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Bi/SnO₂/TiO₂-Graphene nanocomposite photocatalyst for solar visible light induced photodegradation of pentachlorophenol

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Abstract:

In this study, for the first time, a TiO₂/Graphene (G) heterostructure was synthesized and doped by Bi and SnO₂ nanoparticles through a hydrothermal treatment. The as-synthesized nanocomposite was employed for photocatalytic degradation of pentachlorophenol (PCP) under visible light irradiation. Structural characterizations such as X-ray photoelectron spectroscopy (XPS) and X-ray diffraction spectroscopy (XRD) proved the valence band alignment at Bi/SnO₂/TiO₂-G interfaces and crystallinity of the nanocomposite, respectively. The as-developed nanocomposite photocatalyst was able to decompose 84% PCP, thanks to the generation of a large number of active OH[•] and O₂^{•-} radicals. To achieve this optimum photodegradation efficiency, various parameters such as pH, catalyst dosage, and PCP concentration were optimized. The results showed that the PCP photodegradation process followed the first-order kinetic model and the reaction rate constant rose from 0.007 min⁻¹ (Bi) to 0.0149 min⁻¹ (Bi/SnO₂/TiO₂-G). The PCP photodegradation efficiency did not decrease significantly after 5 cycles and the nanocomposite photocatalyst still showed a high efficiency of 68% in the last cycle. The excellent photocatalytic activity of Bi/SnO₂/TiO₂-G is ascribed to the novel composition as well as the heterostructure of the nanocomposite photocatalyst.

Keywords: Advanced oxidation processes; solar photocatalysis; reusability; water treatment.

1. Introduction

In the current era, by evolving industrialization and urbanization, two critical concerns of water scarcity and energy resources depletion have emerged (Homaeigohar and Elbahri 2014). One promising solution to tackle such challenges is development of photocatalytic nanomaterials. This

class of advanced materials can offer distinct merits with respect to production of H_2 and O_2 from water (Kudo and Miseki 2009), reduction of CO_2 to carbon fuels (Habisreutinger et al. 2013) and photodegradation of organic pollutants (Gaya and Abdullah 2008; Homaeigohar 2020). Thus, they put promise for next generation of “green” technologies targeting clean energy demand and environmental remediation.

In 1972, Fujishima and Honda for the first time found out that water is split into H_2 and O_2 when an immersed TiO_2 anode, connected to a Pt black cathode, is excited with an external bias. This phenomenon implied that water can be photodecomposed into H_2 and O_2 in the presence of a visible light provoked catalyst (Fujishima and Honda 1972). TiO_2 is indeed one of the most studied photocatalysts for the purpose of water splitting and photodecomposition of organic pollutants (Homaeigohar et al. 2019; S.Sh. Homaeigohar et al. 2012). Despite such versatility, it possesses a wide band gap energy (3.0-3.2 eV) and thus excites photons solely in the UV light range, accounting for ~4% of the solar light (Gaya and Abdullah 2008; Habisreutinger et al. 2013). Given that, the visible light is largely available everywhere on the earth and accounts for ~50% of the solar light, an extensive attention has been paid to development of the photocatalysts operating under visible light (Ghadimiet al. 2020; Gómez-Avilés et al. 2019; Homaeigohar et al. 2017; Khan et al. 2019). Another problem in relevance to TiO_2 , is the possibility of fast recombination of electron-hole pairs (Chen and Mao 2007).

Graphene has shown to be a high potential matrix able to perform as an acceptor and transporter of the photogenerated electrons of TiO_2 . These charge carriers can readily move via the graphene nanosheets, thereby lowering the chance of fast e^-h^+ recombination. Moreover, induced by the presence of the negatively charged functional groups and high surface area, a large adsorption capacity for the water pollutants by the graphene flakes is expected. Particularly, employing GO as the matrix, a larger density of oxygen containing functional groups are available that can bring about effective and fast oxidation and photodecomposition of organic pollutants (Homaeigohar et al. 2018; Hu and Mi 2013). There is also a high chance for chemical bonding between d orbital in TiO_2 and π orbital in graphene. Such an interaction leads to formation of a narrower band-gap thus visible light

photocatalytic activity for the resulting TiO₂/graphene nanocomposite (Kusiak-Nejman and Morawski 2019).

