JOURNAL OF CHEMICAL EDUCATION

Demonstration

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Demonstrating Online Monitoring of Air Pollutant Photodegradation in a 3D Printed Gas-Phase Photocatalysis Reactor

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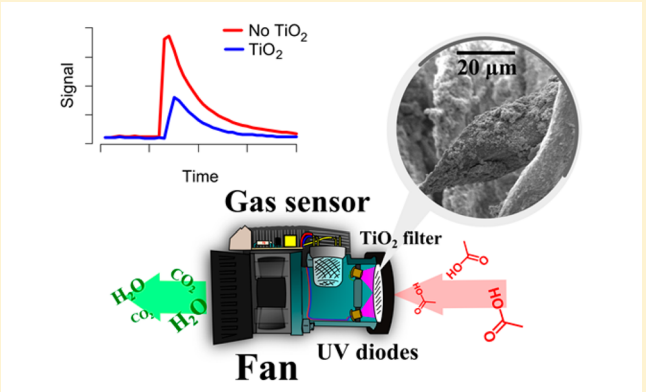
Supporting Information

ABSTRACT: We present a demonstration of online monitoring of gas-phase photocatalytic reactions. A cotton cloth impregnated with commercial titanium dioxide nanoparticles is used as a photocatalytic filter to clean air contaminated with a model pollutant. A fan forces air through the filter while it is irradiated by UV diodes. The concentration of the air pollutant is measured online by an inexpensive, commercially available semiconductor air quality sensor. The structural parts of the reactor were 3D printed in polylactide bioplastic. We provide all schematics, 3D printed model parts, hardware, firmware, and computer code of the reactor and control units. The device can be used for interactive learning of both gas phase photocatalysis and gas sensing, as well as in student laboratory classes for measuring air pollutants and their photodegradation. The experimental setup can also form the basis for a project work for chemical engineering university students, and it can be employed as a building block for development of other gas phase chemical reaction demonstrations.



KEYWORDS: *Chemical Engineering, General Public, Photocatalysis, Gases, Photochemistry, Reactions, Nanotechnology, Laboratory Equipment/Apparatus*

INTRODUCTION

"Sick Buildings" and Indoor Air Quality

People in developed countries spend more than 90% of their life indoors.[1] Poor indoor air can be associated with deteriorating health status, and it is thus highly important to find means to improve the indoor air quality.[2] Buildings with poor indoor air quality have been associated with the term Sick Building Syndrome (SBS) by the World Health Organization (WHO) since 1983.[3] SBS is still a poorly understood multifactorial health condition with a number of nonspecific symptoms, similar for residents in common built environments. Those symptoms are often associated with a number of indoor environmental factors, including for example, lightning and ventilation, but the quality of the indoor air is usually the main component.[4] Poor indoor air quality is a problem that affects both developed countries (due to the use of synthetic building materials, domestic chemistry, and outdoor air pollution in urban areas) and developing countries (due to the burning of poor quality fuels and waste materials for cooking and heating).[5] Poor indoor air quality is responsible for about 2 million deaths per year worldwide, predominantly in the developing countries.[6] Outdoor emissions contribute to a poor indoor air climate. Very recently the International Agency for Research on Cancer (IARC) has, after scrutinizing a large number of research reports, even classified urban outdoor air pollution as being carcinogenic to humans.[7] The main chemical compounds of indoor air pollutants are volatile organic compounds (VOCs), such as BTXS (benzene, toluene, xylenes, and styrene), terpenes (α-pinene, limonene, etc.), and carbonyls (formaldehyde, acetaldehyde, acetone). These are regarded as health issues and are in some case also reported to be cancerogenic.[8,9] The VOCs are released by many sources, such as synthetic materials, surface coatings, building insulation, and domestic chemistry,[10,11] and their accumulation is enhanced through ventilation and air conditioning.[12,13] Air filtration is today becoming of increasing importance due to awareness of the connection between air quality and health.

Apart from traditional mechanical and carbon filter systems, new promising methods to limit and reduce the concentration of VOCs include advanced oxidation processes (AOPs), such as oxidation of VOCs in photocatalytic air filtration systems.

