Photocatalytic Decomposition of Indoor Air Pollution Using Dye-Sensitized TiO$_2$ Induced by Anthocyanin and Ru Complexes

Chiu-Hsuan Lee, Je-Lueng Shie, Ching-Yi Tsai, Yong-Ting Yang, and Ching-Yuan Chang

Abstract—This study investigated the characteristics of dye-sensitized TiO$_2$ (DST) using dyes of anthocyanin and Ru complexes, including natural dyes (raspberry, blueberry, cranberry) and artificial dyes (N3 (RuL$_2$(NCS)$_2$•2H$_2$O), N719(C$_{38}$H$_{42}$O$_{32}$N$_4$S$_2$Ru), prepared by precipitation method following by calcined at muffle furnace and discussed the feasibility of the applications of DST in the removal of volatile organic compounds (VOCs) from the indoor pollution sources using blue, white and red-ultra-violet light emitting diode. UV/Vis absorption spectra, High-resolution scan electron microscopy, Elemental analyses and BET surface area were performed for the characteristic analysis. The results showed that the diluted concentration of dyes affected the decomposition efficiencies ($\eta$). In the case of diluted solution of 30 times raw raspberry juice, $\eta$ was more than 80% and it was higher than that of common TiO$_2$. For N3 and N719-sensitized TiO$_2$, their values of $\eta$ were all in the order of UVLED$>$ BLED$>$ WLED$>$ RLED. Under RLED irradiation, the removal mass of N719DST was 11 times of that of TiO$_2$, showing the optimal special effect on light wavelength. With the irradiation of UVLED, its $\eta$ increased to 95% with the maximum removal mass of 720 mg/g. Visible light intensity for the photocatalytic reaction is still the major factor.

Index Terms—Dye-sensitized, light emitting diode (LED), anthocyanin, Ru complexes, photodegradation.

I. INTRODUCTION

The process of dye sensitization in dye-sensitized solar cell (DSSC) has received significant research for applications in photovoltaic processes. A DSSC is essentially a photoelectrochemical system, in which the light harvesting is accomplished by dye molecules that are adsorbed on the surface of the oxide nanostructures that form the photoelectrode film. Less research has been conducted on the application of dye sensitization in photocatalytic oxidation in indoor air pollutants. Photocatalytic degradation of organic compounds on dye-sensitized TiO$_2$ (DST) is being investigated where the dye serves as both a sensitizer and a substrate to be degraded [1]-[3].

Although visible light can be used in degrading organic compounds on TiO$_2$, it is inactive for the degradation of common pollutants that lack of visible-light absorbing chromophores. The use of the organic substrates themselves as photosensitizers leads to surface photosensitization by organic dyes and coordination metal complexes via photoinduced sensitizer-to-TiO$_2$ charge transfer [4]-[6]. Despite the attractive features of the photosensitization the ability to mediate degradation of non-visible absorbing substrates, report on successful photosensitized photocatalytic system is scarce. It is probably due to the general difficulty in establishing stable surface anchorage of the charge-transfer photosensitizers [5] and degrading dyes on TiO$_2$ from low wavelength irradiation. Therefore, the development of efficient visible-light systems, for example, blue, white and red LEDs (BLED, WLED, RLED) and low intensity ultraviolet LED (UVLED) that can avoid degradation of dye on photocatalysts and enhance the complete degradation of pollutants have been an urgent issue.

In this study, DST nanoparticles of near-uniform size were produced by using nature and artificial dye processes. For our proposed system, anthocyanins from three fruit juices – raspberry, blueberry, cranberry and Ru complexes from N3 (RuL$_2$(NCS)$_2$•2H$_2$O) and N719(C$_{38}$H$_{42}$O$_{32}$N$_4$S$_2$Ru) – were evaluated as our viable sensitizing agents. High-resolution scan electron microscopy (HRSEM), Brunauer Emmett Teller (BET) surface measurement device, Elemental Analyzer (EA), ultraviolet-visible (UV/vis) spectroscopy and gas chromatography/mass spectrometry (GC/MS) were used for the characteristics analysis and the evaluation of the photodegradation effects. In this paper, we mainly studied the anthocyanins and Ru sensitized process into TiO$_2$ films and the photocatalytic ability of DST under the irradiation of LED light sources.

