

GAS PHASE OXIDATION OF FORMALDEHYDE BY $\text{TiO}_2/\text{TiO}_2\text{-V}_2\text{O}_5/\text{POLYPYRROLE}$ ENERGY STORAGE PHOTOCATALYST

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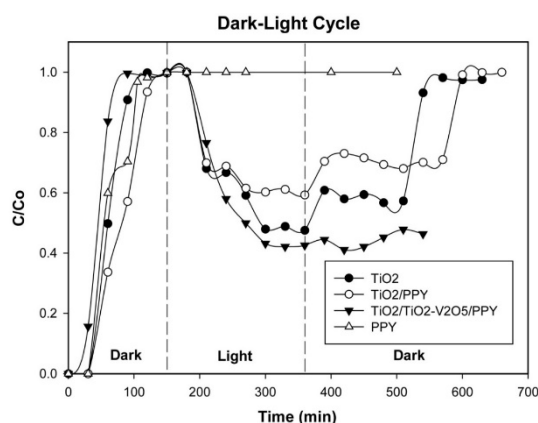
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Graphical abstract



Abstract

Photocatalytic oxidation of formaldehyde was performed through an electron storage photocatalyst named $\text{TiO}_2/\text{TiO}_2\text{-V}_2\text{O}_5/\text{PPy}$ nanocomposites, consisting of TiO_2 responsible for an electron generating source, $\text{TiO}_2\text{-V}_2\text{O}_5$ functional as an electron storage substance, and PPy (polypyrrole) as an electron conducting substance between the formers. It was found that the $\text{TiO}_2/\text{TiO}_2\text{-V}_2\text{O}_5/\text{PPy}$ nanocomposites showed both adsorption and photocatalytic activity for formaldehyde removal. Under UV irradiation, the catalytic activity of the $\text{TiO}_2/\text{TiO}_2\text{-V}_2\text{O}_5/\text{PPy}$ catalyst was 57%, which was 0.1 and 0.4 times higher than that of TiO_2 and TiO_2/PPy catalysts, respectively. Moreover, the $\text{TiO}_2/\text{TiO}_2\text{-V}_2\text{O}_5/\text{PPy}$ catalyst retained its function for at least 3 hours, after UV irradiation for 3.5 hours. The presence of $\text{TiO}_2\text{-V}_2\text{O}_5$ was found to enhance the photocatalytic activity of the TiO_2 catalyst, including the ability to function in the absence of UV light. This is due to the lower energy band gap of the $\text{TiO}_2/\text{TiO}_2\text{-V}_2\text{O}_5/\text{PPy}$, compared to that of TiO_2 ; the $\text{TiO}_2\text{-V}_2\text{O}_5$ also possesses energy storage ability. Further, the reaction rate of photocatalytic oxidation of formaldehyde by the electron storage photocatalyst was determined. The formaldehyde destruction rate is a function of formaldehyde concentration and can be formulated using a simplified Langmuir-Hinshelwood.

Keywords: Formaldehyde, Energy storage photocatalyst, Polypyrrole, TiO_2 , V_2O_5

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1.0 INTRODUCTION

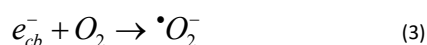
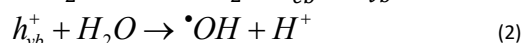
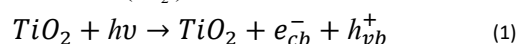
The impacts of the COVID-19 pandemic have brought about significant changes in health behavior i.e., sleep, physical activity, tobacco use, working, and staying longer periods at home [1,2]. Therefore, the awareness of the indoor environment

is of enormous interest, particularly indoor air quality. Poor indoor air quality leads to adverse health outcomes for residents, like the risk of cardiovascular disease, allergic symptoms, and cancer. The most common indoor air pollutants are benzene, toluene, and particularly formaldehyde, which is responsible for the "Sick building syndrome". Possible sources of formaldehyde are building material (e.g., insulating material),

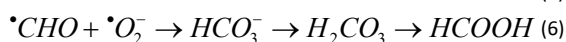
household products (e.g., cleaning solution, printing ink), composite wood products, paint, and smoking [3]. Moreover, the physical properties of formaldehyde i.e., the high vapor pressure at room temperature (3883 mm Hg at 25°C) and very low boiling temperature (-19.3°C) could be the reason for its notoriety as a harmful pollutant of indoor air. Thus, the attempt to improve the effective method for the removal of formaldehyde is of considerable interest [4].

