Synthesis of CuAPTPP-TDI-TiO$_2$ Conjugated Microspheres and its Photocatalytic Activity

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The metal complex 5-(4-aminophenyl)-10,15,20-triphenylporphyrin copper (CuAPTPP) was covalently linked on the surface of TiO$_2$ microspheres by using toluene disocyanate (TDI) as a bridging bond unit. The hydroxyl group (-OH) of TiO$_2$ microspheres surface and the amino group (-NH$_2$) of CuAPTPP reacted respectively with the active -NCO groups of TDI to form a surface conjugated microsphere CuAPTPP-TDI-TiO$_2$ that was confirmed by FT-IR spectra. The CuAPTPP-TDI-TiO$_2$ microspheres were characterized with UV-visible, elemental analysis, XRD, SEM, and UV-Vis diffuse reflectance spectra. The effect of amounts of linked TDI on the performance of photocatalytic microspheres was discussed, and the optimal molar ratio of TDI:TiO$_2$ was established. The photocatalytic activity of CuAPTPP-TDI-TiO$_2$ was evaluated using the photocatalytic degradation of methylene blue (MB) under visible-light irradiation. The results showed that, TDI, as a bond unit, was used to form a steady chemical bridging bond linking CuAPTPP and the surface of TiO$_2$ microspheres, and the prepared catalyst exhibited higher photocatalytic activity under visible-light irradiation for MB degradation. The degradation rate of 20 mg/L MB could reach 98.7% under Xe-lamp (150 W) irradiation in 120 min. The degradation of MB followed the first-order reaction model under visible light irradiation, and the rate constant of $5.1 \times 10^{-2}$ min$^{-1}$ and the half-life of 11.3 min were achieved. And the new photocatalyst can be recycled for 4 times, remaining 90.0% MB degradation rate.

Key words: Conjugated microspheres, Surface modification, Sensitization, Visible-light photocatalysis, Methylene blue

I. INTRODUCTION

Due to its excellent performance and environmentally friendly features, titanium dioxide (TiO$_2$) has been regarded as the most promising environment-friendly photocatalytic material that can be utilized for treatment and degradation of organic pollutants in waste water [1, 2]. However, the drawbacks, including the wide band gap (3.2 eV), the low quantum efficiency and exhibition of excellent photocatalytic activity only when irradiated under UV light, greatly restricted its practical application. Numerous studies indicate surface modification could significantly improve photocatalytic activity of TiO$_2$ [3, 4]. Many methods have been proposed for modification. In recent years, researchers have been focusing on the surface modification of TiO$_2$. TiO$_2$ was endowed with novel photo-absorption properties and physicochemical performance through surface modified by active substances, such as organic dyes [5, 6], polymer [7-9], fullerene C$_{60}$ [10, 11], graphene [12, 13], nanotube NT [14, 15], metal [16, 17], metal oxides [18-20]. Metalloporphyrin and its derivatives are dyes with excellent performance, optical and thermal stability. As a sensitizing material, metalloporphyrin can effectively broaden the photo response range of TiO$_2$ [21-23]. Huang et al. reported that porphyrin and iron metalloporphyrin sensitized TiO$_2$ was used to degrade Rhodamine B under UV-light irradiation [24]. The results showed that the photocatalytic properties of TiO$_2$ sensitized by iron-porphyrin was significantly improved, the degradation rate of Rhodamine B approached 86.3% in 30 min under the high-pressure mercury lamp irradiation. Lu et al. synthesized a series of tetraphenylporphyrin derivatives with different functional groups (-OH, -CO$_2$C$_2$H$_5$, -COOH) which were utilized to sensitize TiO$_2$. The photocatalytic performance of sensitized TiO$_2$ was improved [25]. Chang et al. utilized nickel-porphyrin sensitized TiO$_2$ to degrade 2,4-dichlorophenol in waste water under visible-light irradiation, the maximum degradation rate was up to 81% in 240 min [22]. Murphya et al. utilized 4-(4-carboxyphenyl) porphyrin to modify TiO$_2$, which de-
graded pharmaceutical famotidine under visible-light irradiation [6]. The results showed that the obtained catalysts exhibited more optimized performance than Degussa P25. However, for the metalloporphyrin sensitized TiO$_2$, the sensitizer existed on the surface of TiO$_2$ only through simple physical adsorption, instead of strong chemical bond [26, 27]. Therefore, in the process of photocatalytic degradation, sensitizer would be prone to shedding, which would affect sensitization and reduce photocatalytic efficiency [28, 29].

