wastewater. This technique normally leads to secondary sludge waste. The photodegradation method usually uses UV light to break the polymer chain of MPs. However, the technique's scalability is limited by its high energy consumption and lengthy reaction time [4].

Visible light photocatalysis using semiconductor nanoparticles is regarded as an environmentally friendly process capable of degrading MPs in less time with less energy consumption. Over the years, various semiconductors nanoparticles, especially titanium dioxide (TiO_2) [5, 6] and zinc oxide (ZnO)[7-9] have been extensively studied in the photocatalysis of MPs in water. In spite of the fact that these materials demonstrated degradation of MPs, complete degradation has not yet been reported. Moreover, their applications were often restricted by the limited absorption of visible light and the short lifetime of electron-hole pairs [10]. Tin oxide is an n-type semiconductor, which is well known for its wide band gap (3.6 eV at 300 K), large exciton binding energy (130 meV), and high electron mobility (100-200 $cm^2\ V^{-1}\ S^{-1}$) [11]. Due to its wide band gap, tin oxide itself exhibits a relatively low photocatalytic effect. However, in comparison to SnO_2 to TiO_2 and ZnO, it is known to be a better electron acceptor due to the presence of a more

positive conductive band (CB). Hence, coupling with other metal oxides or doping with transitional metals or noble metals effectively reduces the photogenerated electrons-holes pairs recombination during the photocatalytic reaction [12].

Our previous study reported on the hydrothermal synthesis of metal doped SnO_2 nanorods and their performance as ethanol gas sensors. The results revealed that doping improves the physiochemical properties of SnO_2 [13, 14]. Thus, in the current study, cobalt (Co) and palladium (Pd) doped tin oxide nanorods were synthesized using the hydrothermal method and tested their photocatalytic performance on polypropylene (PP) sample, which is one of the most widely found microplastic pollutants in wastewater.

Materials and Methods

Chemicals

Tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$), cobalt chloride hexahydrate ($CoCl_2.6H_2O$), and palladium chloride ($PdCl_2$) were purchased from Sigma-Aldrich. All chemical reagents were analytical grade without any further purification. Sodium hydroxide (NaOH) was purchased from Qrec Asia Sdn. Bhd, Malaysia, and absolute ethanol (C_2H_5OH) were procured from HmbG Chemicals. All the solutions were prepared using distilled water. MPs sample was prepared from fully aged Polypropylene (PP), which was obtained from a local home storage manufacturer, ASOTV, Kuala Lumpur.

Synthesis of tin oxide nanorods

The synthesis of doped SnO_2 nanorods using the hydrothermal method is described elsewhere [14]. Briefly, tin oxide, 0.32 mol of tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$) was dissolved in 40 ml absolute ethanol - distilled water solvent (1:1 v/v) while stirring continuously. Co and Pd dopants (10 mol%) were added separately in the solution above. Simultaneously the pH of the reaction solution was adjusted to pH 13 by slowly adding an equal volume of 6 M NaOH aqueous solution and absolute ethanol. The pH was monitored throughout the reaction. The final volume of the reaction mixture was completed to 80 mL by adding in absolute ethanol – distilled water solvent (1:1 v/v). A white slurry for undoped SnO_2, a peach color slurry for Co-doped SnO_2, and a grey color slurry for Pd-doped SnO_2 were obtained at the end of the reaction. The samples were then transferred into a 100 mL Teflon -linen stainless-steel autoclave, sealed, and heated at 180 °C for 24 hrs. After being naturally cooled at room temperature, the product was centrifuged and repeatedly washed with distilled water followed by ethanol and then dried in the oven at 60 °C for 24 hrs. The undoped SnO_2 nanorod sample was prepared similarly but without the dopant. Figure 1 shows the final product produced via the hydrothermal process.

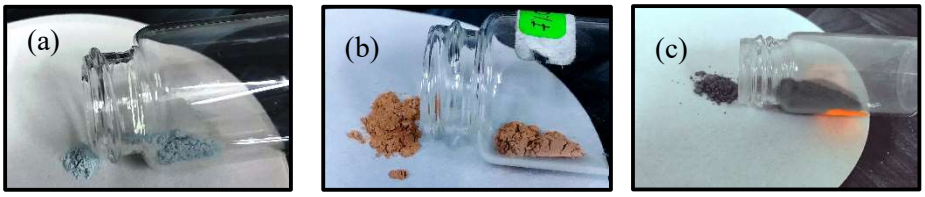

Figure 1. (a) Undoped SnO_2, (b) Co doped SnO_2, and (c) Pd doped SnO_2 powder samples

