



Visible Light- or UV-Activated Carbon Nanotube-TiO₂ Composite Nanofibers for Indoor BTEX Purification†

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Poly vinyl acetate (PVAc)-supported carbon nanotube (CNT)-TiO₂ composite nanofibers (PCTCNs) with different CNT to TiO₂ weight ratios were prepared using a combined sol-gel and electrospinning technique. The photocatalytic performance of the as-prepared PCTCNs for degradation of an indoor concentration level of benzene, toluene, ethyl benzene and *o*-xylene (BTEX) was evaluated under visible-light or UV irradiation. For comparison, a PVA-supported TiO₂ composite nanofiber (PTN) was also investigated for its photocatalytic performance. The characteristics of the PCTCNs and the PTN were determined using scanning electron microscopy and diffuse reflectance UV-visible spectra. For the target compounds, the average photocatalytic degradation efficiencies obtained from PCTCNs were higher than that obtained from PTN. Specifically, the average photocatalytic degradation efficiencies of BTEX obtained from PCTCN-0.056 were 10, 44, 75 and 88 %, respectively, while those obtained from PTN were 4, 11, 30 and 34 %, respectively. Moreover, the PCTCN-0.056 exhibited the highest photocatalytic degradation efficiencies among the as-prepared PCTCNs, although it did not have the highest MWCNT to TiO₂ mixing ratio. Similar to the visible-light irradiation conditions, PCTCN-0.056 revealed the highest photocatalytic degradation efficiencies of BTEX under UV irradiation conditions. However, unlike the visible-light irradiation conditions, the photocatalytic performance of certain PCTCNs were lower than those of PTN. Taken together, PCTCNs exposed to visible light could reveal superior performance for photocatalytic degradation of toxic indoor pollutants, when appropriate ratios of MWCNT to TiO₂ were utilized for the preparation of PCTCNs.

Keywords: Polymer support, Carbon nanotube to TiO₂ ratio, Optimal ratio, Light source type, Indoor pollutant degradation.

INTRODUCTION

Nanosized titanium dioxide (TiO₂) particles coupled with carbon materials including granular and fibrous activated carbon (AC) and carbon nanotubes have attracted a great attention for environmental applications because of their enhanced photocatalytic performance compared to pure TiO₂ particles¹⁻⁴. In carbon-TiO₂ composites, carbon materials seem to assist the TiO₂ powders by concentrating the pollutants and intermediates around the carbon materials followed by subsequent migration of these species to the surface of TiO₂ powders through a diffusion process⁴. Carbon nanotube (CNT) materials are preferred to granular or fibrous activated carbon mainly due to their controllable structural as well as unique electrical natures⁵. They also have a high electron-storage capacity with one electron per 32 carbon atoms^{6,7}. Moreover, there is a space-charge

separation region at the CNT-TiO₂ barrier, which has been attributed to increase recombination times for photon-induced electron-hole pairs⁵. Accordingly, several research groups⁸⁻¹⁰ have suggested CNT-TiO₂ composites as a promising photocatalyst for environmental applications.

Conducting polymer fibers are another supporting material with strong environmental stability and high conductivity¹¹. Expecting a synergistic effect of two supporting materials on photocatalytic activity, previous studies^{12,13} have combined CNT-TiO₂ composites with conducting polymer materials to prepare CNT-TiO₂ composite nanofibers (CTCNs) and demonstrated the feasibility of their potential application for environmental purification. However, the effect of CNT to TiO₂ ratios on the photocatalytic activity of CTCNs is an issue that remains to be further addressed. In addition, previous studies were performed under UV irradiation for photocatalytic activity tests

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of their CTCNs. It is noteworthy that CNTs can further enhance the TiO₂ photocatalytic performance by acting as a photosensitizing initiate, so that photocatalysis can be extended into the visible range^{14,15}. Unlike aqueous applications, the applications of CTCNs to organic vapor purification are not found in literature, even though photon absorbance kinetics and reaction kinetics of environmental pollutants differ between the liquid-solid and gas-solid interfaces¹⁶.