Photocatalysis to the Rescue

According to the International Union for Pure and Applied Chemistry (IUPAC), photocatalysis is the initiation of a chemical reaction, or the change in its rate, under the action of ultraviolet (UV), visible, or infrared (IR) radiation in the presence of a photocatalyst.[14] Materials with beneficial photocatalytic properties are found among a number of semiconductors, typically wide band gap transition metal oxides. Among them, titanium dioxide (TiO_2) is by far the most investigated material.[15]

dx.doi.org/10.1021/ed500604e | J. Chem. Educ. XXXX, XXX, XXX−XXX

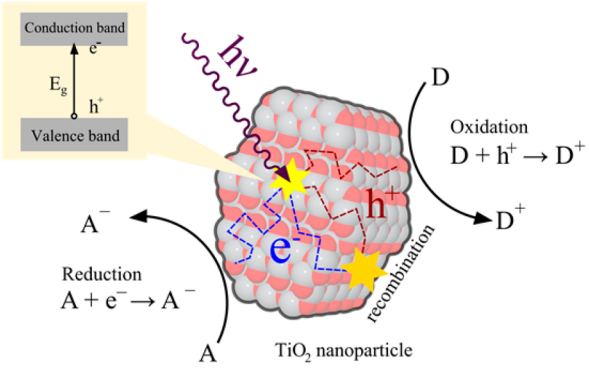


Figure 1. Illustration of elementary photoinduced reaction steps in a semiconductor nanoparticle.

A simplified overview of the mechanism of photocatalytic action of a semiconductor nanoparticle is presented schematically in Figure 1; the nanoparticle's electronic structure is described with a filled valence band (VB) and an empty conduction band (CB). They are separated by a bandgap, E_g, corresponding to the minimum energy required for an electronic transition from VB to CB, which for bulk TiO_2 is E_g = 3.2 eV, or λ_g = 388 nm. When a photon with energy larger than E_g is absorbed an electron (e^-) is excited from VB to CB. This leaves an empty state in the VB, known as a hole (h^+). The excited electron and hole is called an electron–hole (e–h) pair, and the attraction between them takes place via electrostatic forces.

There are two possible scenarios for the fate of the e–h pairs. First, they may recombined, with the electron returning back to the VB through a nonradiative transition. In this case, the absorbed energy is lost in the form of heat. This process is undesired in photocatalysis. It is, however, the dominant process in materials like TiO_2 and leads to their generally low quantum yield, typically <1%.

In the second (desired) pathway the e–h pairs migrate to the surface of the particle and react with adsorbed species. As indicated in Figure 1, such species may participate in surface reactions either as electron acceptors (A), reacting with the photogenerated electrons, or electron donors (D), reacting with the photogenerated holes. Thus, the photocatalyst can participate in oxidation or reduction reactions.

TiO_2 photocatalysts are used in a number of important applications such as superhydrophilic and self-cleaning surfaces,[16] solar-energy conversion devices,[17] antibacterial coatings,[18] and systems for water and air cleaning.[19,20] For the latter applications, it has been shown that TiO_2 can be used to eliminate virtually all VOCs by mineralizing the organics to CO_2 and H_2O (and trace mineral acids if the VOC contains noncarbon anions).[21−24] In fact, TiO_2 and the hydroxyl radicals generated in the photoreaction have a higher oxidation potential than in other commonly used techniques for water cleaning, such as ozone- or hydrogen-peroxide-based treatments (2.80 eV for the photogenerated hydroxyl radical, and 2.07 and 1.78 eV, respectively, for ozone and hydrogen peroxide; for comparison, the oxidizing potential of a hole on the surface of TiO_2 is 3.21 eV).[25] Removing VOCs from indoor air through TiO_2 photocatalysis is an example of how nanotechnology and heterogeneous catalysis can be used to solve imminent problems in our environment. It is clearly urgent to educate students in the field of photocatalysis and to attract them to work on problems related to air quality and air purification in their future careers.