In this work, the toluene disocyanate (TDI) was used as a “bridging bond” molecule, the reaction between the highly reactive group (-NCO) of TDI molecule and the surface hydroxyl group (-OH) of TiO$_2$ was used to firmly fix TDI molecule on the surface of TiO$_2$ microspheres, another group (-NCO) of TDI molecule reacted with the amino group (-NH$_2$) of CuAPTPP complex to obtain the stable conjugate microspheres (CuAPTPP-TDI-TiO$_2$). The structure and morphology of the conjugate microspheres were investigated. The photocatalytic activity of the CuAPTPP-TDI-TiO$_2$ was also evaluated by the degradation of methylene blue (MB), in comparison with pure TiO$_2$, TDI-TiO$_2$ and CuAPTPP-TiO$_2$.

II. EXPERIMENTS

A. Main materials

Pyrrole, benzaldehyde, 4-nitrobenzaldehyde, cupric acetate, methylene blue, titanium(IV) sulfate (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., toluene disocyanate from Xi’an Chemical Reagent Factory, chloroform, methanol, N,N-dimethylformamide, ethanol (AR) from Tianli Chemical Reagent Co., Ltd., and propanoic acid (AR) from Tianjin Fuyu Fine Chemical Co., Ltd. Ultrapure deionized water was used throughout the experiments.

B. Synthesis of CuAPTPP complex

6.50 mL of benzaldehyde and 2.85 g 4-nitrobenzaldehyde (molar ratio of benzaldehyde to 4-nitrobenzaldehyde=3:1) were dissolved in the 150 mL of propionic acid in the three-neck flask equipped with reflux condenser. The three-neck flask with mixture was heated at 140 °C. Subsequently 4.60 mL of pyrrole was dripped into the reaction solution slowly within 60 min. The mixture solution was refluxed continuously for 120 min. After cooling, the mixture solution was distilled at 70 °C and a majority of propionic acid was removed. The remaining solution was transferred to 80 mL of methanol on the ice-bath until the purple crystal precipitated. The precipitated material was 5-(4-nitro)-10,15,20-triphenylporphyrin (NPTPP). The crude product was dissolved in a small amount of CHCl$_3$ and filtered to remove insoluble substance. The CHCl$_3$ solution was purified by the chromatography on a silica gel column with chloroform, the first color band was collected, concentrated and dried, and then the purification of NPTPP was complete.

The NPTPP and copper acetate (molar ratio of NPTPP to copper acetate=1:1) were dissolved in DMF. The mixture solution were heated at 150 °C under stirring and refluxed continuously for 180 min in the oil bath. After cooling, the mixture solution was distilled at 85 °C under vacuum and the DMF was removed. The resulting sepiya sticky substance was transferred into an oven and dried at 80 °C for 12 h. The obtained substance was dissolved in chloroform and filtered to discard the insoluble substance. The chloroform extraction solution was washed by deionized water for 2–3 times. The extraction liquid was dried by MgSO$_4$ for 12 h and then filtered to remove MgSO$_4$. The extraction solution was distilled at 60 °C in vacuum. The 5-(4-nitro)-10,15,20-triphenylporphyrin cupper (CuNPTPP) was generated. A certain amount of SnCl$_2$ concentrated hydrochloric acid solution (0.620 g of SnCl$_2$·H$_2$O was dissolved in 10 mL of concentrated hydrochloric acid) reacted with CuNPTPP at 78 °C for 90 min. After cooling, the mixture solution was extracted by chloroform. The extraction solution was washed by deionized water for 1–2 times and dried by MgSO$_4$ for 12 h. Then the MgSO$_4$ was removed by filtration. The extraction solution was distilled at 60 °C in vacuum, concentrated and dried. The 5-(4-aminophenyl)-10,15,20-triphenylporphyrin cupper(CuAPPTP) was generated. The synthesis of CuAPPTP is shown in Fig.1.