Despite the abovementioned merits for construction of a TiO₂/graphene heterostructure, light harvesting efficiency of TiO₂ is challenged in the presence of graphene and this reduces the number of the photogenerated charge carriers, thus photocatalytic activity. For the purpose of taking the most advantage of solar energy and also minimizing the recombination rate of charge carriers, metal ions doping is regarded as a practical supplementary approach (Ahmadpour et al. 2020; Grinberget al. 2019). In this regard, it has been demonstrated that some particular p-block metals are able to offer orbitals that can hybridize O2p orbitals of TiO₂, thereby generating a more accessible hybridized valence band (VB). The well-known relevant metals include Ag(I), Bi(III), and Sn(II) providing Ag 4d, Bi 6s, and Sn 5s orbitals, respectively, for hybridization leading to promoted mobility of photogenerated charge carriers, narrowing the band gap of the photocatalyst and raising the visible light absorption (Hosogiet al. 2008; Kudo and Miseki 2009). In this regard, various research groups have investigated numerous relevant systems including Sn-doped TiO₂ nanoparticles supported onto reduced graphene oxide (rGO)(Nguyen-Phanet al. 2014), Mn-doped TiO₂ grown on graphene (Chenet al. 2016), and Bi-doped TiO₂ nanotube/graphene (Alamet al. 2017).

Here, we synthesize a TiO₂/graphene heterostructure, that is reinforced via metal ion doping by inclusion of Bi and SnO₂ nanoparticles. While the former strategy, i.e. formation of a heterostructure, assures a larger adsorption capacity for organic pollutants and hampers the fast recombination of the charge carriers, the latter one provides a narrower band gap and enables solar visible light photocatalysis. This synergetic effect is assumed to end up with the highest photocatalytic activity under visible light illumination, beneficial for photodegradation of pentachlorophenol, as an organic pollutant model. Pentachlorophenol has been successfully degraded by V-modified TiO₂ nanorod-aggregates (Han et al. 2019). To the best of our knowledge, such a sophisticated composition and nanostructure has not yet been reported in the literature.

2. Materials and Methods

2.1. Materials

In this study, high purity (99.5%) graphene (CAS number: 7782-42-5) was obtained from US Research Nanomaterials, Inc. (3302 Twig Leaf Lane, Houston, TX 77084, USA). Sodium hydroxide, bismuth nitrate, tin chloride, ammonia, ethanol, nitric acid, ethylene glycol, and tetra butyl ortho titanate (TBOT) were purchased from Merck (Darmstadt, Germany). Pentachlorophenol (PCP) with the chemical formula of C_6Cl_5OH was obtained from Sigma Aldrich (US).

2.2. Sample preparation

Initially, 1.07 g of $Bi(NO_3)_3 \cdot 5H_2O$ (2.2 mmol) was added to 50 mL of 0.1 mol/L mannitol solution, then 20 mL $NH_3 \cdot H_2O$ (5 mol/L) was added to the solution slowly with vigorously stirring. After stirring for about 30 min, the formed white precipitate was collected and washed with deionized water by centrifugation for five times. The white precipitate and 0.3 g of PVP were then introduced into 50 mL EG. The mixture was stirred and sonicated until all the chemicals were well dispersed. Thereafter, it was transferred into a stainless steel autoclave with a Teflon liner. The autoclave was sealed and maintained at 180 °C for 12 h. After cooling down to room temperature, the obtained black solution was centrifuged and the solid product was collected, then washed with ethanol three times and eventually dried in an oven at 70 °C for 12 h (Wu et al. 2011).