Photocatalysis reaction setup

The photocatalytic performance of the as-synthesized tin oxide nanorod sample was tested on PP. A known amount of PP microplastics sample (1 g, size particle~125 µm) was suspended in 100 ml distilled water. The photocatalytic reaction was carried out at room temperature under visible light (LED Blu-ray, 18 Watt, λ, 460 -462 nm) irradiation. 0.5 mg of tin oxide nanorods photocatalyst was added to the MPs sample. To obtain a uniform distribution of PP with a photocatalyst, the sample was shaken at the speed of 150 rpm using an orbital shaker for the duration of 72 hrs. To study the effect of pH, doped SnO_2 samples were tested at different pH conditions (5,7, and 9). After the reaction, the PP and photocatalyst were filtered out using a vacuum pump and dried at room

temperature for 24 hours. Figure 2 shows the experimental setup for the photocatalytic reaction.

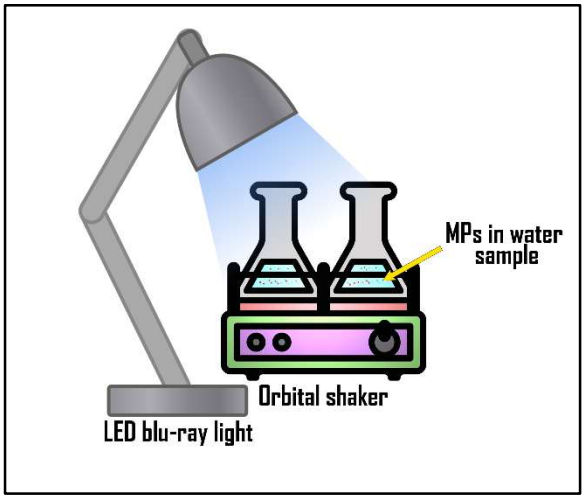

Figure 2. Schematic diagram of photocatalytic reaction under visible light (LED blu-ray) source

Characterization

The morphology and composition of the SnO_2 were determined using HRTEM (high-resolution transmission electron microscopy (HRTEM) (TECNAI G2 20 S-TWIN, FEI, China) and X-ray diffraction technique (PW 3040/60 X'PERT PRO (PANanalytical, Neterland). The X-ray diffraction (XRD) patterns are obtained using Cu Kα radiation (λ=0.1541 nm) in the 2θ range of 20° to 90°. The band gap was calculated using a UV-Vis spectrometer (Perkin Elmer Lambda 35, United States). The photodegradation was verified using Fourier transform Infrared (FTIR) spectrometer (Perkin Elmer's System 2000 FTIR, United States). The infrared spectra were collected in the range of 4000-400 cm^{-1}. For oxidized PP, carbonyl groups were identified in the wide infrared range at 1500-1800 cm^{-1}, with the peak at 2800-2950 cm^{-1} utilized as a reference, which is related to CH bending and CH_3. SEM (HITACHI, TM3030Plus, Japan) was used to observe and determine the morphology of the microplastics with a photocatalyst. The SEM images were taken at a magnification of 600x to 5000x.

Results and Discussion

Figure 3 shows the XRD patterns of undoped SnO_2, Co, and Pd-doped SnO_2 nanorod powder samples. All diffraction peaks could be assigned to the rutile-type tetragonal phase (space group, *P42/mnm*); which was indexed on the basis of ICSD 092552, and no trace of other metallic or metal oxide phases have been detected. The broadening of diffraction peaks shows that the dopants not only reduced the particle size but also lowered the crystallinity of nanoparticles. The prominent reflection of (101), (110), and (211) peaks indicate the preferential crystal planes of the nanostructure [15].