C. Synthesis of TDI-modified TiO$_2$

TiO$_2$ was dispersed into acetone by ultrasonic dispersion in a three-neck flask to form a suspension. The suspension was stirred slowly on heat, while TDI (molar ratio of TiO$_2$ to TDI=1:0.5) was dripped into the flask. And then the mixture solution was refluxed 30 min at 50 °C. The mixture solution was filtered and washed with acetone 3–4 times, and let dry naturally. Then the TDI cross-linked TiO$_2$ (TDI-modified TiO$_2$) was obtained. The synthesis of TDI-modified TiO$_2$ is shown in Fig.2.

D. Preparation of CuAPTPP-TDI-TiO$_2$ conjugate microspheres

20 mg of CuAPTPP was dissolved in 100 mL of acetone. An appropriate amount of TDI-TiO$_2$ was added to the CuAPTPP solution with ultrasonic dispersion for 30 min. The mixture solution was transferred into a 250 mL three-necked flask with stirring at 50 °C and refluxed for 120 min in oil bath. The mixture solution was distilled in vacuum to remove acetone, then the TDI-modified TiO$_2$ was sensitized by using CuAPTPP.
FIG. 1 Synthesis of CuAPTPP complex.

FIG. 2 Synthesis of TDI-modified TiO$_2$.

to obtain the conjugate microspheres (CuAPTPP-TDI-TiO$_2$). Figure 3 shows the synthetic pathway of the CuAPTPP-TDI-TiO$_2$ conjugate microspheres.

**E. Preparation of CuAPTPP-TiO$_2$**

20 mg of CuAPTPP was dissolved in 100 mL of acetone. An appropriate amount of TiO$_2$ was added to the CuAPTPP solution with ultrasonic dispersion for 30 min. The mixture solution was transferred into a 250 mL three-necked flask with stirring at 50 °C and refluxed for 120 min in oil bath. The mixture solution was distilled in vacuum to remove acetone, then the TiO$_2$ sensitized by CuAPTPP was obtained (CuAPTPP-TiO$_2$).

**F. Characterization of conjugate microspheres**

The FT-IR spectra were obtained using a Shimadzu FT-IR 8900 (Japan) with the reference of KBr. The morphology of the conjugate microspheres was observed by JSM-6700F field emission scanning electron microscope (Japan). The crystalline phase analysis of sample was characterized by Shimadzu XRD-7000S X-ray diffractometer (Japan) at tube current of 30 mA, tube voltage of 40 kV, and scanning speed of 10°/min. Elemental analysis (N, C, H) was performed by Vario EL cube elemental analyzer instrument (Germany). The metalkoporphyrin and its derivates were characterized by UV-2102 PC UV-visible spectrophotometer (China). The UV-Vis diffuse reflectance spectra (DRS) of obtained photocatalytic microspheres were characterized by TU-1901 double-beam UV-Vis diffuse reflectance spectrophotometer (China) with BaSO$_4$ as reference.

**G. Evaluation of visible-light catalytic activity**

Self-made photocatalytic reaction device was used for the evaluation of photocatalytic activity of samples. The reactor includes a light source (Xe lamp, 150 W), sample tube (100 mL quartz tube: length 22.0 cm, diameter 2.0 cm, from the light source 10 cm), a cold trap, a snorkel and other accessories. 0.05 g of photocatalysts and 50 mL of MB solution (20 mg/L) were added into the sample tube. The air tube was inserted into the bottom of the sample tube, maintaining a controlled...
air flow at 3 L/min to achieve the suspended catalyst in the degradation solution. Adsorption was performed in dark for 30 min, and then sampling every 15 min with pipette. The absorbance of the supernatant from high-speed centrifugation was measured at 665 nm. According to the relationship between the absorbance and MB concentration, the degradation rate was calculated using the equation

$$\eta = \frac{A_0 - A_t}{A_0} \times 100%$$  \hspace{1cm} (1)

where $A_0$ is the initial absorbance of MB solution, $A_t$ is the absorbance of MB solution at different time, $\eta$ is used to evaluate the photocatalytic activity of synthetic samples.