Consequently, in the current study CTCNs with different weight ratios of MWCNT to TiO₂ were synthesized and their photocatalytic activities for the degradation of indoor air pollutants under visible-light as well as UV irradiation were evaluated. Poly vinyl acetate (PVAc) was used as a supporting polymer material for CTCN, because of its hydrophobicity, low price and chemical crosslinking reaction with a titanium precursor, which provide macroscopically homogeneous conditions, preventing undesired phase separation^{17,18}. It was another advantage of the CTCN application for air purification that a coating process onto the inside wall of a Pyrex tube-type photocatalytic reactor that was required when coupled with powder-type photocatalysts¹⁹ was unnecessary. Four gas-phase compounds, benzene, toluene, ethyl benzene and *o*-xylene (BTEX), were chosen as target pollutants based on their prevalence in the indoor air of residential buildings in urban and suburban areas^{20,21} and their hazardous health effects²²⁻²⁴.

EXPERIMENTAL

Preparation of polyvinyl acetate-supported CTCN:

PVAc-supported CTCNs (PCTCNs) with different weight ratios of MWCNT to TiO₂ were prepared in two steps: first, preparation of carboxyl-functionalized MWCNT (MWCNT-COOH) and second, an electrospinning process. The MWCNT-COOH was prepared by refluxing MWCNTs (95.9 %, Carbon Nano-material Technology Co., Ltd, Korea) with concentrated nitric acid (HNO₃, 60 %, Sigma Aldrich co.). For this process, 2 g of MWCNTs were mixed with 120 mL of HNO₃ and then this mixture was sonicated for 0.5 h for homogeneous mixing. The resultant solution was refluxed for 20 h at 110 °C and subsequently, filtered under vacuum through a membrane filter (0.22 millipore polycarbonate membrane). The filtered media was washed with distilled water, dried for 48 h at 50 °C.

The as-prepared MWCNT-COOH was combined with TiO₂ fiber using the electrospinning process to synthesize PCTCNs with different ratios of MWCNT to TiO₂. 3.8 mL acetic acid was added to 6.2 mL titanium isopropoxide (TIP, Sigma Aldrich co.). In addition, 1.35 g polyvinyl acetate (Sigma Aldrich co.) was added to 10 mL N,N-dimethylformamide (DMF, Sigma Aldrich co.). Subsequently, the 2 mL TIP-acetic acid solution was added to 10 mL PVAc-DMF solution and stirred vigorously with Teflon-coated magnetic bars. This solution was mixed again with 5 mL of early-prepared MWCNT-COOH (0.001, 0.002, 0.005 or 0.025 g) dispersed in acetic acid while sonicating at a high frequency (220 W, 44 KHz) for 0.5 h. These four MWCNT-COOH weights were used to prepare PCTCNs with weight ratios of MWCNT to TiO₂ of 0.01, 0.019, 0.037, 0.056 and 0.084, respectively, which were designated as PCTCN-0.01, PCTCN-0.019, PCTCN-0.037, PCTCN-0.056 and PCTCN-0.084, respectively. The final product was loaded

into a plastic syringe (15 mL). A DC voltage of 19 kV was used for electrospinning. For comparison, a PVA-supported TiO₂ nanofiber (PTN) was prepared using the same procedure as used for the PCTCNs, but without addition of MWCNTs. The characteristics of the PCTCNs and the PTN were determined using scanning electron microscopy (SEM)/Energy-dispersive X-ray (EDX), X-ray diffraction (XRD) and diffuse reflectance UV-VIS-NIR spectra.