Removal of formaldehyde from the air has been attempted by several routes, i.e., adsorption, plasma decomposition, and thermal catalytic oxidation. The disadvantages of these methods are efficiency loss after full adsorption, high energy consumption for the generation of plasma cluster ions that can destroy the pollutant, and high-temperature requirement for catalyst activation, respectively. Of these, photocatalytic oxidation is the most promising method for formaldehyde abatement, owing to its capability of decomposing formaldehyde under ambient conditions and self-regeneration. Several photocatalysts have been used for photocatalytic oxidation, e.g., ZnO, WO₃, Fe₂O₃, and TiO₂. TiO₂ is the most promising material for volatile organic compounds (VOCs) abatement including formaldehyde, as it is relatively inexpensive, chemically stable, and commercially available [4].

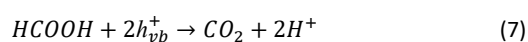
Titanium dioxide (TiO₂) generally has 2 major structures, which are anatase and rutile with the difference in band gap energy of 3.2 and 3.0 eV, respectively. The former has a higher photocatalytic activity than the latter because the conduction band position exhibits stronger reducing power. However, the wide band gaps of both structures limit their application in visible light, i.e., absorption of only UV, which accounts for 4-6% of the solar spectrum. The mechanism of photocatalytic oxidation is as follows; TiO₂ particle absorbs the UV light to excite electrons from the conduction band to the valence band (e_{cb}^-), while the holes are simultaneously generated at the valence band (h_{vb}^+) as shown in eq. (1). The generated holes are responsible for the oxidation of adsorbed water on the TiO₂ surface; on the other hand, the excited electrons are responsible for the reduction of adsorbed oxygen on the TiO₂ surface, as shown in eq. (2) and eq. (3), respectively. Consequently, the extremely high oxidizing power of the hydroxyl radical ($\bullet OH$) and superoxide radical ($\bullet O_2^-$) are generated [5].



These oxidative radicals further react with formaldehyde (HCHO) to form formic acid (HCOOH) which is the major intermediate product, as shown in eq. (4) - eq. (6).



Formic acid is further made to react by holes and the resultant products are carbon dioxide and hydrogen ion, as illustrated in eq. (7).



Photocatalytic oxidation kinetics of formaldehyde in the air by TiO₂ have been extensively studied [6]. The mechanism depends on the adsorption-desorption of various gas molecules on the active sites. The interaction between adsorbed formaldehyde and adsorbed oxygen was proposed as the rate-limiting step. Therefore, the adsorption of each reactant gas expressed based on the Langmuir adsorption isotherm is shown below.

$$\theta_{HCHO} = \frac{K_{HCHO}C_{HCHO}}{1+K_{HCHO}C_{HCHO}} \quad (8)$$

$$\theta_{O_2} = \frac{K_{O_2}C_{O_2}}{1+K_{O_2}C_{O_2}} \quad (9)$$

where θ_{HCHO} and θ_{O_2} are the concentration of adsorbed HCHO and that of O₂, respectively; K_{HCHO} and K_{O_2} are the adsorption equilibrium constant of HCHO and that of O₂, respectively; and C_{HCHO} and C_{O_2} are defined as the concentration of HCHO and that of O₂ in gas, respectively. Thus, the rate of photocatalytic oxidation of formaldehyde could be expressed as eq. (10)

$$r = k\theta_{HCHO}\theta_{O_2} = \frac{kK_{HCHO}C_{HCHO}K_{O_2}C_{O_2}}{(1+K_{HCHO}C_{HCHO})(1+K_{O_2}C_{O_2})} \quad (10)$$

The rate was determined at a low initial concentration of formaldehyde; therefore, the concentration of O₂ was much higher than that of formaldehyde ($K_{O_2}C_{O_2} \approx (1 + K_{HCHO}C_{HCHO})$). The reaction rate could be simplified as shown in eq. (11)

$$r = k\theta_{HCHO} = \frac{kK_{HCHO}C_{HCHO}}{(1+K_{HCHO}C_{HCHO})} \quad (11)$$