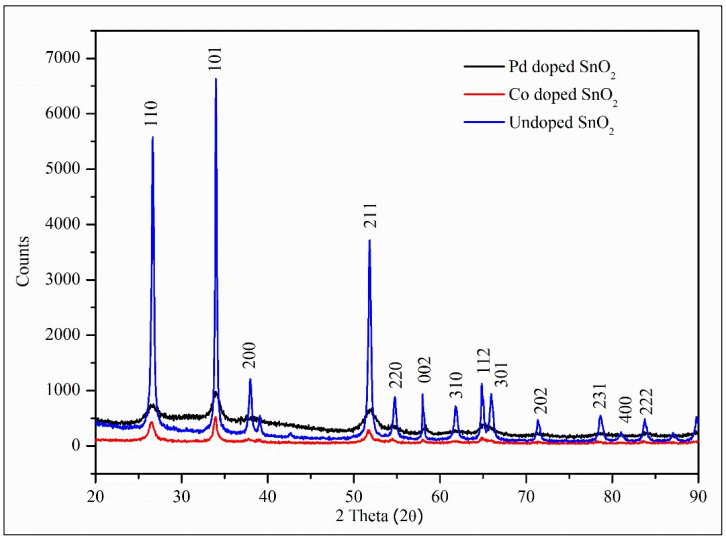

Figure 3. XRD diffraction patterns of undoped and doped SnO_2 nanostructures

The morphology of as-synthesized SnO_2 samples was analyzed by using SEM and HRTEM. Figure 4 exhibits the SEM images of SnO_2 samples. From the SEM images, it can be seen clearly that the SnO_2 are in the form of nanorods. A comparison of the morphology images revealed that the presence of 10% Co and 10% Pd dopants did not affect the shape of the nanorods; However, in comparison to the undoped SnO_2, the size of the nanorods has been significantly reduced. This result suggested that the Co and Pd greatly inhibited SnO_2 grain size, which is in line with XRD data, where the broadening of peaks was observed clearly in doped SnO_2 samples [15].

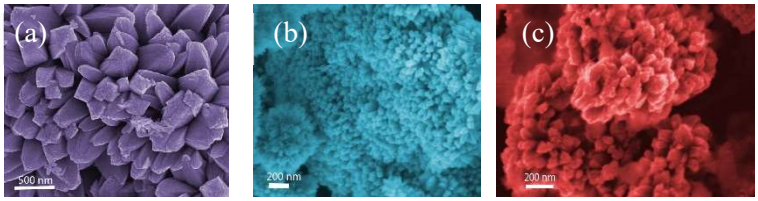

Figure 4. SEM images of (a) undoped SnO_2, (b) Co doped SnO_2 and (c) Pd doped SnO_2 nanorods

Additionally, to study the size and shape of particles, HRTEM analysis was performed on the samples. Figure 5(a) depicts an undoped SnO_2 spear rod-shaped nanorods cluster with an estimated average diameter and length of 23.0 ± 4.2 nm and 152.0 ±7.6 nm, respectively. While Co doped, SnO_2 exhibits needle-like nanorods with an average diameter and length of 14.2± 2.4 nm and 77.2 ± 8.3 nm, respectively (Figure 5 (c)). In contrast, Pd doped SnO_2 formed nanorods with a rounded tip (Figure 5 (c)). The calculated average diameter and length are 8.5 ± 2.9 nm and 43.9 ± 2.7 nm, respectively. The aspect ratio for undoped SnO_2, Co doped SnO_2, and Pd doped SnO_2 changed from 6.6, 5.4 to 5.2, respectively. The result shows that the nanorods formed in the Pd doped SnO_2 sample were the smallest. The drastic decrease in the particle size may be due to the fact that the ionic radii of Co^{2+} (0.72 Å) and Pd^{2+} (0.86 Å) are much bigger than Sn^{4+} (0.69 Å); the introduction of these dopant ions results in lattice strain and a reduction in particle size as well as crystalline size [16].

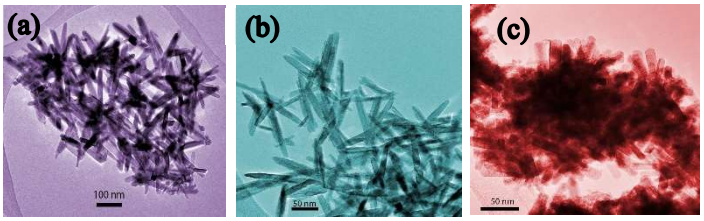

Figure 5. HRTEM images of (a) undoped SnO_2, (b) Co doped SnO_2 and (c) Pd doped SnO_2 nanorods