Tests of photocatalytic performance: The photocatalytic performance of as-prepared PCTCNs and PTN were investigated for the decomposition of BTEX in a cylindrical-type continuous flow Pyrex reactor (25 cm length and 3.8 cm inside diameter), whose inner wall was surrounded with aluminum foil-supported PCTCN or PTN. A cylindrical UV or visible lamp was inserted inside the Pyrex reactor and served as the inner surface of this reactor. The UV radiation was supplied by an 8-W fluorescent black light (F8T5DL, Youngwha Lamp Co.) with a maximum spectral intensity at 352 nm and visible-light irradiation by an 8-W fluorescent daylight lamp (F8T5DL, Youngwha Lamp Co.) with a spectral range at 400-720 nm. The stream flow rate was measured using mass flow controllers and fixed at 1 L min⁻¹. The relative humidity was measured at inlet and outlet of the reactor using a humidity meter and fixed at 45 %. Standard gas (0.1 ppm for each compound) was prepared by injecting the target compounds into a mixing chamber *via* a syringe pump (KdScientific Model 210) and then was fed to the reactor. Gas measurements were performed at inlet and outlet of the photocatalytic reactor to determine the decomposition efficiency of the target compounds. Collected gaseous compounds were analyzed using a gas chromatography (GC, Perkin Elmer Clarus 680)/Mass spectrometer (MS, Perkin Elmer Clarus SQ8 T) coupled with an automated thermal desorber (Perkin Elmer ATD 350). The quality control procedure for organic vapor measurements included analyses of laboratory blank traps and spiked samples. The method detection limits ranged from 0.2 and 0.5 ppb, depending on target compounds.

RESULTS AND DISCUSSION

Characteristics of as-prepared composite nanofibers:

The characteristics of the as-prepared composite nanofibers (PTN, PCTCN-13, PCTCN-19, PCTCN-30, PCTCN-39 and PCTCN-58) were investigated using SEM, XRD and UV-visible spectroscopy. Fig. 1 represents the SEM images of the composite nanofibers with different MWCNT to TiO₂ mixing ratios. The results presented in this figure demonstrated that nanofibers could successfully be produced using the electrospinning method followed by the calcination step. Similarly, Aryal *et al.*¹⁷ reported that MWCNT and TiO₂ could be successfully incorporated to form composite nanofibers using a sol-gel process followed by an electrospinning process. The diameter of PCTCNs was larger than that of PTN and they increased as the MWCNT to TiO₂ ratio increased, due to elevated amounts of MWCNT for PCTCNs with high MWCNT to TiO₂ ratios.

Fig. 2 shows the UV-visible spectra of the PTN and PCTCNs with different MWCNT to TiO₂ mixing ratios. The PTN revealed lower absorption intensity for visible range edge