Demonstrating Photocatalytic Reactions

It is straightforward to show liquid phase photocatalysis in simple experiments, and there are a number of demonstrations that can be performed in the classroom.[26−28] Typically, a solution containing an organic dye is brought in contact with TiO_2 nanoparticles dispersed in the solution (usually employing TiO_2 concentrations between 0.1 and 1 g/L) and irradiated with UV or solar light. A visible color change of the solution is observed within 5 to 30 min, which can readily be quantified spectrophotometrically.[29] In contrast, tutorial demonstration of gas phase photocatalysis for educational purposes is more challenging and, as there is no visible change, advanced analytical equipment such as gas chromatography (GC), mass spectrometry (MS), GC–MS, or advanced IR spectroscopy setups is required,[30] which complicates online (in situ) analysis.

The present work demonstrates a simple experimental setup for a tutorial demonstration of gas phase photocatalysis without requiring elaborate analytical equipment to measure air pollutants. It is a gas-phase photocatalytic reactor, equipped with a simple photocatalytic filter and a semiconductor air quality sensor, which measures electrical resistance changes. Through the use of an inexpensive analogue-to-digital converter, online monitoring of the resistivity changes and, hence, pollutant concentrations is possible.

CONSTRUCTION OF THE PHOTOCATALYTIC GAS PHASE REACTOR

Reaction Cell

Figure 2 shows the photocatalytic reactor. The reactor, and all other structural components, is 3D printed using polylactide (PLA) bioplastic (Velleman K8200 3D printer, 500 μm resolution). The 3D models are provided in the Supporting Information

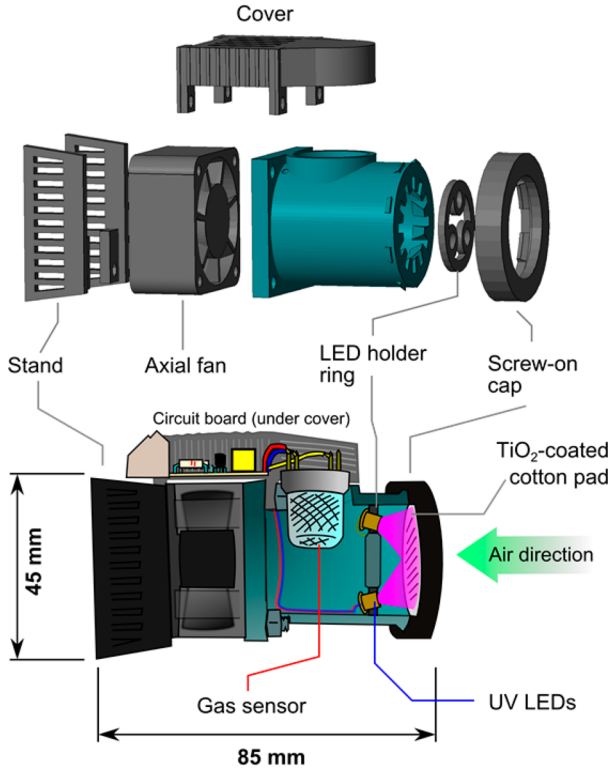


Figure 2. Schematic drawing of the photocatalytic gas phase reactor showing an exploded 3D view (top) and a side-view (bottom).

dx.doi.org/10.1021/ed500604e | J. Chem. Educ. XXXX, XXX, XXX−XXX

as .STL files. The reactor body comprises a cylindrical plastic housing with 36 mm outer diameter and 4 mm wall thickness. A 40 × 40 × 20 mm fan (KD1204PKB2, Sunon Group, Taiwan, http://www.sunon.com/) is mounted at one end of the cylindrical housing. A 36 mm diameter circular cotton cloth impregnated with a TiO_2 photocatalyst is attached at the opposite end and is held in place by a number of tooth-shaped protrusions providing support and a plastic screw-on cap to secure its position. The fan forces air through the cotton cloth in the direction shown in Figure 2.

