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Photoelectrocatalytic Degradation of C.I. Basic Blue 9 in Water under UV and Visible Light Illumination Using Copper/Sulfur Co-Doped Titanium Dioxide Nanotubes †

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Abstract: Titanium dioxide has long been investigated for its excellent photocatalytic activity under UV illumination. However, its sluggish activity under visible light illumination remains a challenge. Doping titanium dioxide with transition metals and non-metals was done in the past to improve its catalytic properties, yet the expensive synthesis protocols involved in doping titanium dioxide limit its applications. Herein, a one-pot approach of doping titanium dioxide nanotubes was used. In particular, the Cu/S-TiNTs electrode was synthesized by electrochemical anodization using an electrolyte solution spike with $CuSO_4$. The resulting nanostructured Cu/S-TiNTs electrode was used as a photoanode for the photoelectrocatalytic degradation of synthetic dye solution (50 ppm C.I. Basic Blue 9 in deionized water) in a 125-mL reactor. The Cu/S-TiNTs were shown to be catalytically active under both ultraviolet and visible light. Co-doping pristine TiNTs with copper and sulfur significantly enhanced the photoelectrocatalytic degradation rates of BB 9. Cu/S-TiNTs achieved 67% faster degradation rate ($k_1 = 1.5054 \pm 0.0193 \times 10^{-2}$ min^{-1}) compared to pristine TiNTs ($k_1 = 8.9106 \pm 0.0647 \times 10^{-3}$ min^{-1}) under visible light illumination. At the end of 60 min, the Cu/S-TiNTs were able to degrade 59.69% of the initial dye concentration under visible light compared to 45.43% degradation using pristine TiNTs. The synthesized photoanodes demonstrated good reusability and stability after several cycles of use, even at a low dopant loading. These findings bring us closer to the possible large-scale adaptation of advanced oxidation processes, such as photoelectrocatalysis, for environmental remediation of recalcitrant organic compounds in wastewater.

Keywords: photoelectrocatalysis; methylene blue; titanium dioxide; doping; wastewater

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1. Introduction

Titanium dioxide, a widely-available metal oxide semiconductor, has been used by many researchers for a variety of applications since the first reports of Fujishima and Honda [1] on UV-induced chemical reactions on its surface. Among its common uses is photocatalytic degradation of organics in water [2,3] and photoelectrochemical water splitting [4,5], among others.

Despite the extensive use of titanium dioxide in literature, commercial applications are minimal due to various key challenges that remain unaddressed to be feasible for large-scale use. Among these issues [6], enabling visible-light photoactivity and minimizing electron-hole recombination remains a challenge.

Doping titanium dioxide is the most popular method to address extend its photoactivity to the visible-light region. Cationic doping is more widely-studied; common cationic dopants are noble metals [7,8], transition metals [9,10], and rare earth metals [11,12]. First-principles calculations involving transition metal-doped TiO_2 previously showed that transition metals introduce intermediated energy levels (IELs) that are previously absent in pristine TiO_2 due to the delocalization of *3d* or *4d* states of the transition metals and sometimes the hybridization of these states with the Ti *3d* and O *2p* states. This alters its electronic structure and improves its visible light absorption ability by narrowing the bandgap [13,14]. On the other hand, anionic dopants such as nitrogen [15], sulfur [16], and carbon [17] were also used to enhance visible-light photocatalysis by extending the optical absorption edge of TiO_2. Because anions are less electronegative than O, substitutional-doping causes the anionic *p*-states to be pushed up out of the TiO_2 valence band into the bandgap [6].

Despite the effectiveness of doping in improving the visible-light photoactivity of TiO_2, many issues still limit its application in water treatment. For example, cationic doping causes induced thermal instability which causes activity loss during calcination. Transition metals can also enhance electron-hole recombination by acting as electron traps which significantly reduces the photocatalytic activity of TiO_2 [18]. In the case of anionic doping, calcination could lead to reduced dopant concentration due to sintering [19]. To address these issues, co-doping TiO_2 with two or more elements has been explored by some researchers [20,21].

Meanwhile, even though co-doping TiO_2 can potentially improve its visible-light activity through bandgap modification, electron-hole recombination is still an issue. Efforts to address exciton and charge transfer issues, particularly electron-hole recombination upon photo-activation by a light source, have been limited. The most promising method to address charge transfer issues is to introduce an external bias such that the photogenerated electrons can be continuously harvested through an external circuit towards the counter-electrode, thus arresting the recombination of photogenerated electrons and holes. This process, known as photoelectrocatalysis (PEC), belong to advanced oxidation processes (AOPs) that has the potential to overcome electron-hole recombination experienced in conventional photocatalysis [22]. Preventing electron-hole recombination could enhance the production of reactive free radicals which can be exploited for various catalytic applications such as the degradation of organic pollutants in water [23,24], among others.