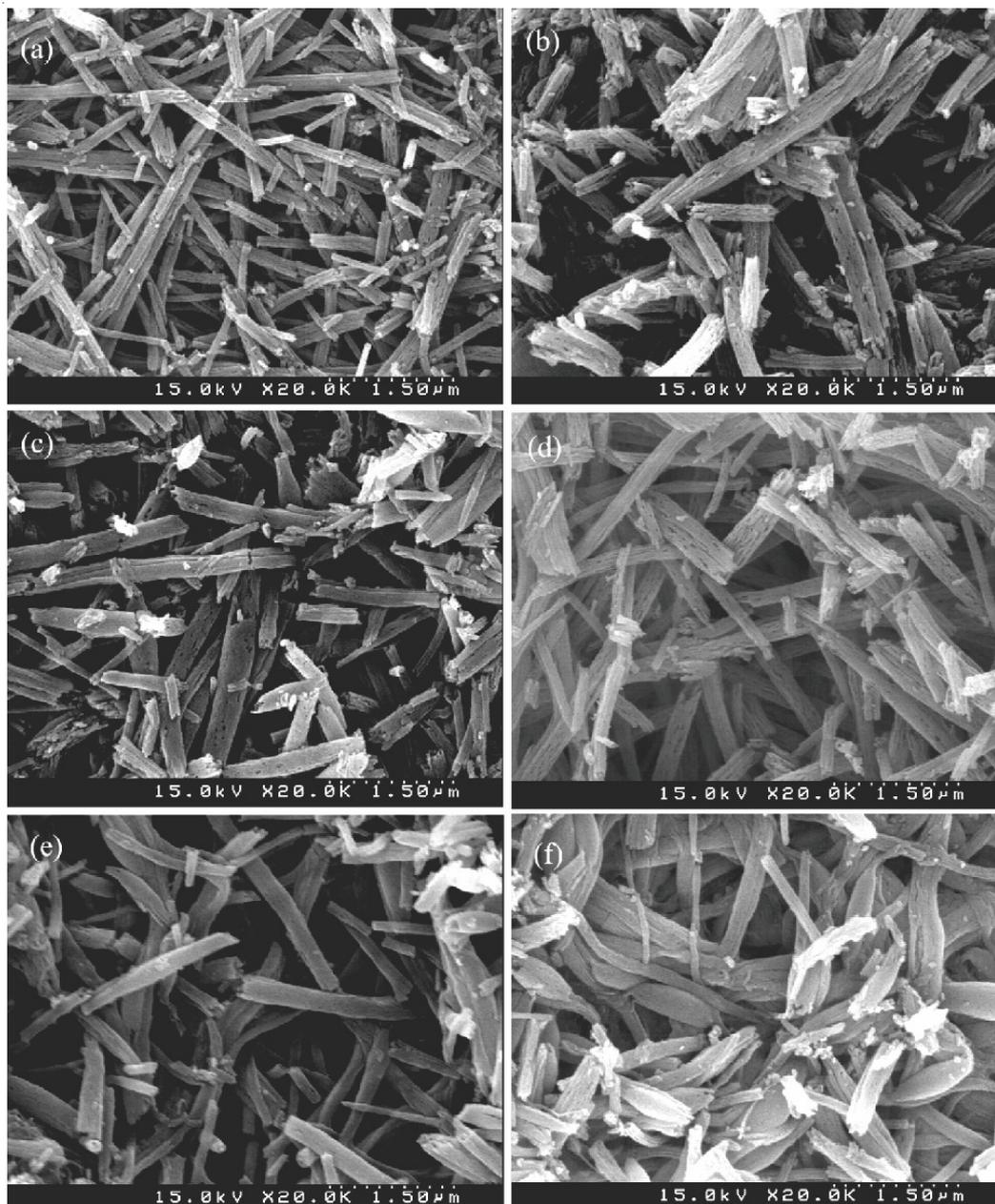


Fig. 1. Scanning electron microscopy of a reference PTN, PCTCN-0.01, PCTCN-0.019, PCTCN-0.037, PCTCN-0.056 and PCTCN-0.084

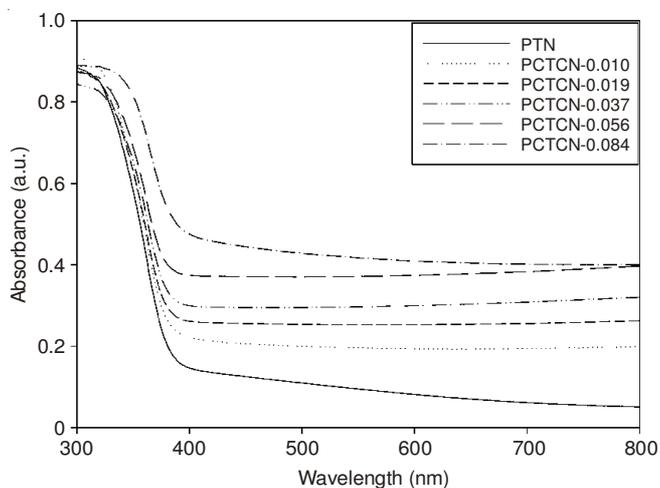


Fig. 2. UV-Visible spectra of PTN, PCTCN-0.01, PCTCN-0.019, PCTCN-0.037, PCTCN-0.056 and PCTCN-0.084

compared to PCTCNs. Additionally, the visible-light absorption intensity of PCTCNs increased as the MWCNT to TiO₂ mixing ratios increased, due to elevated MWCNT amounts for PCTCNs with high MWCNT to TiO₂ mixing ratios. In contrast, previous studies^{19,25} have shown that Degussa P25 TiO₂ exhibited an absorption edge at around 420 nm. Conversely, the absorption edge of the PCTCNs photocatalysts prepared in the present study shifted well to the visible-light range (> 700 nm). This absorption shift was attributed to the presence of carbon species at interstitial positions of TiO₂ lattice⁵. These findings further indicated that the as-prepared PCTCNs could act as an effective photocatalyst under visible-light as well as UV irradiation.