However, limitations for the practical application of TiO₂ are the fast recombination rate of the photo-excited electron-hole and the wide band gap of TiO₂. Those limitations can be addressed by the heterojunction of semiconductor materials with different band gaps [7] or loading/doping with noble metals [8], respectively. Suppression of the electron-hole recombination has been achieved by the heterojunctions between TiO₂ and other different band gap-semiconductors to improve charge separation and prolong the lifetime of charge carriers, e.g., TiO₂ (n-type semiconductor) and BiOI (p-type semiconductor). Under the light radiation, an equilibrium state between TiO₂ and BiOI is generated by reducing the Fermi level of TiO₂ and conversely, raising the energy band of BiOI. Therefore, the consequent electronic field-driven the transfer of excited electrons and holes to TiO₂ and BiOI particles, respectively. These phenomena hinder electron-hole recombination. Narrowing the band gap of TiO₂ by the doping of metal/ non-metal could be expected due to the formation of new localized electronic states or mid-gap state which requires lower energy to excite electrons and holes, i.e., sufficient energy from visible light [9].

Moreover, the kinetics study on the photocatalytic oxidation of formaldehyde by the modified TiO₂ was also determined [10]. The simplified Langmuir-Hinshelwood mechanism, which is a model of bimolecular chemical reactions on solid surfaces, was found to be fit for the photocatalytic oxidation of formaldehyde in the gas phase by Au/TiO₂ powders as shown in eq. (12)

$$r = -\frac{dC}{dt} = \frac{kKC}{1+KC} \quad (12)$$

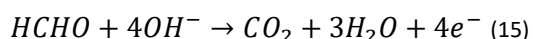
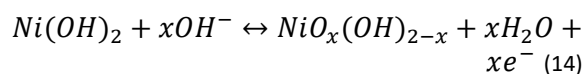
where C is the concentration of formaldehyde at time t , t is the reaction time, k is the kinetic constant and K is the adsorption

equilibrium constant. In the case of the low concentration of formaldehyde ($KC \ll 1$), the simplified Langmuir-Hinshelwood was expected, as shown in eq. (13)

$$r = -\frac{dC}{dt} = kKC \quad (13)$$

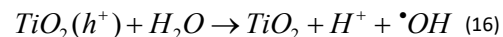
Yet, the photocatalytic activity in the dark or in the absence of light is still nominal. To prolong the photocatalytic activity of TiO_2 after switching off the light, “the energy storage photocatalyst” [11, 12] or “round-the-clock photocatalysis” [13, 14] has been announced. The principle of the energy storage photocatalyst is the coupling of TiO_2 , which is the major photo-excited electrons and holes generator, with energy storage substances having a compatible energy band gap; i.e., the conduction band of the electron storage substance must be below the conduction band of TiO_2 (e.g., WO_3 [11], MoO_3 [15]), the valence band of the hole storage substance must be above the valence band of TiO_2 (e.g., $Ni(OH)_2$ [12]). Under light irradiation, the compatible band gaps of TiO_2 and energy storage substance drive the charge transfer from TiO_2 to the energy storage substance. The storage electrons/holes are released by the reduction/oxidation of the absorbed molecule on the surface in the dark; therefore, the photocatalytic activity of energy storage photocatalyst can prolong for versatile applications e.g., degradation of water-air pollutant, disinfection, and anti-corrosion even in the dark, including photodegradation of formaldehyde [13].

The TiO_2 - $Ni(OH)_2$ bilayer film, a so-called hole storage photocatalyst, exhibited the degradation of formaldehyde in the dark after the film was exposed to UV light with an intensity of 30 mW/cm^2 for 4 hours. The mineralization of formaldehyde to CO_2 was manifest by the storage hole in terms of hydroxide ion (OH^-) into the TiO_2 - $Ni(OH)_2$ bilayer film after being photoelectrochemically charged, as shown in eq. (14-15) [16]