III. RESULTS AND DISCUSSION

A. UV-Vis analysis

Figure 4(a) shows the UV-Vis absorption spectra of the TPP, CuTPP, CuNPTPP, and CuAPTPP samples. The characteristic Soret band of TPP was captured at 419 nm. There are four weak peaks of TPP between 500–700 nm: 515.7 nm ($\lambda_1$), 550.6 nm ($\lambda_2$), 590.5 nm ($\lambda_3$), and 647.3 nm ($\lambda_4$), which are the characteristic peaks of Q-band absorption of TPP [30]. Figure 4(b) shows the Q-band absorption spectra of samples. In comparison with the absorption peaks of TPP, absorption peaks of CuTPP, CuNPTPP and CuAPTPP differed greatly. The peak position of Soret band essentially remained unchanged. Only one absorption peak ($\lambda_1$) was present in the Q-band, and the other three absorption peaks disappeared. The $\lambda_1$ absorption peaks of metalloporphyrin spectrum exhibited red shift from 515.7 nm to 539.0 nm.

B. FT-IR analysis

Figure 5 shows the FT-IR spectra of TPP, CuTPP, CuNPTPP, and CuAPTPP. From the FT-IR spectrum of TPP, the peak at 3307 cm$^{-1}$ was a result of stretching vibration of the two N–H bonds at the center of porphyrin ring. Formation of metal ligand leads to disappearance of N–H vibration absorption peak [30]. Compared with TPP, CuTPP, CuNPTPP, and CuAPTPP spectra have peaks at 1000 cm$^{-1}$, due to bond stretching/bending vibration between Cu$^{2+}$ and porphyrin [32, 33]. The FT-IR spectrum of CuNPTPP shows the peak at 1344 cm$^{-1}$, due to the $\lambda_1$ absorption peaks of metalloporphyrin spectrum exhibited red shift from 515.7 nm to 539.0 nm.
The elemental analysis results of synthesized TPP and porphyrin derivatives are shown in Table I. The experimental element contents of NPTPP, APTPP and metalloporphyrin derivatives (CuNPTPP, CuAPTPP) matched the theoretical value. The experimental results show that, the synthesized NPTPP, APTPP, and metalloporphyrin derivatives were nitro-monosubstituted and amino-mono substituted derivatives.

D. XRD analysis

Figure 7 shows XRD patterns of pure TiO₂, TDI-TiO₂, CuAPTPP-TiO₂, and CuAPTPP-TDI-TiO₂ samples. It is clear that the four kinds of photocatalysts were anatase phase structure. Various distinct characteristic diffraction peaks corresponded to different crystalline surface. The synthesized pure TiO₂ has an anatase crystalline phase [101], 25.28° corresponds to [101] plane, 37.80° corresponds to [004] plane, 48.04° corresponds to [200] plane, 53.89° and 55.60° correspond to [105] and [211] planes, 62.68° corresponds to [204] plane, 76.01° corresponds to [301] plane, and 83.14° corresponds to [312] plane. After surface modification and sensitization, the characteristic diffraction peaks of CuAPTPP-TDI-TiO₂ in XRD patterns do not exhibit relocation or any change in the peak shapes. It was apparent that modification and sensitization only occurred on the surface of TiO₂ and there were no significant effect on the crystalline phase of catalyst. CuAPTPP-TDI-TiO₂ crystalline anatase phase still dominated [36].

E. SEM analysis

As shown in Fig.8, TiO₂ (inset) appears smooth surface and uniform size, and the diameter average size is about 40 nm. In comparison, the microstructures of prepared CuAPTPP-TDI-TiO₂ appear loose and irregular spheres with rough surface. The average size of these microspheres diameter estimated from

<table>
<thead>
<tr>
<th>Samples</th>
<th>N/[%]</th>
<th>C/[%]</th>
<th>H/[%]</th>
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<td>Pure TPP</td>
<td>9.12</td>
<td>9.47</td>
<td>85.9</td>
</tr>
<tr>
<td>NPTPP</td>
<td>10.6</td>
<td>10.4</td>
<td>80.1</td>
</tr>
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<td>9.03</td>
<td>73.2</td>
</tr>
<tr>
<td>CuAPTPP</td>
<td>10.1</td>
<td>7.68</td>
<td>76.4</td>
</tr>
</tbody>
</table>

C. Elemental analysis

The experimental results show that, the synthesized NPTPP, APTPP, and metalloporphyrin derivatives were nitro-monosubstituted and amino-mono substituted derivatives.
improve the photo response activity of TiO$_2$. It indicates that TDI, as sensitizer, could evidently strengthen the absorption of TDI from 200 nm to 400 nm in the ultraviolet light range. This phenomenon of TDI is attributed to the modification of TiO$_2$ with TDI, which lead to the photo-absorption decrease. The agglomerate phenomenon may be due to the cladding of TDI with TDI and the formation of a small organic molecule shell, which results in the worsened dispersibility of TiO$_2$.