Photocatalytic performance of as-prepared composite nanofibers: The photocatalytic performance of PTN and PCTCNs synthesized with different weight ratios of MWCNT to TiO₂ were examined for the degradation of four gas-phase

compounds (BTEX) under visible-light or UV irradiation. Fig. 3 shows the time-series photocatalytic degradation efficiencies of BTEX as determined *via* a reference PTN, PCTCN-0.01, PCTCN-0.019, PCTCN-0.037, PCTCN-0.056 and PCTCN-0.084 under visible-light irradiation. For the target compounds, the average photocatalytic degradation efficiencies obtained from PCTCNs were higher than that obtained from PTN. Moreover, the PCTCN-0.056 exhibited the highest photocatalytic degradation efficiencies among the as-prepared PCTCNs, although it did not have the highest MWCNT to TiO₂ mixing ratio. These results suggested the presence of optimal MWCNT to TiO₂ mixing ratio for the synthesis of PCTCNs. Similarly, Kedem *et al.*¹³ reported that the photocatalytic activity for the decomposition of rhodamine B in aqueous phase obtained *via* a poly acrylonitrile (PAN)-supported CTCNs were higher than those obtained *via* a PAN-TiO₂. The enhanced photocatalytic activity of PCTCNs was attributed to synergistic effects of MWCNT, TiO₂ and conducting polymer on photocatalytic degradation of environmental pollutants^{12,13}. Consequently, these findings indicated that polymer-supported CTCNs exposed to visible light would reveal enhanced performance for photocatalytic degradation of toxic indoor pollutants.

Fig. 4 exhibits the the time-series photocatalytic degradation efficiencies of BTEX as determined *via* a reference PTN, PCTCN-0.01, PCTCN-0.019, PCTCN-0.037, PCTCN-0.056

and PCTCN-0.084 under UV irradiation. Similar to the visible-light irradiation conditions, PCTCN-0.056 revealed the highest photocatalytic degradation efficiencies of BTEX under UV irradiation conditions. Specifically, the average photocatalytic degradation efficiencies of BTEX obtained *via* PCTCN-0.056 were 78, 94, 96 and 97 %, respectively, whereas those obtained *via* PTN were 60, 88, 93 and 94 %, respectively. However, unlike the visible-light irradiation conditions, the photocatalytic activities of the other PCTCNs were lower than those of PTN. These results were likely due to less UV absorption of PCTCNs relative to PTN, because of strong UV absorption properties of MWNT that interfere with UV absorption by TiO₂ crystals.

Conclusion

The present study examined the application of PTCNs prepared with different weight ratios of MWCNT to TiO₂ using an electrospinning technique for the photocatalytic decomposition of airborne aromatic compounds (BTEX). The characteristics of as-prepared PTN and PTCNs could be successfully determined by SEM/EDX, XRD and UV-visible spectrophotometers. We found that PTCNs exposed to visible light could reveal superior performance for photocatalytic degradation of toxic indoor pollutants, when appropriate ratios of MWCNT to TiO₂ were utilized for the preparation of PCTCNs. In addition, the presence of an optimal ratio of MWCNT to TiO₂ for the preparation of