In our previous work, the enhancement of electron storage ability has been achieved by synthesis of the hybrid metal oxides (TiO_2 coupled with the electron storage substance, namely the TiO_2 - V_2O_5 compound [17]) with the conducting polymer (i.e., polyaniline (PANI) [18], polypyrrole (PPy) [19]). The design principle for high activity energy storage photocatalyst was found to depend on 1) the charge generated materials (e.g., TiO_2 , PPy- TiO_2 [20]) with lower stimulated energy, 2) the high capacity of the charge storage substance (e.g., TiO_2 - V_2O_5 compound or TVC [17]) and 3) the effectiveness of the electron mobility between TiO_2 and the charge storage substance by using a semi-conducting polymeric binder. The composite film consisting of TiO_2 and TVC which is in situ polymerized with PANI exhibited an electron storage efficiency of 96.3% by the addition of PANI of 2.17 wt% in the film, which is higher than that of the film without PANI [18]. Moreover, the TiO_2 / TiO_2 - V_2O_5 /PPy nanocomposites have been successfully synthesized with a lower energy band gap than pristine TiO_2 , and hence, the activity under visible light is possible [19]. Further, TiO_2 / TiO_2 - V_2O_5 /PPy composites also exhibited the ability to degrade the methylene

blue solution in the dark, after those particles were exposed to UV/Visible light. These phenomena acknowledge the electrons stored within TVC, as shown in eq. (16-17) [18].



To date, the ability to destroy formaldehyde by an electron storage photocatalyst has not been achieved or reported [13, 14]. This work aims to extend the application of TiO_2 / TiO_2 - V_2O_5 /PPy composites, the so-called electron storage photocatalyst, to the photocatalytic oxidation of formaldehyde in the air under UV light irradiation and in dark conditions. Moreover, we explore the kinetics of formaldehyde degradation with a higher initial concentration of formaldehyde in the air owing to the pollution of the indoor environment through much applied cleaning solutions, more smoking at home, etc. during the COVID-19 pandemic.

2.0 METHODOLOGY

Chemicals

TiO_2 nanoparticles were purchased from Carlo Erba, consisting of 98.5% anatase. TiO_2 - V_2O_5 nanoparticles were synthesized by the procedure reported by Ngaotrakanwivat and Meeyoo [17]. Pyrrole (98% reagent grade) was obtained from Sigma-Aldrich, Hydrochloric acid (37% analytical grade) from Merck, and Iron (III) chloride from Sigma-Aldrich. All chemicals used in this research were used without further treatment.

Catalyst Preparation and Characterization

The TiO_2 / TiO_2 - V_2O_5 /PPy nanocomposites were synthesized by *in situ* oxidative polymerization. Typically, 0.2 g of the TiO_2 nanoparticles and 0.65 g of TiO_2 - V_2O_5 nanoparticles were dispersed in 100 ml of 1.5 M HCl (aq.) by a sonication bath for 30 min. The resulting suspension was cooled at 0 °C. Then, 0.1 g of pyrrole was introduced into the suspension and stirred for 30 min. Thereafter, the solution was prepared by dissolving 0.4 g of $FeCl_3$ into 1 ml of 1.5 M HCl (aq.). The solution was added in drops to the above-cooled suspension and polymerization was allowed to take place for 6 h. The obtained product was washed with 1.5 M HCl (aq.) and distilled water, followed by vacuum drying at 60 °C for 24 h. A similar procedure was applied for the synthesis of TiO_2 /PPy nanocomposites without the addition of TiO_2 - V_2O_5 nanoparticles. The as-prepared samples were characterized by BET surface area, X-ray diffraction, and TEM. The phase structure of the synthesized TiO_2 / TiO_2 - V_2O_5 /PPy nanocomposites was explored by Bruker Euler Cradle for D8 Advance X-ray diffraction with Cu $K\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) operated at 40 kV and 40 mA over a 2θ range of 10-90°. The images of the nanocomposites were taken by a transmission electron microscope (TEM), Jeol, JEM-2100 with an accelerating voltage of 200 kV. The N_2 physisorption was conducted by using a surface analyzer (Quantachrome; model N12-5). The surface area of the nanocomposite was analyzed by the Brunauer-Emmett-Teller (BET) method.

Catalytic activity test

Photocatalytic activity tests for formaldehyde oxidation were carried out in a differential quartz tubular reactor (i.d. 6 mm). Typically, 0.1 g of the catalyst was packed between two layers of glass wool. The reactor was placed next to the UV lamp (Phillip 10 W) fitted into a wooden box. Formaldehyde was vaporized from a saturator at 10 °C using air as a carrier gas. The concentration of formaldehyde was controlled by mixing it with another stream of air. The concentration of formaldehyde was fixed at 500 ppm to compare the activity of each type of catalyst under UV irradiation and after switching off the light. To study the kinetics of formaldehyde photocatalytic oxidation, the concentrations of formaldehyde were adjusted in the range of 500, 700, 900, 1100, and 1300 ppm. The total flow rate of feed gases was kept at 40 ml/min using mass flow controllers (Brooks). A micro-electrical fan was used to control the surrounding temperature at 24 °C. The product gases were chromatographically analyzed with a gas chromatograph (Shimadzu GC-17A) equipped with an Agilent HP-FAPP column for an FID detector and Helium was used as a carrier gas. The precision of formaldehyde quantification by GC-FID was $\pm 3\%$.