II. MATERIALS AND METHODS

A. Dyes

TiO$_2$ of Degussa P-25 was supplied by Degussa, used without any pretreatment. The DSTs were prepared by the precipitated impregnation with dyes on TiO$_2$. The natural dyes used in these experiments were obtained from commercially available fresh fruit which was pressed to extract the juice. Raw extracts were purified and filtered using disposable $1 \mu$m pore size filters with 125 mm diameter (Advantec comp.). The final solution, without further purification, was used as the dye for sensitization of TiO$_2$ implemented in the photodegradation experiments (diluted solution). The yield of juice from nature dye was 400 mL kg$^{-1}$. DOI: 10.7763/JOCET.2013.V1.27
and the fresh juice was diluted into different concentrations for use. The sensitizers of artificial dyes were chosen Ru complexes, including N3 (RuL2(NCS)2•2H2O) and N719 (C58H86O8N8S2Ru), taking 0.005g sample mass diluted in alcohol to quantitatively 50 mL for use.

B. Catalyst Characteristics Analyses

Dye-sensitized photocatalysts were prepared by 0.5g TiO2 embedded into different dye solutions of 10 mL, and then dried in 333 K oven for 24 hr. Then High resolution scanning electron microscope (HRSEM) (Hitachi Tabletop TM-3000, Japan), Brunauer Emmett Teller (BET) surface measurement device (Model ASAP 2100, Micromeritics, USA), Elemental Analyzer (EA) (Elementar VarioEL-III, German) and ultraviolet-visible (UV/vis) spectrophotometer (ELEVATION-220, Thermo., USA) were used for the characteristic analyses of these samples.

C. Apparatus

In this study, Fig. 1 shows the photodegradation reactor. The top cover and bottom plates of the reactor were made from stainless steel 316. The 185 glass sticks (diameter: 1.5 mm, length: 25 cm, half illuminated area of total 185 glass sticks: 1177.5 cm²), outside surface coated with different DST (0.5 g), were inserted into the vessel. After complete mixing with stirrer and cycling pump, the temperature of the vessel was kept at 303 K by constant temperature circulating bath (Model-B403, First Scientific, Taiwan) to avoid the temperature disturbance.

The pure dry air was introduced for 30 min to push the residual gas in the reactor. Then, toluene was injected into the reactor. For coating purpose, 4 g TiO2 was suspended in solutions of 40 mL DI water, 20 mL acetylacetone (2,4-Pentanedione, Nacalai Tesque Inc., Kyoto, Japan) and 1 mL Triton X-100 (Nacalai Tesque Inc., Kyoto, Japan). Then, the TiO2 solution was uniformly coated on the supports of glass sticks, calcined at 723 K for 30 min, precipitated and immersed with dyes for 30 min, and then dried in 333 K oven for 10 min. After the sampling of the initial concentration of toluene, the reactor was kept in darkness for 1 hr to allow the adsorption equilibrium. Then the light source of blue light emitting diode bar (BLED) (wavelength (λ) = 465-470 nm), white light emitting diode bar (WLED) (wavelength (λ) = 300-700 nm) or red light emitting diode bar (RLED) (wavelength (λ) = 625-630 nm) was turned on and the toluene was analyzed using GC/MS (Focus GC and DSQ, USA). The LED is more novel, and has lower power, electromotive force (emf) demand and price, but higher efficiency, life-span and security as compared to a lamp. Also, it does not generate heat.

The chromatographic column of the GC-MS is a Rtx-1 capillary GC column (26 m long, 0.53 mm i. d., 3 μm film thickness). The operating conditions of the GC-MS were set as follows: injector temperature 473 K, detector temperature 473 K, column temperature (following the sampling injection) being increased from 333 to 373 by program, helium carrier gas flow rate 1 mL min⁻¹, helium make-up gas 50 mL min⁻¹, and sample volume 150 μL. Quantitative analysis of gaseous products was conducted using the linear calibration response equations of standards. The equation was generated for each compound of gas standard using a minimum of five different concentrations with three replicates at each concentration. All correlation coefficients (r²) of linear calibration response curves exceed 99.5%.

