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Room-light-induced indoor air purification using an efficient Pt/N-TiO_2 photocatalyst

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ABSTRACT

A conceptual air purifier harvesting fluorescent room lights was tested in this study. Visible photocatalysis was applied to facilitate the degradation of volatile organic compounds (VOCs) on a highly efficient visible light photocatalyst, Pt/N-TiO_2 synthesised via a sol–gel process. The as-prepared photocatalyst was characterised by many techniques, such as XRD, XPS, UV–vis DRS, N_2 adsorption and SEM, etc. XPS spectra revealed that platinum was at a chemical state of 2+, while nitrogen existed as NO_x species. The unique chemical compositions made the photocatalyst respond to visible light with a band gap of 2.69 eV, and present a broad absorption shoulder extended further into infrared region. The photocatalytic activities under irradiations of $\lambda > 387$, 430 and 490 nm were evaluated by photodegradation of phenol solutions. Under UV–vis light, the Pt/N-TiO_2 exhibited 5.5 times higher activity than Degussa P25. Various gaseous pollutants were degraded by employing the Pt/N-TiO_2 in a batch reactor. The capability of photodegradation of VOCs under room lights was also proven by the decomposition of gaseous toluene in a continuous reactor using fluorescent lamps (6×10 W). The mechanism of the enhanced activity in degradation of VOCs and potential application were discussed.

1. Introduction

Indoor air quality (IAQ) has become a critical community concern due to increased personal time (over 80%) spent in indoor environment, such as home, office, car and shopping center. Unfortunately, IAQ was suggested to be even worse than outdoor environment, attributing to the continuously emitting sources of combustion by-products, cooking, construction materials, office equipment, and consumer products. The detected pollutants from such sources mainly include nitrogen oxides (NO_x), carbon oxides (CO and CO_2), particulates, and volatile organic compounds (VOCs) [1]. Many VOCs are known to be toxic and considered as carcinogenic, mutagenic, or teratogenic. Long-term exposure to VOCs leads to sick building syndrome (SBS), such as dizziness, dry or itchy skin, eye, nose and throat irritation, a dry cough, fatigue, headache, or asthma attack [2].

To improve IAQ, three strategies, e.g. source control, increased ventilation, and air cleaning have been suggested to remove VOCs in indoor environment. Source control is often ungovernable and avoidable in metropolis and increased ventilation just transfers pollutants from indoor to outdoor environment. For air cleaning, advanced oxidation processes (AOPs) have shown their superiority over conventional adsorption, as they can completely destroy VOCs to H_2O and CO_2 [3], other than phase transfer from gas to solid [4]. Thermal oxidation destruction had been extensively studied and was generally operated at a higher temperature of 200–1200 °C, hence being cost intensive [5]. Moreover, thermally catalytic oxidation is not economically feasible at low pollutant concentrations, which is typical in indoor air.

Photodegradation has been proposed as a promising approach since it not only completely oxidises VOCs, but also occurs at room temperature and ambient pressure [6,7]. Due to high activity, long-term stability, non-toxicity and low cost, TiO_2 has been employed as a typical semiconductor-based photocatalyst [6,8–11]. In photocatalysis, a photocatalyst is activated by the photons with greater energy than the band gap, producing electron/hole pairs to carry out redox reactions [12]. The band gap of anatase TiO_2 is 3.2 eV, which requires the wavelength of light shorter than 387.5 nm, in ultraviolet (UV) region. It is known that UV exposure is severely dangerous, even more harmful to humans than VOCs in indoor. The photodegradation of VOCs under visible light therefore becomes highly desirable for the viable application, i.e. air purifier using visible light photocatalysis.

The key issue in the photocatalytic removal of VOCs under visible light lies in the extension of the absorption threshold of TiO_2. Previous studies suggested that nitrogen doping was an effective method to make TiO_2 respond to visible light region, and nitrogen doped TiO_2 was generally applied to degrade aqueous

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pollutants [13–15]. Recently, N-TiO_2 has been employed to decompose VOCs for indoor air purification [10,16]. However, the visible light extension was weak and the activity was rather low. In gas-phase reaction, deactivation of a photocatalyst by intermediates or carbonisation was another concern. Co-doping of a metal with nitrogen into TiO_2 has been proposed to both extend the absorption and enhance the photocatalytic stability under visible light irradiations. Higashimoto et al. [17] reported that photocatalytic activity of N-TiO_2 would be significantly increased by surface modification with vanadium species in the decomposition of VOCs and that the interaction of oxidation states between +IV and +V on N-TiO_2 surface played the key role in the enhancement. Nitrogen and nickel co-doped TiO_2 was prepared by Zhang and Liu [18], who reported that Ni_2O_3 was dispersed on the surface of TiO_2 to suppress the recombination of photo-induced electron/hole pairs. Apart from lanthanoid and transition metals, noble metals such as silver, palladium and platinum have shown much effectiveness in improving the activity of N-TiO_2 [19–21]. In the degradation of VOCs, Li et al. [22] reported that an increased quantum efficiency of photodegradation of VOCs was observed over Pt/$TiO_{2-x}N_x$. The enhancement was attributed to the better separation efficiency of photogenerated electron/hole pairs, higher interface electron transfer rate, and an increased number of surface hydroxyl radicals.