According to the relationship between semiconductor band gap and UV-Vis absorption coefficient:

$$\alpha h\nu = K(h\nu - E_g)^{1/2}$$

where $h\nu$ is the photo energy, $\alpha$ is the absorption coefficient, $K$ is the semiconductor constant and $E_g$ is the band energy gap. The $(\alpha h\nu)^2$ vs. $h\nu$ curves of different samples are shown in inset of Fig.9. According to the value from tangent of curve intersects the axis abscissa, the band gap values were calculated. Figure 9 shows that the band gap of pure TiO$_2$ is 3.19 eV, the band gap of TiO$_2$ modified with TDI decreased in varying degree: $E_g$(TDI$_{0.01}$-TiO$_2$)=3.09 eV, $E_g$(TDI$_{0.05}$-TiO$_2$)=3.06 eV, $E_g$(TDI$_{0.1}$-TiO$_2$)=3.13 eV, $E_g$(TDI$_{0.5}$-TiO$_2$)=3.08 eV, $E_g$(TDI$_1$-TiO$_2$)=3.12 eV. The narrow band gap energy indicated that the modification of TDI can extend the range of TDI light absorption. The decrease of transition energy of photogenerated electrons is caused by the UV-absorption property of TDI.

Figure 10 is UV-Vis DRS spectra for TDI, TiO$_2$, and a series of catalysts. It shows that the spectra of CuAPTTP-TiO$_2$ and CuAPTTP-TDI-TiO$_2$ exhibited strong characteristic absorption peaks of phyrin at 420 nm, indicating that TDI-TiO$_2$ has been sensitized by CuAPTTP. The surface modified TiO$_2$ with TDI showed more intensive characteristic absorption peaks of phyrin at the same amount of sensitizer, indicating the surface of TDI-TiO$_2$ could be fixed with more CuAPTTP via -NCO band. The results showed that
sensitization of CuAPTPP improved the photoresponse activity of TDI-TiO$_2$ greatly.

G. Evaluation of photocatalytic activity

1. Degradation experiments of MB by CuAPTPP-TDI-TiO$_2$

MB is a chromogenic agent of diltiazem benzene. In the process of photocatalytic degradation, the -(CH$_3$)$_2$ within molecules accepted the photo-generated electron and then demethylation occurred. The degradation process was indicated by the reduction of characteristic absorption peak ($\lambda=664$ nm). After formation of phenyl thioridazine, the small organic were degraded and mineralized to inorganic molecules gradually [37].

As shown in Fig.11, the absorption peaks of MB solution are gradually reduced during the photocatalytic degradation by a series of samples under Xe lamp (150 W) irradiation. In Fig.12(a), the degradation rate of 10 mL MB solution by CuAPTPP-TDI-TiO$_2$ was up to 98.7% within 120 min. It was significantly higher than the degradation rates of CuAPTPP-TiO$_2$ (Fig.11(b), 65.1%), TDI-TiO$_2$ (Fig.11(c), 62.0%) and pure TiO$_2$ (Fig.11(d), 33.7%). It can be apparently seen that the absorbance of the characteristic peaks at 290 and 664 nm both decline continually and nearly disappear finally in Fig.11(a). It implies that MB not only decolorized but also mineralized under visible light irradiation. The unique and excellent photocatalytic activity of sample may be due to the role of CuAPTPP-TDI, which has increased the hydrophobicity of TiO$_2$ and favored samples adsorption. Before bridging bond linked by CuAPTPP-TDI, only a small amount of MB is adsorbed on TiO$_2$ surface and then degraded, the hydrophobic attractions between CuAPTPP-TDI and MB are increased, leading to enhancement of the surface coverage of MB on CuAPTPP-TDI-TiO$_2$ powders. In addition, for the CuAPTPP-TDI-TiO$_2$ composite, the complex structure established the conjugated interaction between TiO$_2$ and CuAPTPP molecules, the sensitization efficiency was improved. As mentioned above, CuAPTPP-TDI-TiO$_2$ shows stronger adsorption and higher degradation capability than others.