To include SnO_2 nanoparticle, 0.3 g of Bi nanoparticle was dispersed in 30 ml deionized water and sonicated (for the sonochemical process) or stirred (for the hydrothermal process). Then, 30 mL of an ethanolic solution containing 1.4 g $SnCl_2$ and 1.0 g hexamine was added drop wise. This mixture was sonicated for 30 min and then transferred into a Teflon stainless steel autoclave for hydrothermal treatment. The autoclave was sealed, kept at 180 °C for 12 h and allowed to cool naturally down to room temperature. Finally, the precipitate was collected, washed several times with water followed by absolute ethanol, and finally dried at 120 °C for 4 h. Further, it was calcinated at 500 °C for 2 h in a muffle furnace fitted with a PID temperature controller (Su et al. 2012; Tang et al. 2013).

To synthesize $Bi/SnO_2/TiO_2$ nanoparticles, 0.35 g of Bi/SnO_2 was dispersed in 50 ml of deionized water and ultrasonicated for 20 min. Subsequently, tetra butyl ortho titanate (TBOT) (4 ml) was dissolved in 40 ml of ethanol and drops wise added to the Bi/SnO_2 -G containing suspension and vigorously stirred for 2 h. The resulting mixture was transferred into an autoclave and heated at 120

°C for 3 h. After cooling down to room temperature, the product was centrifuged and washed several times with deionized water. The precipitate was then dried in an oven for 12 h, ending up with a gray powder that was Bi/SnO₂/TiO₂ photocatalyst (Zhu et al. 2018).

The synthesis of Bi/SnO₂/TiO₂-G was done via a hydrothermal method. 0.3 g of Bi/SnO₂/TiO₂ nanoparticles and 0.5 mg graphene nanoplatelets were added into 10 mL of absolute ethanol and stirred for 10 min. The mixed solution was then sonicated for 40 min and transferred into a 25 mL capacity stainless steel autoclave which was maintained at 180 °C for 12h. The resulting sample was collected by centrifugation, washed with deionized water, and dried at 70 °C for 12 h.

2.3. Structural Characterizations

The crystalline structure of the nanocomposite photocatalyst was characterized by X-ray diffraction (Rigaku MiniFlex 600, Japan) using Cu-K α radiation ($\lambda=0.15418$ nm). The morphology of the nanocomposite nanoparticles was investigated by using Field Emission Scanning Electron Microscopy (FESEM) (TE-SCAN, MIRA3 FESEM model). X-Ray Photoelectron Spectroscopy (XPS) (Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer, USA) and Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu, FTIR1650 spectrophotometer, Japan) were also applied to determine the chemical features of the nanocomposite photocatalyst. Zeta potential measurements were performed to assess zeta potential and isoelectric point of the nanoparticles using a Zetasizer (3000HS) machine. Thermo gravimetry Analysis (TGA) was done using a Perkin Elmer device (USA) for a temperature sweep of 50 to 800 °C under nitrogen atmosphere. The UV-Vis spectra of the specimens were measured by a UV-Vis spectrophotometer (Shimadzu, UV-2550, Japan).

2.4. UV-light Induced Photodecomposition Efficiency Analysis

Batch photodecomposition experiments were performed in a 250 ml cylinder reactor containing 100 ml of PCP solution (30 mg/l) at room temperature. In each experiment, a certain amount of the photocatalyst was added to the reactor vessel. The pH values were adjusted by addition of HCl (0.1 M) and NaOH (0.1 M) and controlled using a pH meter (Istek, 915PDC, Korea). At predetermined intervals, 3 ml of the solution was taken, centrifuged immediately and the PCP concentration was

measured via high-performance liquid chromatography (HPLC) (Agilent Technologies, Infinity1260, USA). An air pump (Hailea, ACO-5504, China) was attached to the set-up to homogenize the solution during the experiment.

2.5. Visible-light Induced Photodecomposition Efficiency Analysis

This series of experiments was carried out inside a quartz reactor with a sunlight collector to reflect light to the reactor. These experiments were performed for 2 h from 11 am to 13 pm under the optimum conditions, already determined based on the UV-light induced photodegradation tests. The pH of natural aquatic media lies in the neutral range. Therefore, for the current measurements based on visible light irradiation, the pH value of 7 was considered. For the sake of homogenization of the solution to be analyzed, an air pump was attached to the set-up.