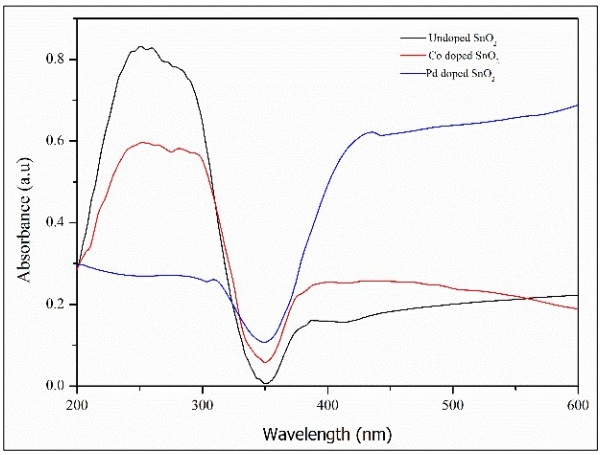

Figure 6: UV-Vis spectra of as-synthesized SnO_2 samples

The UV-Vis absorption spectra of as-synthesized SnO_2 nanorods are shown in Figure 6. The absorption edges of Co-doped SnO_2 and Pd-doped SnO_2 show a redshift (300 -350 nm) which could cause by the high concentration of oxygen vacancies or defects in the SnO_2. The high uptake at the wavelength of 380 nm to 450 nm in Co and Pd doped SnO_2 nanorod samples reveals the sp-d exchange interactions between the band electrons and localized d electrons of dopant ions that replace Sn^{4+} ions in the crystal lattice. Consequently, this finding suggests that the absorption capacity of the Co and Pd doped SnO_2 nanorods is improved from the UV region to the visible region, which is essential for visible light photocatalysis. A similar trend was also obtained in previous studies [17]. The bandgap energy was estimated following Tauc's relation. The bandgap energies of the resulted samples are 3.88 eV, 3.61 eV and 3.55 eV for undoped SnO_2, Co doped SnO_2 and Pd doped SnO_2, respectively, suggest that doping has reduces the bandgap energy [18].

Photodegradation of PP microplastics under visible light

The photocatalytic reactions were conducted for 72 hours under visible light irradiation to test the SnO_2 nanorods as a photocatalyst for degrading the PP MPs in water. The PP residues were filtered and dried before being characterized using an FTIR spectrometer. As can be seen in Figure 7, some chemical reactions occurred during the photocatalytic process. This reaction led to the formation of new functional groups such as carbonyl, hydroperoxide, peroxides, and unsaturated groups, which are assigned to the peaks at 1700-1630 cm^{-1}, 3500-3300 cm^{-1}, 3000-2750 cm^{-1} and 1374 cm^{-1}, respectively. This result is in agreement with previous literature [9]. During the degradation process under visible light, radiation of oxidizing agents, particularly reactive oxygen radical species, would react with PP and eventually produce new functional groups. The combination of visible light irradiation with a chemical attack by reactive oxygen species induced by photocatalysts has

effectively promoted the degradation of PP microplastics [19]. Based on the FTIR spectra, the Co and Pd doped SnO_2 sample exhibit more new peaks than the undoped SnO_2. This may be due to smaller particle size, narrow bandgap, and the presence of oxygen vacancies in Co and Pd-doped SnO_2 nanorods samples.

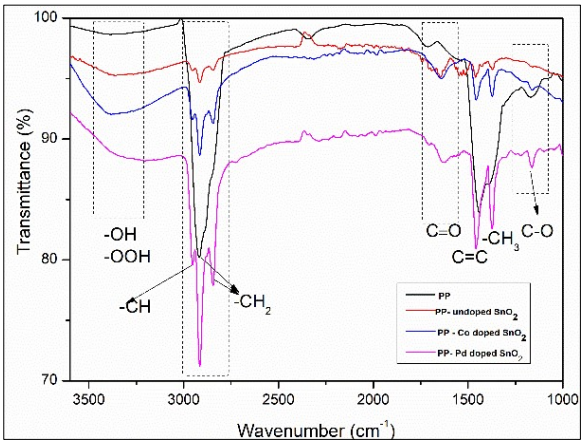

Figure 7. FTIR spectra of PP MPs photodegradation reaction after 72 hours under visible light irradiation

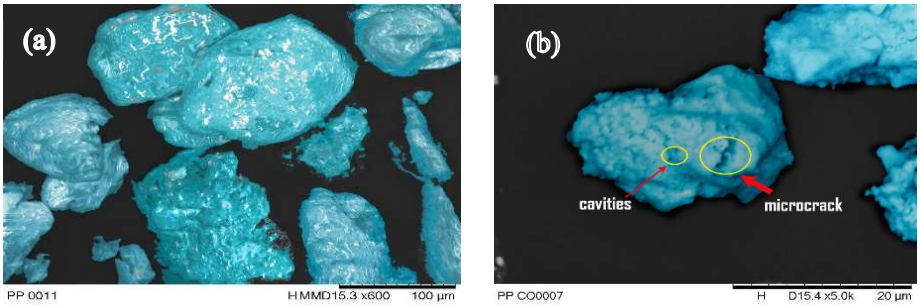

Figure 8. SEM images of PP MPs (a) before the photodegradation reaction (b) after 72 hours of photodegradation under visible light using Pd doped SnO_2 nanorods as the photocatalyst