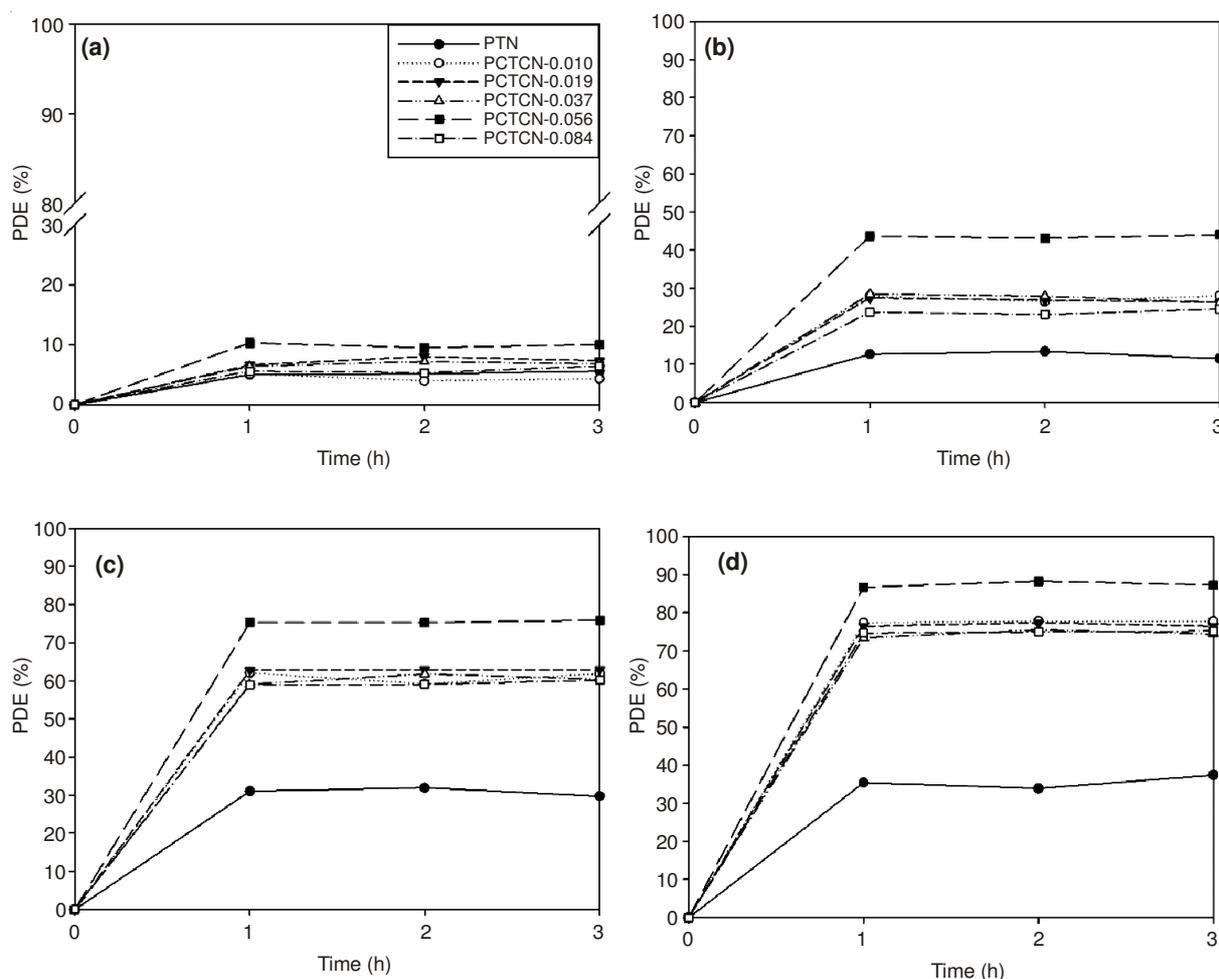


Fig. 3. Time-series photocatalytic degradation efficiencies (PDE, %) of gas-phase pollutants (a, benzene; b, toluene; c, ethyl benzene; d, *o*-xylene) as determined *via* a reference PTN, PCTCN-0.01, PCTCN-0.019, PCTCN-0.037, PCTCN-0.056 and PCTCN-0.084 under visible-light irradiation