2.6. Photodegradation kinetics

The kinetics of PCP photodegradation reactions in the presence of the Bi/SnO₂/TiO₂-G photocatalyst was measured via Equation (1):

$$\ln \left(\frac{c}{c_0} \right) = -kt \quad (1)$$

where c and c_0 are the momentary and initial concentrations, respectively. k and t are the reaction rate and time constants, respectively (Elmolla and Chaudhuri 2010).

3. Results and discussion

3.1 Crystalline structure

To validate the formation of the multiphasic nanocomposite photocatalyst, XRD analysis was performed and the corresponding crystalline phases of each component were precisely determined. Fig. 1a demonstrates the XRD pattern of G, Bi-G, Bi/SnO₂-G and Bi/SnO₂/TiO₂-G nanocomposites. As can be seen here, graphene has three distinct peaks at 27.6°, 54.7° and 56.4°, which can be indexed to (002), (004) and (110) diffraction planes, respectively (according to JCPDS-No. 75-2078). For G/Bi, the characteristic peaks at 23.6° (003), 37.1° (104), 39.5° (110), 43.9° (015), 63.8° (112), and

73.7° (009) were in good agreement with the typical peaks of the rhombohedral phase of Bi (JCPDS-No. 18-0244). The diffraction peaks at $2\theta=26.71^\circ$, 33.79° , 54.94° , 57.81° , 61.96° , and 66.03° correspond to (110), (101), (211), (220), (310) and (301) diffraction planes of SnO₂ core, respectively (JCPDS card No. 41-1445). The observed TiO₂ diffraction peaks at $2\theta= 25.6^\circ$, 48.3° , and 62.5° are associated with (101), (200), and (204) planes, respectively (JCPDS-No. 71-0574) (Sayadiet al. 2019). The crystallite size of the specimens was calculated via the Debye-Scherrer formula (equation (2)):

$$D = \frac{k\lambda}{\beta} \cos \Theta \quad (2)$$

where K is the grain shape factor (0.9), λ is the wavelength of X-ray (nm), d is the average crystallite size (nm), β is the full width at half max in radians and Θ is the Bragg diffraction angle of the peak in degree. According to this equation, an average crystallite size of 40 nm was measured.

3.2 Fourier Transform Infrared (FTIR) analysis

Fig. 1b shows the FT-IR spectra of the Bi/SnO₂/TiO₂-G nanocomposite. For graphene, the peaks appearing at 1060 cm^{-1} , 1372 cm^{-1} , 1635 cm^{-1} , 1726 cm^{-1} , and 3430 cm^{-1} , are attributed to the C-O stretching vibrations of epoxy groups, OH deformation vibrations of tertiary C-OH, OH deformation vibrations of COOH groups, C=O stretching of carbonyl groups and OH stretching vibrations of adsorbed water, respectively (Wanget al. 2013). The first peak located at 530 cm^{-1} and the one at 646 cm^{-1} are associated to Bi-O. The peaks located at 846 cm^{-1} and 1384 cm^{-1} are attributed to Bi-O-C and Bi-O-Bi stretching vibration, respectively (Liu et al. 2020). In the case of SnO₂, the peak emerging at about 513 cm^{-1} relates to vibrations of Sn-O. Moreover, the peaks at 463 cm^{-1} and 601 cm^{-1} can be associated to the symmetric vibrations of O-Sn-O and the asymmetric vibrations of Sn-O-Sn, respectively (Sayadiet al. 2019; Tamminaet al. 2016; Tamminaet al. 2017). Lastly, the peaks appearing at 817 cm^{-1} and 1029 cm^{-1} can be related to O-Ti-O flexural vibration and Ti-O-Ti tensile vibration, respectively (Rajakumaret al. 2014).