III. RESULTS AND DISCUSSION

A. Characteristics of Dye-Sensitized TiO2

1) UV/Vis absorption spectra

Fig. 2 shows UV/Vis absorption spectra graphs of dye solutions. The major absorption wavelengths of nature dye solutions are between 221.5-292 nm. The absorption wavelengths are belonged to the field of ultraviolet, however, only Cranberry solution has obvious third absorption wavelengths of 511.5-516.5 nm which is near the green light wavelength. This may be due to Cranberry being rich in anthocyanins and can be used as usable viable sensitizing agents. There are three major absorption wavelengths of N3 and N719 dye solutions and they are in the ranges of 306-310.5, 392.5-398.5 and 522.5-532 nm. The absorption wavelengths of Ru complexes are belonged to the fields of ultraviolet and visible light, moreover, higher absorption intensity in the visible light range while comparative to the nature dyes.

2) HRSEM

The HRSEM spectra of DSTs are illustrated in Fig. 3
DST (BDST), cranberry DST (CDST), N3 DST (N3DST) and N719 DST (N719DST) are 471, 471, 600, 525 and 589 nm, respectively. The particle aggregated obviously after the precipitated impregnation with dyes on TiO2. The dye-aggregated phenomena may be due to the electrostatic and adhesive attraction of dyes with a comparative result of TiO2 size of 50-60 nm solely [7].

3) Elemental analyses
The results of the elemental analyses for N3DST, N719DST, RDST, BDST and CDST are listed in Table I. Comparison with the sum of all elements, including N, C, S, and H, CDST has the highest mass percentage, and the value is about 29.65 wt.%. In all nature dyes, C is the major element and the range is between 76.4-83.4 wt.% with the order of CDST > RDST > BDST.

About artificial dyes, the elemental adsorption capacity is not obvious, the total elements of N719DST and N3DST are 0.94 × 10^{-5} g/m and the range is between 76.4-83.4 wt.% with the order of CDST > RDST > BDST.

4) BET surface area
The BET surface areas of TiO2, N3DST, N719DST, RDST, BDST and CDST calculated by BET equation are listed in Table II. BET surface areas of N3DST and N719DST are 50.08 and 48.91 m²g⁻¹, a little lower than that of commercial TiO2. However, BET surface areas of CDST, RDST and BDST are far lower than those of N3DST, N719DST and commercial TiO2 and the reason is due to the viscosity and aggregation from anthocyanin dyes.

**TABLE I: ELEMENTAL ANALYSIS OF DYES-SENSITIZED TiO2**

<table>
<thead>
<tr>
<th>Dyes</th>
<th>N3DST</th>
<th>N719DST</th>
<th>RDST</th>
<th>BDST</th>
<th>CDST</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.06</td>
<td>0.25</td>
<td>1.23</td>
<td>0.49</td>
<td>0.08</td>
</tr>
<tr>
<td>C</td>
<td>0.32</td>
<td>0.51</td>
<td>15.16</td>
<td>10.96</td>
<td>24.74</td>
</tr>
<tr>
<td>S</td>
<td>0.24</td>
<td>0.76</td>
<td>0.79</td>
<td>0.44</td>
<td>0.55</td>
</tr>
<tr>
<td>H</td>
<td>0.32</td>
<td>0.27</td>
<td>2.66</td>
<td>2.32</td>
<td>4.29</td>
</tr>
<tr>
<td>Total</td>
<td>0.94</td>
<td>1.79</td>
<td>19.84</td>
<td>14.21</td>
<td>29.65</td>
</tr>
</tbody>
</table>

**TABLE II: BET SURFACE AREAS OF DYE-SENSITIZED TiO2**

<table>
<thead>
<tr>
<th>Dyes</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3DST</td>
<td>50.08</td>
</tr>
<tr>
<td>N719DST</td>
<td>48.91</td>
</tr>
<tr>
<td>RDST</td>
<td>3.07</td>
</tr>
<tr>
<td>BDST</td>
<td>8.39</td>
</tr>
<tr>
<td>CDST</td>
<td>-</td>
</tr>
</tbody>
</table>

B. Photodegradation Efficiency of Toluene under Different Light Source
An initial test of photocatalysis of various initial concentrations of toluene using different DST was conducted to evaluate the decomposition or conversion efficiency (η) at different light source and shown in Figs 4-13. The η is calculated by the following equation:

\[
\eta = \frac{(C_o - C)}{C_o} \times 100\% \quad (1)
\]

where

C_o: initial concentration of toluene (ppmv),
C: concentration of toluene at time t (ppmv).