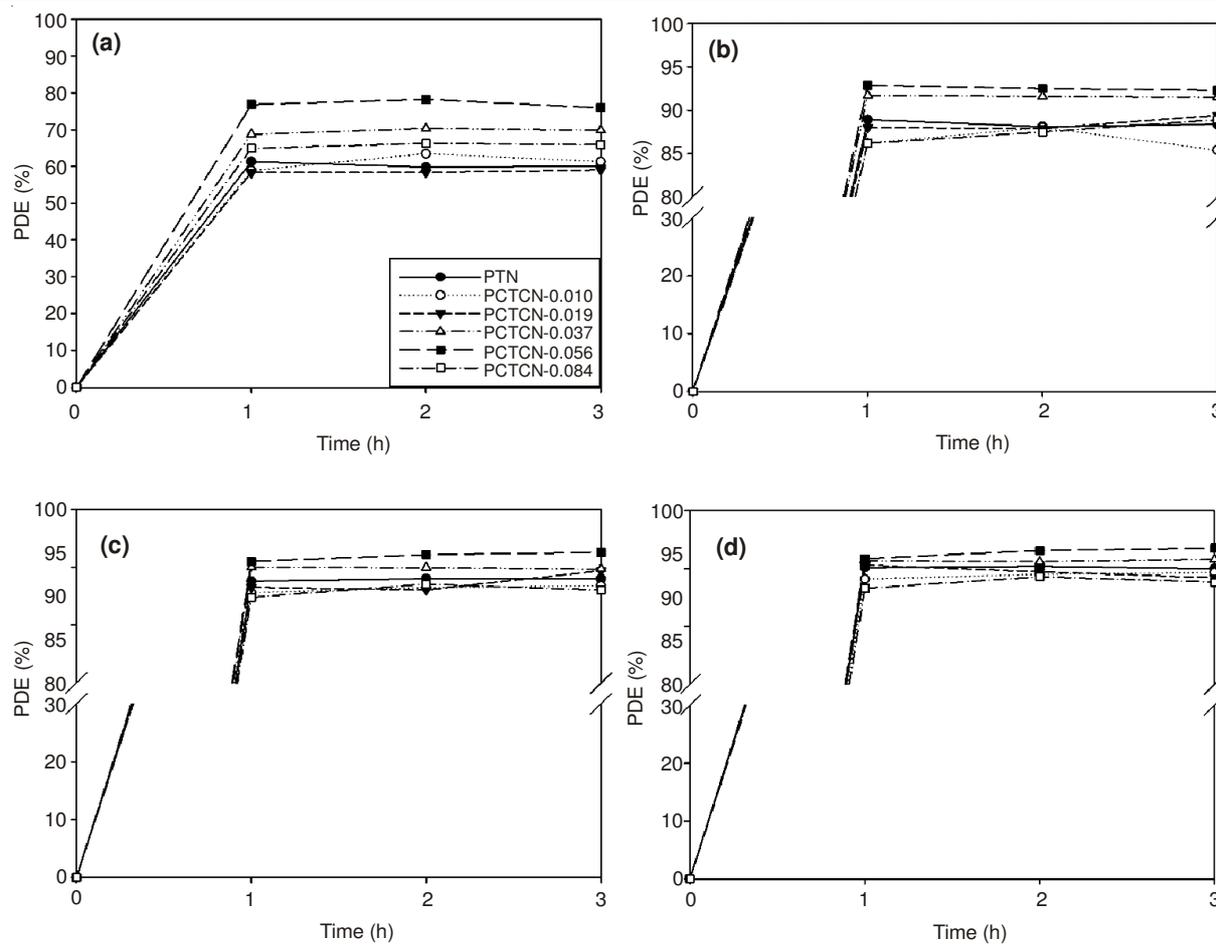


Fig. 4. Time-series photocatalytic degradation efficiencies (PDE, %) of gas-phase pollutants (a, benzene; b, toluene; c, ethyl benzene; d, *o*-xylene) as determined via a reference PTN, PCTCN-0.01, PCTCN-0.019, PCTCN-0.037, PCTCN-0.056 and PCTCN-0.084 under UV-light irradiation

PCTCNs was demonstrated. Similar to the visible-light irradiation conditions, PCTCN-0.056 revealed the highest photocatalytic degradation efficiencies of BTEX under UV irradiation conditions. However, it is noteworthy that, unlike the visible-light irradiation conditions, the photocatalytic performance of certain PCTCNs under UV irradiation conditions were lower than those of PTN.

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