2. MB degradation kinetics analysis

Figure 12 shows the relationship between $\ln(c_0/c_t)$ and reaction time $t$ for MB degradation by pure TiO$_2$ and a series of synthesized photocatalysts. From the Fig.12, the CuAPTPP-TDI-TiO$_2$ microspheres possess the optimal photocatalytic performance. Furthermore, its degradation rate was higher than the either sensitized or modified TiO$_2$. The results show, the isocyanate groups of TDI on the surface of TiO$_2$ are able to fix firmly the CuAPTPP molecules and inhibit the generation of inactive CuAPTPP dimer [38]. As a result, the sensitization efficiency of CuAPTPP was improved significantly. The dye molecules were able to inject the photo-generated electrons to the conduction band of TiO$_2$ as the dye molecules were irradiated. TDI molecule between CuAPTPP and TiO$_2$, as a conjugated tunnel, could control the amounts of injected electrons, prohibit recombination of $e^-h^+$ and enhance the coefficient of utilization for photo-generated electrons. Since the organic molecules on the surface of TiO$_2$ strengthened the compatibility with MB molecules, the adsorption rate increased greatly.

Table II shows the initial reaction rate of MB degradation kinetic equation, the linear correlation coefficient $k$, and the half-life $t_{1/2}$. The reaction rate kinetics constant $k$ of MB degradation by CuAPTPP-TDI-TiO$_2$ is $5.12 \times 10^{-2}$ min$^{-1}$, which was seven times bigger than that of the pure TiO$_2$. The degradation half-life $t_{1/2}$ is 11.3 min, which is the shortest degradation half-life among all catalysts tested.

3. Stability of the catalyst

In order to investigate the stability of CuAPTPP-TDI-TiO$_2$ and CuAPTPP-TiO$_2$, the samples were recovered after each photocatalytic degradation experiment, and then were reused in the next photocatalytic experiment. Figure 13 shows the MB degradation curves by CuAPTPP-TDI-TiO$_2$ reused for 4 times, and degradation rate remained at about 90%. In comparison with CuAPTPP-TDI-TiO$_2$, the degradation rate of MB by CuAPTPP-TiO$_2$ decreased rapidly.
after reusing, this result was due to the fall off of CuAPTPP. Because the CuAPTPP on the surface of TiO$_2$ is merely physical adsorption and not chemical bond. This shows that, TDI could form a steady chemical bridging bond linking between CuAPTPP and the surface of TiO$_2$ microspheres and enhanced the photocatalytic performance of sample. The catalytic activity of CuAPTPP-TDI-TiO$_2$ did not reduce after repeated utilization. This implies that as-prepared photocatalyst was reusable.

**IV. CONCLUSION**

CuAPTPP-TDI-TiO$_2$ conjugated photocatalyst was successfully synthesized. The characterizations of the conjugated structure of the composite catalyst indicate that the bridging bond linking was formed to immobilize the dye sensitizer on the surface of TiO$_2$. Two isocyanate groups -NCO of TDI molecules reacted with -NH$_2$ of CuAPTPP molecule and -OH of TiO$_2$ surface respectively. The immobilization of dye sensitizers overcame effectively the fall off of CuAPTPP, the utiliza-
tion rate of dye sensitizer was improved. The size of CuAPTPP-TDI-TiO₂ photocatalytic microspheres was in the range of 4–10 µm with loosen surface and exhibited excellent photocatalytic activity on the degradation of MB under visible-light irradiation. The degradation rate of MB on CuAPTPP-TDI-TiO₂ was up to 98.7% under Xe lamp irradiation within 120 min. The TDI linking on the surface of TiO₂ enhanced the compatibility of TiO₂ with MB, the adsorption properties of photocatalysts were strengthened considerably. The higher photo-response activity of CuAPTPP-TDI-TiO₂ may be due to the establishment of bridging bond linking between dye molecules and TiO₂ substrate. The kinetics of photocatalytic degradation of MB was investigated, suggesting a pseudo first-order kinetics model. The CuAPTPP-TDI-TiO₂ sample was robust and able to use at least for four runs without obvious loss.

V. ACKNOWLEDGMENTS

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