3.0 RESULTS AND DISCUSSION

Catalyst Characterizations

The surface area of the photocatalyst can be considered one of the main factors for enhancing the photocatalytic activity, as the adsorbed substance on the surface of the photocatalyst can be decomposed by the oxidative radicals [9]. The PPy, which plays an important role as an electronic bridge in the charge storage photocatalyst consisting of TiO₂ (photo-excited electron generator) and the TiO₂-V₂O₅ compound (an electron storage material) should not cause a reduction in the surface area. Then, BET surface areas of the materials were measured as listed in Table 1. The surface areas of the materials were found to be in the range of 16 to 31 m²/g. The appropriate amount of polypyrrole (PPy) in the charge storage photocatalyst (TiO₂/TiO₂-V₂O₅) leads to a higher surface area. This phenomenon is in accordance with our previous work (TiO₂/TiO₂-V₂O₅-PANI) [19].

Table 1 BET Surface Area of Materials.

Samples	Specific Surface Area (m ² /g)
PPy	15.6
TiO ₂	19.4
TiO ₂ /PPy	20.3
TiO ₂ /TiO ₂ -V ₂ O ₅ /PPy	31.5

The phase structure of the TiO₂/TiO₂-V₂O₅/PPy nanocomposites was characterized by XRD, and the results are shown in Figure 1. Feature peaks of TiO₂ were found with phase contents of anatase and rutile, no feature peaks of PPy were detected owing to its amorphous structure, which conforms to works [20, 21]. Moreover, the feature peaks indicating the V₂O₅ particle could not be observed, in tune with the XRD patterns of the TiO₂-V₂O₅ particle that are similar to that of its parent oxide (TiO₂), suggesting the incorporation of vanadium atoms to the TiO₂ crystalline structure [17].