Inside the reactor housing three UV LEDs (T5F36, Seoul Semiconductors, South Korea) are mounted and directed onto the impregnated cotton cloth, thus providing UV irradiation (λ_{max} = 365 ± 18 nm, 1.5 mW nominal optical output, 130° emission angle). The UV diodes are attached to a small plastic ring inside the reactor body. They are positioned 120° apart, and tilted so that the center of the emission cone is directed at the center of the cotton cloth.

An In_2O_3 semiconductor sensor (NAP-11AS, Nemoto & Co., LTD, Japan; http://www.nemoto.co.kr/) was used for online measurements of gas phase air pollutants. It is a general indoor odor sensor and provides good response for a wide range of organic and inorganic gases. Its response is proportional to the concentration of a gas pollutant in the air (most gases are in the range 0.2−10 ppm). It is inexpensive and available off-the-shelf; there are, however, a number of similar gas sensors available for under $10 and, for example MQ-5 (Hanwei Electronics Co., Ltd., http://www.hwsensor.com) can be obtained by third parties on a printed circuit board (PCB) ready to connect to the Arduino microcontroller used here.

The sensor is inserted through an opening on the side of the main body of the reactor (Figure 2). The sensor is positioned about 3 cm downstream from the UV irradiated TiO_2 impregnated cotton cloth.

Electronics and Software

A minimal amount of supporting electronics is needed. The gas sensor requires a 5 V power supply, and a single transistor is used to control the fan. All electronic components are soldered on a small piece of prototyping board mounted inside the 3D printed plastic cover. The entire schematics and a complete list of materials are provided as Supporting Information.

In our demonstrations two reactors of the kind described above have been employed in a serial configuration, as described in the Demonstration section below. They were wired to Arduino Uno boards (Arduino LLC, Italy, http://www.arduino.cc/) and both reactors were controlled simultaneously. Four wires run to each reactor: two to a 9 V power supply, one for fan speed control, and one for reading the sensor signal. Up to six such reactors may be controlled with one Arduino board.

A computer script running on the Arduino was used to set the fan rotation speed and return the ADC converted value from the sensor on request from the computer via the USB serial interface. A small client program was written on the host computer in Visual Basic .NET to adjust air flow and for online plotting of sensor signal versus time. All computer code and software are available as Supporting Information.

Impregnation of Cotton with TiO_2

Cotton fabric was impregnated with photocatalytic TiO_2 nanoparticles via the following steps (Figure 3):

1. Circular cloths with 36 mm diameter were cut out from cotton fabric and soaked in 10 mL of distilled water (panel 1 in Figure 3).

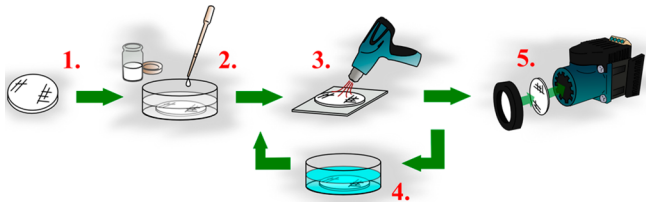


Figure 3. Preparation of the TiO_2-impregnated cotton cloths.

2. A suspension was prepared by dispersing 1 g of TiO_2 (Aeroxide P25, Evonik Industries AG, Germany) in 5 mL of absolute ethanol. Aeroxide P25 is known to contain 70−80 mol % TiO_2 nanoparticles of anatase phase, with the remainder being rutile. The suspension was sonicated for 15 min. Then, 1 mL of the TiO_2 suspension was added to each cloth, which was left overnight in a covered Petri dish (panel 2).
3. The cloths were subsequently dried using a heat gun (panel 3).
4. The cloths were then rinsed thoroughly in distilled water (panel 4), and again dried with the heat gun. The process was repeated two times.
5. The as-prepared TiO_2-impregnated cotton cloths were mounted in the reactor and fixed with the plastic screw-on-cap (panel 5).

Scanning electron microscopy (SEM) images of cotton cloths with and without TiO_2 impregnation are shown in Figure 4.