Fig. 1

3.3. Morphology

The structure and morphology of the nanocomposite photocatalyst were observed by Scanning Electron Microscopy (SEM). Fig. 2a&b shows the SEM images of Bi/SnO₂/TiO₂-G samples. The functionality of the graphene nanosheets results in formation of spherical Bi, SnO₂, and TiO₂ nanoparticles with a uniform distribution and small particle size ranging from 36 to 46 nm (Fig. 2c).

Fig.2

3.4 X-ray photoelectron spectroscopy (XPS) analysis

The surface chemistry of the Bi/SnO₂/TiO₂-G nanocomposite was examined through XPS analysis. Fig. 3a shows the general XPS spectrum of Bi/SnO₂/TiO₂-G implying the existence of carbon, oxygen, bismuth, tin and titanium. Fig. 3b exhibits the C1s peak of graphene wherein the main peak is attributed to sp²-hybridization (C-C bond, 284.5 eV). The three minor peaks appearing at 285.94, 287.51 and 288.81 eV, correspond to C-O bonds, carbonyl (C=O), and carboxylate (O-C=O) functional groups, respectively (Kumaret al. 2016). Fig. 3c reveals Bi 4f peaks situated at 159.05 eV and 164.29 eV, implying that Bi exists as Bi³⁺ in the composite (Jianget al. 2011). The peaks of Sn 4s, 3p, 4p, 3d, and 4d for SnO₂ are also visible in Fig. 3d. As shown in this Figure, the Sn 3d spectrum includes two peaks at 487.23 and 495.67 eV that are attributable to Sn 3d_{3/2} and Sn 3d_{5/2} spin orbit peaks of SnO₂, verifying the formation of SnO₂ nanoparticles on the surface of graphene nanosheets (Kumaret al. 2015). Fig. 3e displays the TiO₂ spectrum, therein doublet peaks of Ti 2P_{1/2} (458.63 eV) and Ti 2P_{3/2} (464.26 eV) are clearly seen. These peaks clarify the Ti⁴⁺ chemical state and imply that titanium exists in the form of TiO₂ (Benjwal and Kar 2015).

Fig. 3

3.5 BET analysis

Fig. 4 shows the N₂ adsorption-desorption isotherms curve of Bi/SnO₂/TiO₂-G nanocomposite. From the adsorption segment of the isotherm curve, the specific surface area of Bi/SnO₂/TiO₂-G nanocomposite can be calculated through the multipoint Brunauer–Emmett–Teller method, as large as 33.38 m² g⁻¹. The specific surface area of Bi@SnO₂/TiO₂-G nanocomposite is mainly attributed to the contribution of graphene. From the desorption segment of the isotherm curve, pore size distribution of Bi/SnO₂/TiO₂-G nanocomposite can be calculated through the Barrett-Joyner-Halenda (BJH) model,

in the range of a typical mesoporous structure (inset). As shown here, the pores are mainly as small as 38.5 nm, and the total pore volume based on the pores whose size varies from 0 to 100 nm is 0.315 cm³g⁻¹.

3.6 TGA analysis

Fig. 5a shows the thermal analysis result for the Bi/SnO₂/TiO₂-G nanocomposite. The presence of impurities remaining after a high temperature heating process on the nanocomposite photocatalyst was investigated via TGA analysis. Weight losses took place in three temperature ranges of: 1) 26–150°C due to the evaporation of absorbed water. 2) 250–400°C, due to the evaporation of some organic precursors, and 3) 400–600°C, thereafter the nanocomposite remains stable even at temperatures above 600°C.

3.6 UV-vis DRS spectra

Fig. 5b displays the UV-Vis optical absorption spectra for TiO₂, Bi, Bi/SnO₂ and Bi/SnO₂/TiO₂-G within the wavelength range of 300–800 nm. The main absorption bands are seen in the visible region for Bi (460 nm), SnO₂ (480 nm) and G (490 nm). The neat TiO₂'s characteristic absorption band appears at 420 nm. As other semiconductors, the band-gap energy (E_g) of the photocatalysts synthesized in this study can be calculated via equation 3 (Wanget al. 2017):

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \quad (3)$$

where E_g , $h\nu$, α and A represent the band gap energy, photon energy, absorption coefficient and a constant, respectively (Huet al. 2015; Wanget al. 2017). The estimated band-gap energies of neat TiO₂, Bi, Bi/SnO₂ and Bi/SnO₂/TiO₂-G were measured to be 3.05 eV, 2.94 eV, 2.63 eV and 2.42 eV, respectively. A narrow-band gap is useful for improving the visible light absorption, thus Bi/SnO₂/TiO₂-G can show an advanced photocatalytic performance.