Herein, we explored the use of copper and sulfur co-doped titanium dioxide nanotubes (Cu/S-TiNTs) as photoelectrodes for photoelectrocatalytic degradation of textile dyes. In-situ doping was done to synthesize the Cu/S-TiNTs through double-anodization of Ti sheets with the dopant precursor dissolved in the electrolyte solution. The Cu/S-TiNTs were and then used for the batch degradation of C.I. Basic Blue 9 (BB 9). The catalytic performance of the synthesized nanotubes over repeated cycles of use was also investigated.

2. Materials and Methods

2.1. Materials

Titanium sheets (99.58% Ti, ASTM B265) were used as metal substrates for the synthesis of pristine TiNTs and Cu/S-TiNTs. Ethanol (≥99.5% CH_3CH_2OH), nitric acid (70% max. HNO_3), hydrochloric acid (37% max. HCl), copper sulfate pentahydrate (≥98.0%, $CuSO_4{\cdot}5H_2O$), C.I. Basic Blue 9 (≥95% $C_{16}H_{18}ClN_3S_3H_2O$), and anhydrous sodium sulfate (≥95% Na_2SO_4) were obtained from Ajax Finechem Ltd. (Taren Point, Australia). Acetone (≥99.5% CH_3CH_2COOH) was purchased from RCI Labscan Ltd. (Bangkok, Thailand). Meanwhile, ammonium fluoride (≥98.0% NH_4F) and platinum wire (≥99.99% Pt, 0.1 mm diameter) were obtained from Sigma-Aldrich (St. Louis, MO, USA). All chemicals are of analytical grade and are used as-received without purification. All preparations were done using ultrapure water (Milli-Q, ≤18.2 MΩ·cm at 25 °C, Merck, Rahway, NJ, USA).

2.2. Synthesis of Pristine (TiNTs) and Copper/Sulfur Co-Doped (Cu/S-TiNTs) Titanium Dioxide Nanotus

Briefly, titanium sheets (20 × 50 × 0.1 mm) were sonicated in ethanol, acetone, and ultrapure water at 35 °C, 15 min in each solvent, to remove the impurities on its surface. The pre-treated Ti sheets were etched in freshly-prepared aqua regia for 3 min to dissolve any adhering oxide layer [25]. The etched Ti sheets were washed using free-flowing ultrapure water and then oven-dried prior to use.

Pristine TiNTs were synthesized by anodizing the treated Ti sheets at 30.0 V for 60 min at 20 °C using a Pt wire as the counter electrode. The anodization electrolyte consists of 0.3 wt% NH_4F and 2 vol% ultrapure water dissolved in ethylene glycol as solvent. Meanwhile, Cu/S-TiNTs were synthesized using the same anodization recipe, but a sufficient amount of $CuSO_4$ was added to the anodization electrolyte to make a 1.0 wt.% $CuSO_4$ solution which served as a precursor to achieving in-situ Cu/S co-doping. The as-anodized Ti sheets were sonicated in ethanol for 2 min at 30 °C, washed with ultrapure water, and then oven-dried to remove the TiO_2 barrier layer and expose the nanoporous template where ordered TiO_2 nanotubes can grow. The sonicated samples were anodized using the same anodization recipe for another 60 min. The double-anodized TiNTs were washed in ultrapure water, oven-dried, and then calcined in a muffle furnace (Constance FN-1208) at 450 °C for 3 h at a 10 °C/min heating and cooling ramp. The calcined pristine TiNTs and Cu/S-TiNTs were stored in a desiccator prior to characterization and degradation experiments.

2.3. Textile Dye Degradation in a Batch Photoelectrochemical Reactor

The photoelectrocatalytic activity of pristine TiNTs and Cu/S-TiNTs in degrading C.I. Basic Blue 9 (BB 9) was investigated in a batch, agitated, and borosilicate-made photoelectrochemical reactor with a total working volume of 125 mL and housed in an air-cooled black box. Four pieces of 40 W low-pressure mercury lamp (λ_{max} = 365 nm) in series with a total average UV intensity of 2000 μW cm^{-2} were used for UV-assisted experiments. Meanwhile, a halogen lamp with an average intensity of 10,000 lumens was used to simulate solar-assisted photoelectrocatalysis. Meanwhile, a benchtop DC power supply (V_{max} = 60.0 V, I_{max} = 5.0 A, Top Power Ltd., Singapore) was used as an electrical source and was operated at a constant current density of 0.5 mA cm^{-2}.