Further analysis was executed using SEM to investigate the morphology of PP MPs prior to and after photocatalytic reaction; the images are presented in Figure 8. Referring to the figure, the treated PP exhibits surface structural changes such as brittleness, microcracks, and cavities. In conjunction with FTIR findings, the formation of low molecular weight compounds has led to the development of these surface defects, which evidence the degradation process [9]. Generally, in photocatalysis reaction, electron/holes are generated when metal oxide photocatalyst is irradiated by light source that has a higher energy than its bandgap. These pairs migrate to the surface and produce species such as hydroxyl radical (ȮH) and superoxide radical ($\cdot O_2^-$). For SnO_2, it was found that ȮH are the primary active species, this is due to the fact that the conduction band (CB) of SnO_2 (0.2 eV) is more positive than that of ($O_2/\cdot O_2^-$) (-0.05 eV). Hence, when some holes in valence band of SnO_2 reacted with water produced ȮH radicals which subsequently degraded the PP MPs [20, 21] .

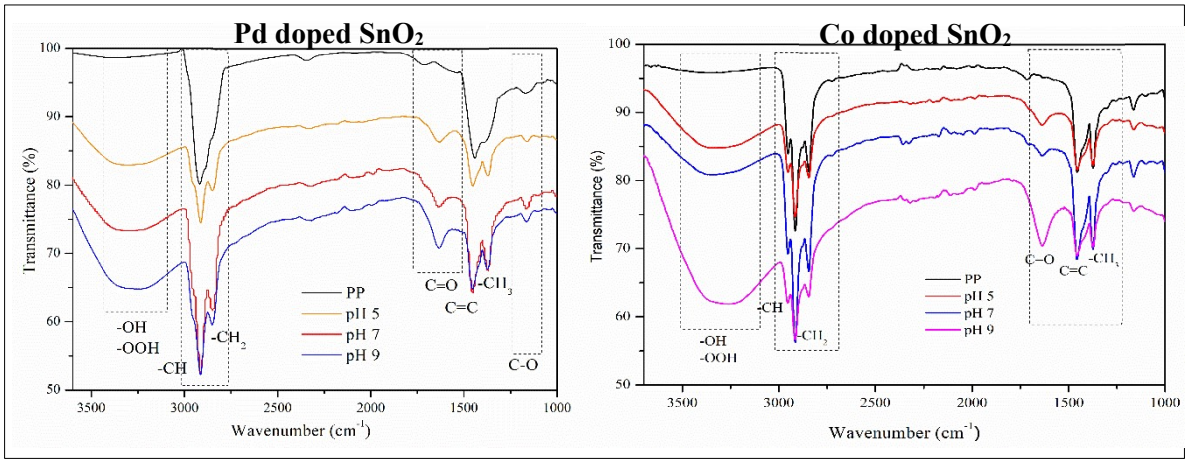

Figure 9. FTIR spectra of PP MPs before and after the 72 hours photodegradation reaction using Pd doped SnO_2 and Co doped SnO_2 as the photocatalysts under different pH conditions.

In order to study the effect of pH, the photocatalytic reaction was performed at different pH (5,7, and 9) using Pd and Co doped SnO_2. Figure 9 depicts the spectra of PP before the treatment and PP MPs residues obtained after 72 hours of photodegradation at various pH under visible light irradiation. The results show for both photocatalysts the intensity of hydroxyl, carbonyl, and peroxide peaks increased when the pH increased. The result suggests that the presence of hydroxide ions increases the degradation of MPs by inducing the formation of more hydroxide radical species [19].

Conclusion

This study successfully demonstrates the degradation of MPs and polypropylene (PP) in water using visible light and hydrothermal synthesized tin oxide nanorods photocatalysts. The photocatalytic reaction led to the formation of low molecular weight compounds such as hydroperoxides, peroxides, carbonyl, and other unsaturated groups, which cause cracks on the surface of PP, and subsequently degrade the MPs. The higher pH of the water sample improves the photodegradation process. In addition, the physical and chemical properties, such as the particle size, bandgap energy, and oxygen vacancies of the photocatalyst, also contribute to enhancing PP degradation. Overall, we conclude that Pd and Co doped SnO_2 nanorods can be applied as an alternative technology to combat global MP pollution.

Acknowledgement

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