3.8 PL spectra

Fig. 5c demonstrates the PL spectra of all samples in the range of 380–510 nm. Based on this figure, TiO₂ shows the strongest emission, implying that the photogenerated electrons and holes are

recombined promptly. In contrast, the emission strength of Bi/SnO₂/TiO₂ and Bi/SnO₂/TiO₂-G is lower, indicating Bi/SnO₂ and graphene can effectively separate the electron-hole pairs photogenerated by TiO₂. This suggests that such a heterostructure could offer a more optimum photocatalytic activity.

3.7 Zeta potential

Fig. 5d shows the variations of zeta potential in the pH range of 2 to 12 for Bi/SnO₂/TiO₂-G nanocomposite. Based on this measurement, the zeta potential of Bi/SnO₂/TiO₂-G takes place at pH 7.3.

Fig. 5

3.8 UV-light induced photodecomposition of PCP

3.8.1 Effect of pH

pH notably affects pollutants' solubility and photocatalysts' surface charge and hydroxyl radical production ability. Fig. 6a demonstrates the pH dependent PCP photodegradation rate of Bi/SnO₂/TiO₂-G. When pH declines from 11 to 3, the PCP photodegradation rate increases, peaking at pH3.

According to Fig. 6a, the highest amount of PCP degradation occurs under acidic conditions, where a large concentration of H⁺ ions leads to formation of many H⁺ radicals. These radicals bond with the oxygen present in the solution and further generate [•]HO₂ radicals, that can be later converted to [•]OH ones. Upon forming insoluble compounds at high pHs, the PCP degradation rate declines, possibly due to a lower light absorption and less hydroxyl radical production (Sayadi et al. 2019). Rajput et al. investigated the photodegradation process of PCP at the pH range of 3–8. Their results showed that PCP degradation was affected by the solution pH and the highest degradation occurred at pH3 (Rajput et al. 2018).

3.8.2 Effect of the catalyst dosage

The effect of Bi/SnO₂/TiO₂-G catalyst dosage on the PCP degradation rate is presented in Fig. 6b. Up to a certain extent, the higher the catalyst amount, the larger the PCP degradation efficiency

was. The reason for this observation could be related to the increased density of active sites able to produce hydroxyl radicals with the catalyst dosage (Li and Shi 2016). A similar behavior has been reported by Zhang et al. (Zhanget al. 2016). They declare that the extent of photodegradation of phenolic compounds increases with increasing the catalyst content.

3.8.3 Effect of the PCP initial concentration

The correlation of the photodegradation rate with the PCP initial concentration is represented in Fig. 6c. As shown here, the photodegradation rate decreases with increasing the PCP initial concentration. This could be related to this fact that the available active sites on the photocatalyst are rapidly occupied by the PCP molecules. Thus, formation of reactive radicals is hampered. Moreover, at higher PCP initial concentrations, the number of photons reaching the catalyst surface and thereby the photodegradation efficiency is notably reduced (Pourtaheri and Nezamzadeh-Ejhieh 2015). A similar performance has also been observed by Han et al. (Hanet al. 2019).

3.9 Comparison of PCP degradation rates by the synthesized catalysts

The PCP degradation rate of Bi, Bi/SnO₂, and Bi/SnO₂/TiO₂-G catalysts is shown in Fig. 6d. The results indicate that by changing the catalyst type from Bi to Bi/SnO₂/TiO₂-G a significant change in the photodegradation rate (from 45% to 84%) takes place. Accordingly, Bi/SnO₂/TiO₂-G is regarded as the most efficient catalyst for photodegradation of PCP, among the synthesized compounds.