C. Photodegradation under BLED using RDST
In the previous study [7]-[10], the adsorption on TiO2 and degradation in the dark environment were not clearly detected, therefore, the effects of adsorption was neglected in this study. The η for different diluted time (T) of RDST is in the order of 1/30T > 1/50T > 1/100T (Fig. 4). The reason may be due to that there is an optimum concentration of nature dye sensitized on TiO2 for photodegradation. In the case of 1/30T RDST using BLED, the final η was more than 80% with the removal mass of 612 mg/g of toluene (Fig. 4). It is proved that the dye sensitization on TiO2 is an affected factor in the photocatalysis of air pollutants. The possible reason may be due to the conduction band (CB) of DST acts as a mediator for transferring electrons from the excited sensitizer with the electron hole active to the substrate adsorption on TiO2. Although the DST demonstrated the ability of utilizing visible light in degrading pollutants, its photodegradation efficiency was not high maybe due to the much slower interfacial electron transfer to the substrate than the back electron transfer to the oxidized sensitizer [11].

![Fig. 4. The removal mass of toluene from the photocatalytic decomposition reaction using BLED with RDST at different diluted concentrations of raspberry. ▲: 1/30T RDST; ◇: TiO2; △: 1/50T RDST; ●: 1/100T RDST. Reaction times: 8 hours, reaction temperature: 25°C, TiO2: 0.5 g. 1/30T, 1/50T, 1/100T: 30, 50, 100 diluted multiples of raw concentration.](image-url)
N3DST > 1/30BDST > N719DST > 1/30CDST > TiO2.

After 8 hr reaction and at the initial concentrations of 100 ppmv, 1/30RDST had the efficiency of 75% with the mass removal of 560 mg/g. However, comparative to TiO2, the improved η of RDST at WLED (45%) is larger than that of BLED (10%). This effect displace that sensitization of anthocyanin in visible light is more important and obvious.

2) Photodegradation under RLED

Using RLED for the light source, the results show in Fig. 6. It is reasonable that all η are lower than those of BLED and WLED, and this may be due to the illuminated energy of RLED is quick low. The η of TiO2 in RLED is only 3%, however, the value of N719DST is 34%, almost 11 times of that in TiO2.

It is obvious that Ru complex dyes have special absorption in high wavelength for enhancement of photodegradation and it also can be proved from the UV/vis spectra.

3) Photodegradation of Ru complexes dye-sensitized photocatalyst under different light sources

All the study results show that light wavelength (energy intensity) is a very important factor. The η of artificial Ru complexes (N3 and N719) are better than those of nature dyes in visible light range, especial at red light wavelength. In order to get photodegradation completely, UVLED was induced in this study. Figs. 7 and Fig. 8 show the results, and it exhibited the order of both in N3 and N719 DST are have the result UVLED > BLED > WLED > RLED with both N3DST and N719DST. And under the light source UVLED, and initial concentrations of 100 ppmv, N3DST and N719DST can remove over 95% or 720 mg/g of toluene at 2 hr.

IV. CONCLUSION

This study investigated the characteristics of dye-sensitized TiO2 (DST) using dyes of anthocyanin and Ru complexes, including nature dyes (raspberry, blueberry, cranberry) and artificial dyes (N3 (RuL2(NCS)2•2H2O), N719(C58H86O8N8S2R)), prepared by precipitation method following by calcined at muffle furnace and discussed the feasibility of the applications of DST in the removal of volatile organic compounds (VOCs) from the indoor pollution sources with irradiation using light bars of light emitting diode (LED), such as blue LED (BLED), red LED (RLED), white LED (WLED) and ultraviolet LED (UVLED). In the case of TiO2 sensitized by 30 times diluted solution of raspberry (1/30T RDST), η was more than 80% and higher than that of commercial TiO2. For N3 and N719-sensitized TiO2 (N3DST and N719DST) their values of η were in the order of UVLED> BLED> WLED> RLED. Under RLED irradiation, the removal mass of N719DST was 248 mg/g and the value was 11 times of that of TiO2, showing special effect on optimal light wavelength. Irradiation of UVLED, its η increased to 95% with the removal mass of 720 mg/g. Visible light intensity for the photocatalytic reaction is still the major factor. All the results obtained from this study can give information to identify the relationship between the induced photo potential and η of DST.
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REFERENCES


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