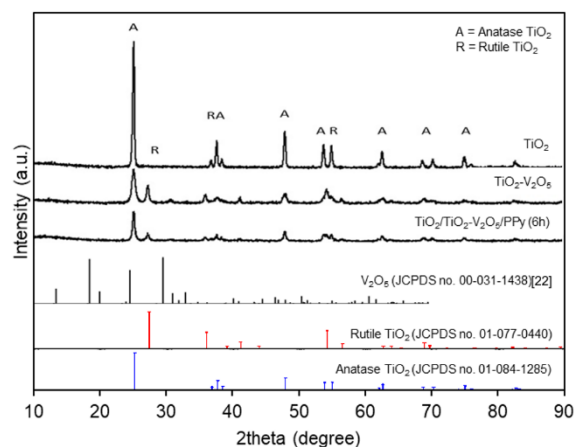


Figure 1 XRD patterns of TiO₂/TiO₂-V₂O₅/PPy, TiO₂, and TiO₂-V₂O₅

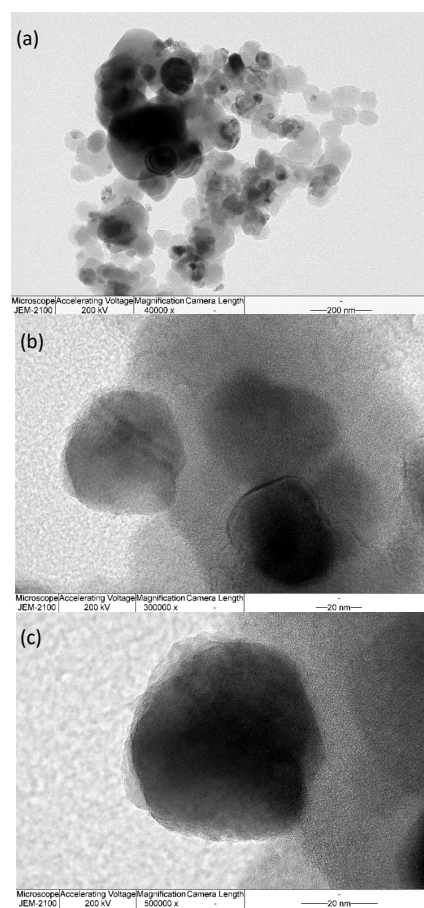


Figure 2 TEM images of TiO₂/TiO₂-V₂O₅/PPy

Moreover, the presence of PPy on the surface of metal oxides was confirmed by FTIR analysis, and the full analysis of the FTIR spectrum was reported in our previous work [19]. However, the presence of PPy was declared by TEM images, as illustrated in Figure 2. Opaque particles and translucent sheets that indicated the metal/metal oxide particles and organic substance, respectively, could be observed in Figure 2(a). At high magnification in Figure 2 (b, c), the opaque spherical particles with a diameter of 20–80 nm with the same appearance as TiO₂-V₂O₅ particles [18] were displayed. Moreover, a translucent

sheet (PPy) was fully covered on the opaque spherical particles and interconnected between those particles. This phenomenon is in agreement with other works [20, 23].

Adsorption/Photocatalytic reaction for formaldehyde oxidation

Before carrying out the photocatalytic reaction, all materials were saturated with formaldehyde. As shown in Figure 3, the adsorption of the TiO₂/TiO₂-V₂O₅/PPy particles reached a plateau after 90 minutes, while those of TiO₂ and TiO₂-PPy were saturated at 120 and 150 minutes, respectively. The adsorption capacity of the catalyst was calculated by the summation of the difference between the initial concentration and the concentration at any measurable time until the adsorption was saturated. The adsorption abilities of the TiO₂/TiO₂-V₂O₅/PPy, TiO₂, and TiO₂-PPy particles were at 7.5, 11.8, and 15.9 mg/g_{cat}, respectively. Although the surface area of the TiO₂-PPy and TiO₂ particles was similar (Table. 1), the former exhibited higher formaldehyde adsorption than the latter, which are parent particles (TiO₂). This could be the advantage of the higher formation of oxygen deficiency on the PPy surface [23]; consequently, the highest adsorption could be expected. Conversely, the TiO₂ and PPy incorporated in the TiO₂/TiO₂-V₂O₅/PPy did not exhibit the adsorption enhancement.

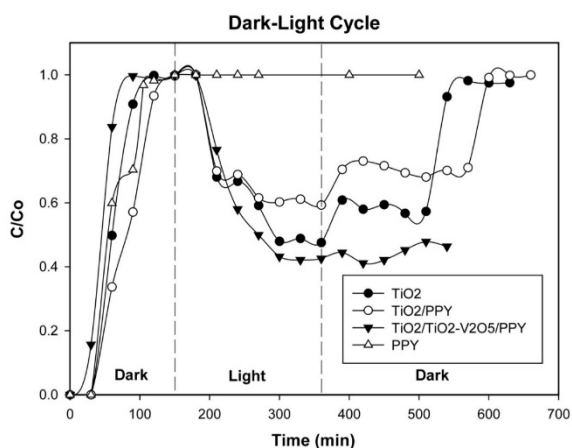


Figure 3 Photocatalytic oxidation of formaldehyde under UV light and dark over TiO₂/TiO₂-V₂O₅/PPy, TiO₂, and TiO₂-V₂O₅.

After the samples reached the saturation point, UV light was introduced. The results showed that all hybrid materials display photocatalytic activities, while PPy did not reveal a photocatalytic activity since it does not have such activity. The formaldehyde removal efficiency was governed by eq. (18)

$$\text{removal efficiency} = \left[1 - \left(\frac{C}{C_0} \right) \right] \times 100 \quad (18)$$

where C is the concentration of formaldehyde at time t and C_0 is the initial concentration of formaldehyde. Although the adsorption ability of TiO₂/TiO₂-V₂O₅/PPy particles was the lowest, interestingly, their photocatalytic oxidation activity under UV light was the highest at 57%, while the activities of TiO₂ and TiO₂-PPy were 52% and 40%, respectively. The formaldehyde removal efficiency of TiO₂/PPy was lower than that of pure TiO₂ owing to the different amount of TiO₂, which is the electron-hole generator, in the catalyst. Therefore, the lower amount of TiO₂ in the TiO₂/PPy particles (0.067 g) could provide less photocatalytic activity than the TiO₂ catalyst (0.1g), based

on the same loading amount of catalyst at 0.1 g. Conversely, only 0.023 g of TiO₂ contained in the TiO₂/TiO₂-V₂O₅/PPy catalyst exhibited enhanced photocatalytic activity up to 3.8 times based on the TiO₂ content. This might be because the compatible energy band gap of the TiO₂ and TiO₂-V₂O₅ compound could improve charge separation, leading to the suppression of the electron-hole recombination [9] and the electron storage phenomena [17].