Fig. 5.

3.10 The PCP photodegradation kinetics

The PCP photodegradation process was analyzed from kinetics point of view. For such an analysis, optimum experimental conditions including pH = 3, 20 mg/l PCP concentration, 0.3 g/l catalyst (Bi, Bi/SnO₂, and Bi/SnO₂/TiO₂-G) concentration (dosage) and 120 min reaction time were taken into account. Fig. 7a shows that the photodegradation process proceeds linearly over time and complies well with the first order kinetics. Additionally, depending on the type of the catalyst, the PCP photodegradation reaction rate constant rises from 0.007 min⁻¹ (Bi) to 0.0149 min⁻¹

(Bi/SnO₂/TiO₂-G)(Table 1). Ba-Abbad et al. (Ba-Abbad et al. 2017) investigated the photocatalytic degradation of PCP using ZnO nanoparticles. Their results showed that the PCP photodegradation process followed the first-order kinetics and the reaction rate constant with the optimum catalyst amount was 0.0052 min⁻¹.

Table 1

3.11 Reusability of Bi/SnO₂/TiO₂-G

Reusability of the Bi/SnO₂/TiO₂-G photocatalyst for UV-light induced photodegradation of PCP was examined in five successive cycles under the optimum environmental conditions previously defined. To do so, the Bi/SnO₂/TiO₂-G photocatalyst was separated from the solution after each use and washed several times with deionized water; then was dried at 60°C and used again for the next PCP photodegradation cycle. As shown in Fig. 7b, the PCP photodegradation efficiency did not decrease significantly after 5 cycles and the nanocomposite photocatalyst still showed a high efficiency of 68% in the last cycle. The reason for loss of efficiency can be associated to the occupation of Bi/SnO₂/TiO₂-G surface active sites by the decomposed organic residues. Furthermore, the Bi/SnO₂/TiO₂-G photocatalyst's mass declines during each cycle of the recovery process and this leads to a lower PCP photodegradation efficiency (Guo et al. 2020). Overall, stability and reusability of the Bi/SnO₂/TiO₂-G photocatalyst hold promise for its further application in photocatalytic degradation of organic pollutants.

XRD was used to assess the structural properties of the catalyst before and after reuse. Fig. 7c shows the XRD patterns of the catalyst before and after five cycles. As seen here, the intensity of the XRD diffraction peaks negligibly declines after reuse. Therefore, no significant change is observed in the XRD patterns of Bi/SnO₂/TiO₂-G before and after reuse. The peaks related to the anatase phase of Ti in the XRD pattern remain almost intact even after five uses, indicating that Bi/SnO₂/TiO₂-G possesses high stability and can be reused for several cycles without remarkable changes in its initial crystalline structure.

3.12 Visible light induced photodegradation of PCP by Bi/SnO₂/TiO₂-G photocatalyst

As shown in Fig. 7d, the visible light induced photodegradation efficiency of Bi/SnO₂/TiO₂-G photocatalyst rises over time. Comparing this performance (photodegradation rate) at two pH values

of 3 and 7, one can see that this catalyst has a higher degradation potential under acidic condition rather than under the neutral one.

Fig. 7

3.13 Visible light induced photocatalysis mechanism

Scheme 1a shows the proposed reaction scheme for the visible light induced photodegradation of PCP by the Bi/SnO₂/TiO₂-G nanocomposite. As seen here, graphene interlinks Bi, SnO₂ and TiO₂ nanoparticles, thereby causing e⁻ and h⁺ separation and hampering recombination. When graphene is irradiated with visible light, the photogenerated electrons are shifted from valence band (VB) to conduction band (CB), leaving h⁺ in VB. On the other hand, the photogenerated electron present in CB could be driven towards Bi, SnO₂ and TiO₂ through the formed junctions. A large number of O₂^{•-} is made over the catalyst surface through the reaction between e⁻ and the absorbed O₂, that can contribute to PCP degradation.