In previous studies, a mercury lamp has been generally selected as UV source, and xenon (or metal halide) lamp as visible light source. Few investigations have been reported using room light. To further explore the advantage of visible light photocatalysis being operated at room temperature and atmospheric pressure, ambient room lights (fluorescent lamps) were employed to photodegrade VOCs in this work. This investigation would underpin an ideal design of harvesting room lights for simultaneous indoor air purification.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide (TTIP) was used as a Ti-precursor and supplied by Aldrich Chemicals with a purity of 97%. Urea was applied as a nitrogen source, supplied by Ajax Finechem with a grade of 99%. Hexachloroplatinic acid (99.9%) was used as a Pt precursor and purchased from Sigma–Aldrich. The VOC gases were prepared by evaporation of liquid acetone, ethanol, trichloroethene (TCE), 2-propanol, *n*-hexane, and toluene received for Chem Supply with a purity of 99.5%. A reference material of TiO_2-P25 was received from Degussa, Germany. A cylinder of toluene at 100 ppm in air was supplied by BOC.

2.2. Preparation of photocatalysts

Pt/N-TiO_2 was prepared by a modified sol–gel process with acid assistance. 100 mL of ethanol, 20 mL of acetic acid and 20 mL of TTIP were mixed to produce *solution A*. 1 L of deionised water, 1 mL of HNO_3 (69.5%), 0.3250 g of $H_2PtCl_6{\cdot}6H_2O$, 15.5474 g of urea and 20 mL of acetic acid were mixed as *solution B*. In an ice bath, *solution A* was added dropwise into *solution B* to carry out a controlled hydrolysis and then aged for 48 h. After evaporation at 80 °C, the dried gels were annealed in air at 400 °C for 4 h. Then a Pt(1.0 at.%)/N-TiO_2 photocatalyst was obtained. Degussa P25 (TiO_2, 75% anatase and 25% rutile, 20 nm, and $S_{BET} = 50\ m^2/g$) was used as a reference sample for a comparison.

2.3. Characterisation of photocatalysts

UV–vis diffuse reflectance spectra (DRS) of samples were recorded on a JASCO V 670 spectrophotometer with an Ø 60 mm integrating sphere, and $BaSO_4$ as a reference material. The crystalline structure of samples was analysed by powder X-ray diffraction (XRD) using a Bruker D8-Advance X-Ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM), performed on a Zeiss Neon 40EsB FIBSEM, was used to evaluate the morphology, size and texture information of the samples. The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were evaluated by nitrogen sorption at −196 °C using a Quantachrome Autosorb AS-1. Chemical compositions of Pt (1.0 at.%)/N-TiO_2 were analysed by X-ray photoelectron spectroscopy (XPS) using Thermo Escalab 250 with a monochromatic Al Kα X-ray source. All binding energies were calibrated by the C 1*s* peak at 284.6 eV arising from adventitious carbon [23].

2.4. Tests of photocatalytic activity

The photocatalytic activity of Pt/N-TiO_2 dependent on the wavelengths was evaluated by degradation of 25 ppm aqueous phenol solutions using a MSR 572/2 metal halide lamp (575 W, Philips) with various cut-off filters. The concentration of phenol solutions was monitored by a high performance liquid chromatograph (HPLC) using a C-18 column, and a UV detector set at $\lambda = 270$ nm.

2.5. Photocatalytic decomposition of VOCs

Two reactors (batch and continuous) were applied to evaluate the performance of Pt/N-TiO_2 in decomposition of various VOCs, such as acetone, ethanol, TCE, 2-propanol, *n*-hexane, and toluene. A 1.2 L stainless steel reactor was employed to carry out the batch tests. Fig. 1(A) schematically shows the batch reactor and associated system. The irradiations were provided by a Newport Oriel Universal Xenon arc lamp (300 W), and were filtered by a cut-off filter to block the lights with wavelengths shorter than 387 nm (UVA < 0.05 W/m^2). The photocatalyst (0.1 g) was immobilised on a Petri dish ($D = 7$ cm), which was fixed by a stainless steel support. In a typical run, the catalyst was loaded into the reactor, which was flushed by an instrument-grade air for 2 h to maintain the humidity constant in each run. Then a certain amount of liquid acetone was injected into the reactor, at a level of ca. 200 ppm in control condition (without a catalyst). The mixed gas was then recycled by a dual syringe pump (Hamilton Microlab 500) and monitored by a GC–MS (Varian 3800/2200) until the concentration was stable. Then the light was switched on and the concentrations at varying reaction time were recorded by the GC–MS.

Fig. 1(B) shows the continuous reaction system using room lights from fluorescent lamps (6 × 10 W) as light sources. A cylinder was used to provide VOC flow (100 ppm toluene in air), and the flow rate was controlled by a mass flow controller at 65 mL/min. The toluene gas was flowing into the continuous reactor with three channels. At the bottom of each channel a stainless steel plate (29 × 20 cm) coated with 0.2 g of photocatalyst was fixed. The lights irradiated the photocatalyst through a Soda glass window. The energy distribution of the fluorescent lamp is centred at ca. 570 nm in the region from 390 to 670 nm. The transparent performance of Soda glass was tested to be higher than 95%. The concentration of toluene was analysed by a GC (SHIMADZU 2010) with a FID detector.

3. Results and discussion

3.1. XPS studies

N (1*s*) and Pt (4*f*) XPS spectra of Pt/N-TiO_2 are shown in Fig. 2(A and B). A weak peak at 399.8 eV was fitted in N (1*s*) spectrum and no signal peak was found at ca. 396 eV. According to previous investigations [13,15], the peaks at the range of 399–401.5 eV arise from