There was a similar finding for the oxidation of methylene blue [19]. After switching off the UV light, the formaldehyde removal is still present in all materials, indicating the continuation of photocatalytic activity. This was due to some OH• radicals remaining on the surface of the materials after UV exposure [9]. The oxidation took place until they were all consumed. Then, the adsorption of formaldehyde took over until it reached adsorption equilibrium. Similar breakthrough characteristics were obtained for both TiO₂ and TiO₂/PPy. The photocatalytic activity of TiO₂/TiO₂-V₂O₅/PPy, on the other hand, remained unchanged, while even those of TiO₂ and TiO₂/PPy were diminished. The continuation of the catalytic activity in the dark cycle might be due to TiO₂-V₂O₅ acting as an energy storage material capable of self-discharging in the absence of light. Since PPy is a semiconducting polymer, the electron can transport through TiO₂-V₂O₅. It was evident that under potentiostat charging at -400 mV, TiO₂/TiO₂-V₂O₅/PPy could store the electrons up to 10 minutes, while TiO₂/PPy could store only 20 seconds. During UV exposure, some of the electrons generated by TiO₂ are stored in TiO₂-V₂O₅ and are released in the absence of light, as described in Figure 4.

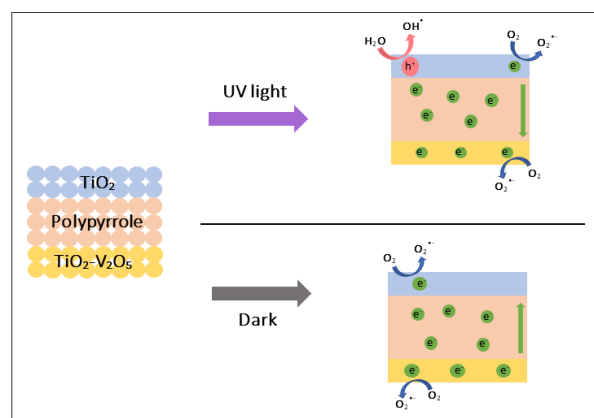


Figure 4 Electron transfer during photocatalytic oxidation of formaldehyde under UV light and in dark over TiO₂/TiO₂-V₂O₅/PPy.

Kinetic studies

Since the photocatalytic mechanism is rather complex, an initial rate approach was adopted and the kinetics of reaction were examined for the inlet concentrations of formaldehyde equivalent to the partial pressure ranges of 0.05-0.13 kPa, while that of oxygen was kept at 21.3 kPa. The apparent power rate took the form

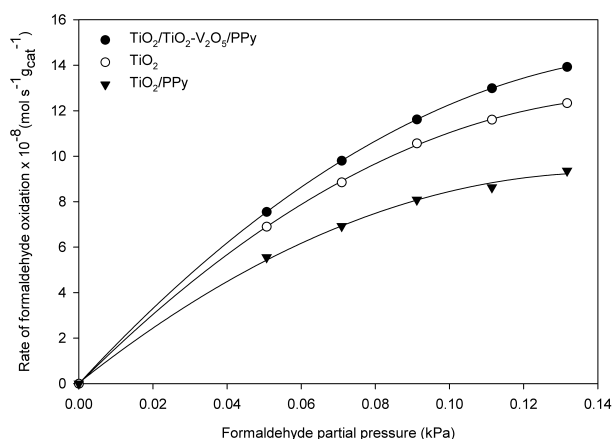
$$-r_{HCHO} = kP_{HCHO}^n \quad (19)$$

where n is the reaction order, P_{HCHO} is the partial pressure of formaldehyde in kPa and k is the first-order rate constant reported in Table 2.

Table 2 Values of Rate Parameters for Photocatalytic Oxidation of Formaldehyde Over TiO₂/TiO₂-V₂O₅/PPy Catalyst.