3.14 Degradation pathways

Scheme 1b proposes the possible reaction pathways for PCP photodegradation. It shows an oxidative dechlorination pathway through substitution of chlorine by HO[•]. 14 intermediates are involved in the PCP photodegradation process. The ion at m/z 265.84 represents PCP. Based on the above, the photodegradation of PCP by the Bi/SnO₂/TiO₂-G nanocomposite refers to two main pathways, including main product ions at m/s 247.67 and 231.92 which were identified as 2,3,5,6-Tetrachloro-1,4-benzenediol (TeCP) and 2,3,5,6-Tetrachlorophenol (TCP) (Antonopoulou et al. 2014). As shown in TCP pathway, during the decomposition, the reaction proceeds based on the isomers of 2,3,5,6-Tetrachlorophenol (TCP), 2,3,6-trichloropheno (m/s 195.73), 2,6-dichlorophenol (m/s 162.89), 2,4,5-trichlorophenol (m/s 195.86) and 2,5-dichlorophenol (m/s 161.91). In another pathway, the chlorination process involving 2,3,5,6-Tetrachloro-1,4-benzenediol (TeCP) results in the formation of possible isomerized intermediates with m/z values of 177.82 and 143.76. Subsequently, cleavage of the azo (C-Cl) bond leads to the formation of benzenoid degradation intermediates with m/z values of 128.42 and 93.96. This consequently gives rise to the formation of phenol, which oxidizes to form maleic acid. All these aromatic intermediates would undergo further oxidation to form aliphatic

carboxylic acids (such as malonic acid). Eventually, the ring-opening reactions would give rise to formation of the products that are oxidized to CO₂, H₂O and Cl⁻ with help of h_{VB}⁺, O₂⁻ and [•]OH species.

Scheme 1.

4. Conclusion

In this study, we devised a novel heterostructure photocatalyst composed of Bi/SnO₂/TiO₂-G that could efficiently photodegrade organic pollutants (here PCP). Upon visible light irradiation, the photocatalyst could generate a large number of OH⁻ and O₂⁻ reactive radicals, playing an important role in PCP photodegradation. The excellent photocatalytic activity of the nanocomposite photocatalyst is ascribed to its novel composition as well as its unique heterostructure. Taken together, a promising, cost-effective, and highly efficient strategy has been introduced for the design and synthesis of a novel visible light driven photocatalyst that can be used for the degradation of organic contaminants in water treatment.

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Table 1 The PCP photodegradation reaction rate constant with various types of the catalysts

Catalyst	catalyst concentration (g/l)	PCP concentration (mg/l)	k (min ⁻¹)	R ²
Bi	0.3	20	0.007	0.9722
Bi/SnO ₂	0.3	20	0.0101	0.9733
Bi/SnO ₂ /TiO ₂ -G	0.3	20	0.0149	0.9778

Fig. 4. N_2 adsorption-desorption isotherms of $\text{Bi}/\text{SnO}_2/\text{TiO}_2\text{-G}$ nanocomposite. Inset pore size distributions from the adsorption branch through the BJH method

Fig. 5. a) TGA spectrum for Bi/SnO₂/TiO₂-G; b) UV-visible absorption spectra for G, Bi-G, Bi/SnO₂-G and Bi/SnO₂/TiO₂-G; c) PL spectra of the as-prepared pure TiO₂, Bi/SnO₂/TiO₂ and Bi/SnO₂/TiO₂-G samples. d) Zeta potential measurement graph for Bi/SnO₂/TiO₂-G.

Fig. 6. The PCP photodegradation rate variations depending on a) pH; b) catalyst dose; c) PCP concentration; d) the catalyst type.

Fig. 7. a) Photodegradation kinetic behavior of the different photocatalysts; b) Reusability assessment for the Bi/SnO₂/TiO₂-G photocatalyst in a cyclic manner; c) XRD pattern of Bi/SnO₂/TiO₂-G catalyst before and after 5 cycles. d) Visible light-induced photodegradation of PCP under sunlight and different pHs.