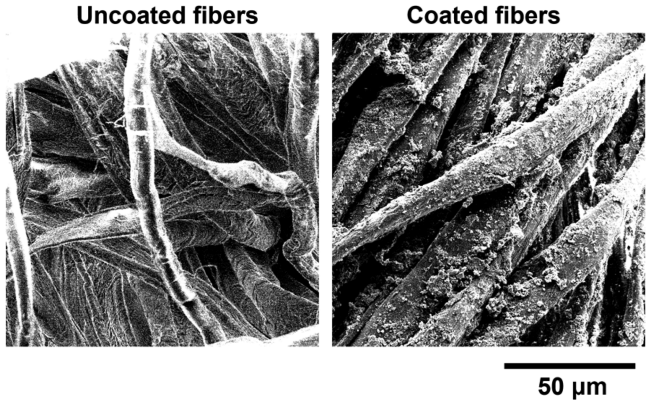


Figure 4. SEM images of cotton cloths without (left) and with (right) TiO_2 nanoparticle impregnation.

■ HAZARDS

Ethanol is flammable and its vapors are irritating when inhaled. During the preparation of the photocatalytic filter, caution must be taken when handling the TiO_2 powder, which is irritating to the respiratory system and may cause inflammation in the lung upon inhalation of large doses.[31] Gloves and respiratory protection should be used. The diodes emit low power (1.5 mW) UVA light at 365 nm, which can be harmful to the skin and eyes by direct exposure.

■ DEMONSTRATION OF GAS-PHASE ETHANOL PHOTODEGRADATION

The photocatalytic gas phase reactor has been used at science festivals as part of a workshop on environmental photocatalysis. The students were introduced to the concept of photocatalysis

dx.doi.org/10.1021/ed500604e | J. Chem. Educ. XXXX, XXX, XXX−XXX

and were first instructed to perform a hands-on demonstration of liquid phase photocatalytic oxidation of an organic dye, as described by Pitcher et al.[26]

A short introduction was then given about VOCs, which can be found in indoor air, and about the way they can accumulate over time as a consequence of air conditioning.[13] The students were introduced to the setup with two photocatalytic gas phase reactors connected in series as depicted in Figure 5. A cotton

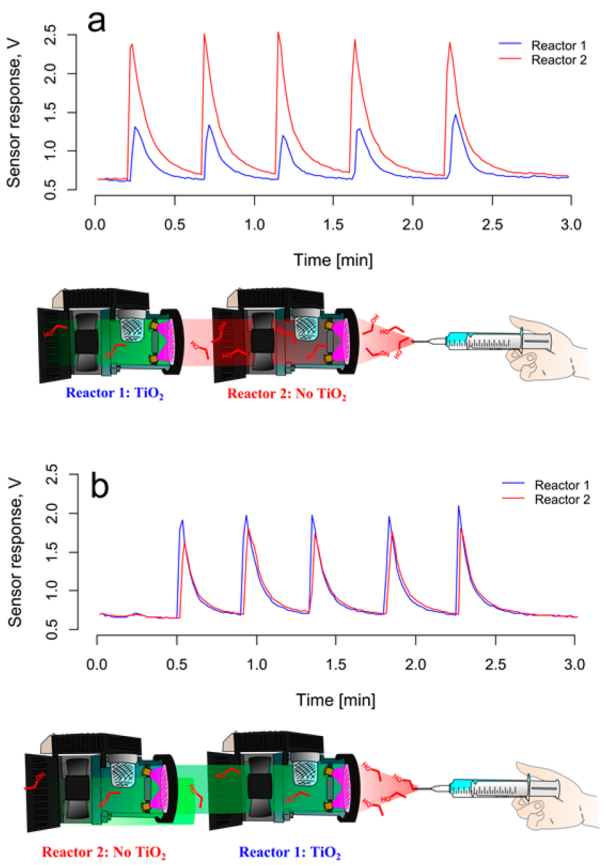


Figure 5. Reactor setups and measured online sensor response as a function of time for two configurations: (a) Reactor 2 in front of Reactor 1 and (b) Reactor 1 in front of Reactor 2, clearly showing that the TiO_2 filter lowers the sensor signal (panel a) and that the reactor with no TiO_2 filter does not influence the signal (panel b). For details of the experimental setups, see main text.

cloth impregnated with the TiO_2 photocatalyst was mounted in reactor 1 and a plain cotton cloth was mounted in reactor 2. The students were able to observe the sensor signals online on a computer screen throughout the whole experiment. They were instructed to increase the speed of the fan, which sucks air into the reactor through the cotton cloth, to a maximum, thus venting the reactor during a few minutes until a steady sensor signal was observed.