Samples	$-r_{HCHO} = kP_{HCHO}^n$		
	n	$k \times 10^7$ ($\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1} \cdot (\text{kPa})^{-n}$)	Correlation Coefficient
TiO ₂	0.59	4.17	0.99
TiO ₂ /PPy	0.52	2.75	0.99
TiO ₂ /TiO ₂ -V ₂ O ₅ /PPy	0.62	5.01	0.99

Samples	$-r_{HCHO} = \frac{k'KP_{HCHO}}{1 + KP_{HCHO}}$		
	$(k'K) \times 10^6$ ($\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1}$)	K (kPa^{-1})	Correlation Coefficient
TiO ₂	2.01	8.51	0.99
TiO ₂ /PPy	1.77	11.4	0.99
TiO ₂ /TiO ₂ -V ₂ O ₅ /PPy	2.08	7.14	0.99

**Figure 5** Experimental reaction rate (r_{HCHO}) vs. formaldehyde partial pressure (P_{HCHO}) for photocatalytic oxidation of formaldehyde over TiO₂/TiO₂-V₂O₅/PPy, TiO₂, and TiO₂-V₂O₅.

As shown in Figure 5, the reaction rate of oxidation increases with the increase in formaldehyde partial pressure. The apparent kinetics using a power-law model showed the reaction order of ca. 0.52-0.62 with a correlation coefficient of 0.99. With the excess of oxygen, this result conforms to the dependence of the partial pressure of formaldehyde, which infers the surface reaction between the adsorbed reactants. The fractional-order of ca. 0.5 infers the complex reaction mechanism, where the oxidation rate depends primarily on the oxygen adsorption rate [24].

Moreover, the simplified Langmuir-Hinshelwood model was adopted from eq. (10) due to the concentration of O₂ being much higher than that of formaldehyde ($K_{O_2}C_{O_2} \approx (1 + K_{O_2}C_{O_2})$). The reaction rate was tested with the experimental data, as shown in eq. (20).

$$-r_{HCHO} = \frac{k'KP_{HCHO}}{1 + KP_{HCHO}} \quad (20)$$

where k' and K are the reaction rate constant and the adsorption equilibrium constant, respectively. P_{HCHO} is the partial pressure of formaldehyde in kPa.

The kinetic parameters k' and K were obtained using linear least square analysis and the results are furnished in Table 2. The solid line drawn in Figure 5 shows a good fitting of the model to the experimental data, confirming the simplified Langmuir-Hinshelwood nature of the photocatalytic reaction mechanism of these catalysts. This is similar to what was reported in the literature for photocatalytic oxidation of VOCs [25-28]. It was suggested that the photocatalytic oxidation rate of VOCs depends simultaneously on both k' and K [25]. However, the photocatalytic oxidation of formaldehyde (in this study) strongly depends on the reaction rate constant. The rate constant was found to be in the order of TiO₂/TiO₂-V₂O₅/PPy > TiO₂ > TiO₂/PPy.

4.0 CONCLUSION

The TiO₂/TiO₂-V₂O₅/PPy electron storage photocatalyst was found to be an effective material for the removal of formaldehyde under UV irradiation and after UV switching off. These phenomena emphasize the ability of storage electrons in the electron storage photocatalyst an alternative route to destroy formaldehyde, instead of storage holes in the hole storage photocatalyst, i.e., TiO₂-Ni(OH)₂. The presence of TiO₂-V₂O₅ was found to enhance the photocatalytic activity of TiO₂, including its ability to function in the absence of UV light. PPy acts as an electron bridge to enable the excited electrons during UV exposure to be transferred and stored in TiO₂-V₂O₅ particles. The catalytic activity of the TiO₂/TiO₂-V₂O₅/PPy photocatalyst under UV irradiation was 57%, which is greater than the pristine TiO₂ at 9.6%. Moreover, the storage electrons could retain the catalytic activity at less than 3 hours after switching off UV light, while the pristine TiO₂ lost the activity within 30 min. Based on kinetic studies, the reaction rate of the photocatalytic oxidation of formaldehyde by the TiO₂/TiO₂-V₂O₅/PPy electron storage photocatalyst depends on the formaldehyde concentration. The simplified Langmuir-Hinshelwood model was successfully applied to correlate the experimental data.

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