Ethanol was used as a model gas phase pollutant. The gas sensor is very sensitive to ethanol vapor. The demonstration may be adapted to other configurations and other pollutants may be used, such as sources of odors, cigarette smoke, or similar ones. The list of gases to which the sensor is sensitive is usually available from the manufacturer. NAP-11AS is a general air quality sensor, sensitive to smoke detection according to the manufacturer. There are many similar sensors, optimized and calibrated for different pollutants, but in general such catalytic gas sensors have a broad and quite nonspecific response toward gas phase pollutants. Using a 1 mL plastic syringe, the students were instructed to withdraw saturated ethanol vapor from a sealed vial containing a few milliliters of ethanol held at room temperature. The ethanol vapor was injected several times into the reactor, using one syringe at a time, by simply emptying the syringe in the air stream controlled by the fan next to the entrance of the reactor (Figure 5).

Figure 5 shows the results of placing two reactors in series in different configurations; either with Reactor 1 in front of Reactor 2 or vice versa. The fan speed was set to about 50% of full speed for the front reactor, and 75% of full speed for the back reactor to ensure that the ethanol vapor passes through both reactors

In the first experiment (Figure 5a), the reactor with a cotton cloth filter (Reactor 2) was placed in front of the reactor with the TiO_2-impregnated cloth filter (Reactor 1). In this configuration, the gas sensor in Reactor 2 is positioned before the TiO_2 filter, and the gas sensor in Reactor 1 behind the TiO_2 filter. A strong difference in the signal was observed, because ethanol is decomposed by the photocatalyst in Reactor 1 (the reactor in the back) before the air stream reaches Reactor 2, but not in Reactor 2, which does not contains a photocatalytic filter. The students were then asked to swap the two reactors so that Reactor 1 was placed in front of Reactor 2 and then repeat the measurement, as schematically shown in Figure 5b. This time only a very small difference is observed in the sensor response of Reactors 1 and 2. Moreover, the sensor response in Reactor 1, with a TiO_2 photocatalyst cotton filter, is much lower, and on par with the sensor response when it was placed behind reactor 2 (see Figure 5a). Both observations are caused by the fact that the two gas sensors now are located after the photocatalytic filter in the air stream.

After the experiments, a discussion was held with the students about what happened to the ethanol in the air stream and how photocatalysis can be used to clean indoor air. The students were also encouraged to admit other gases into the reactors and watch the sensor response.

CONCLUSION

We have presented a simple tutorial setup to demonstrate gas phase photocatalytic reactions. The gas phase photocatalytic experiment complements existing liquid phase photocatalytic demonstrations. In particular, the demonstration allows students to gain direct, hands-on experience on gas phase photocatalysis, which otherwise is difficult to illustrate without advanced analytical techniques, and thereby broadens the scope of photocatalysis as an environmental technology for students. This work is an example on how relatively cheap and readily available off-the-shelf technology can be used to demonstrate advanced scientific topics in chemical engineering. We show that advanced scientific equipment readily can be made and distributed by use of open-source prototyping platforms, solid state gas sensors, and implementation of 3D printing technology

ASSOCIATED CONTENT

Supporting Information

Specific learning objectives of the presented demonstration, all 3D models for printing the reactor parts, and firmware and software for Windows are provided. For more information we refer to the assembly instructions provided as a PDF file. This material is available via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/ed500604e | J. Chem. Educ. XXXX, XXX, XXX−XXX

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was received from the European Research Council under the European Community's Seventh Framework Program (FP7/2007−2013)/ERC Grant Agreement No. 267234 (GRINDOOR).

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