Synthetic dye solutions of BB 9 with an initial concentration of 50.0 mg L^{-1} were prepared, and a sufficient amount of anhydrous Na_2SO_4 was dissolved in the dye solution to achieve a 0.100 M Na_2SO_4 concentration. The resulting solution was used without pH adjustment. Prior to all degradation experiments, the working solution is well-stirred in the dark for 60 min to compensate for the adsorption of BB 9 on the surface of the photoelectrodes. The working solution is maintained at 30 °C using a cold-water bath. After 60 min, the light source and DC source were turned on, and aliquots were obtained at 5-min intervals for 60 min. The aliquots were immediately analyzed for their optical absorbance spectra using a Vis-NIR spectrophotometer (Go-Direct SpectroVis Plus, Vernier, Beaverton, OR, USA). The concentration profiles were fitted using a pseudo-first-order (PFO) kinetic model in their integrated form. All experimental runs were done in triplicates, and three absorbance readings were done for each replicate.

3. Results

3.1. Photoelectrocatalytic Degradation under Ultraviolet Light

Batch photoelectrocatalysis was performed on C.I. Basic Blue 9 (BB 9) in aqueous solutions using pristine TiNTs and Cu/S-TiNTs as photoanodes, respectively, to compare their photoelectrocatalytic degradation performance. The UV intensity and applied potential were fixed at 2000 μW cm^{-2} and 1 mA cm^{-2}, respectively, and the concentration profiles were fitted numerically to the pseudo-first-order (PFO) kinetic model in accordance with the commonly observed degradation model for AOPs [26]. As shown in Figure

1, the Cu/S-TiNTs performed better in degrading BB 9 degradation under UV light illumination. BB 9 degraded over 36% faster using Cu/S-TiNTs ($k_1 = 10.5353 \pm 0.2001 \times 10^{-3}$ min^{-1}) compared to pristine TiNTs ($k_1 = 7.7367 \pm 0.2110 \times 10^{-3}$ min^{-1}). At the end of 60 min, the Cu/S-TiNTs were able to degrade 49.36% of the initial BB 9 concentration. Meanwhile, under similar experimental conditions, 35.94% of the initial BB 9 degraded using pristine TiNTs as photoelectrodes. These results show that co-doping pristine TiNTs with copper and sulfur improves its PEC performance in degrading textile dyes significantly under UV light illumination. The PEC activity of the pristine TiNTs and Cu/S-TiNTs were also tested upon repeated electrode use. As the number of electrode use increases, the PEC activity of the photoelectrodes also dropped, which can be due to the fouling of the photoelectrodes and/or leaching of dopants into the solution during photoelectrocatalysis. Further studies can be done to improve the catalytic activity of the photoelectrodes for repeated use. Nonetheless, in this study, we demonstrated that Cu-S/TiNTs remained superior in terms of its PEC activity under UV light illumination compared to pristine TiNTs even after several cycles of reuse.

3.2. Photoelectrocatalytic Degradation under Visible Light

To determine the role of Cu/S co-doping on the PEC performance of the TiNTs, visible light—assisted photoelectrocatalytic degradation of BB 9 were performed in a batch PEC reactor at a fixed visible light intensity and applied current density. Cu/S co-doping enhanced the PEC activity of pristine TiNTs in degrading BB 9 as evidenced by a faster degradation rate observed using Cu/S-TiNTs compared to pristine TiNTs. Under visible light illumination, the Cu/S-TiNTs achieved 67% faster degradation rate ($k_1 = 1.5054 \pm 0.0193 \times 10^{-2}$ min^{-1}) compared to pristine TiNTs ($k_1 = 8.9106 \pm 0.0647 \times 10^{-3}$ min^{-1}). At the end of 60 min, the Cu/S-TiNTs was able to degrade 59.69% of the initial BB 9 concentration compared to 45.43% degradation of the initial BB 9 using pristine TiNTs under similar experimental conditions. These results show that Cu/S co-doping in pristine TiNTs enhanced its PEC performance in the visible light range, which is important to make solar-assisted PEC possible. As in the case of UV-assisted PEC, the catalytic activity of the photoelectrodes decreased as the number of cycles of use increases. Even so, we were able to demonstrate that the Cu/S-TiNTs synthesized by a simple in-situ doping anodization technique is catalytically-active under both UV light and visible light region of the solar spectrum and achieved an enhanced activity in degrading conventional textile dyes compared to pristine TiNTs alone.

In general, the use of Cu/S-TiNTs as photoelectrodes for the degradation of textile dyes have several key advantages compared to the use of traditional TiO_2 nanopowders. First, the nanotubular structure of Cu/S-TiNTs allows fast carrier transport, which reduces losses due to electron-hole recombination at recombination centers [27]. Second, the use of nanostructured TiNTs as photoelectrode allows higher absorption of incident photons from the UV light source compared to using a flat TiO_2 film [28]. Third, the nanotubular geometry results in a very high surface area and avoids catalyst aggregation experienced in TiO_2 nanoparticles, which leads to an increase in reactivity and specific reaction rates [27]. Fourth, doping with transition metals, copper/sulfur, in this case, creates an electron-trap which prevents electron-hole recombination [29]. Fifth, the increased charge-mobility during PEC as a result of the applied electrical potential allows continuous harvesting of photogenerated-electrons from the photoanode to the counter-electrode, which, in turn, prevents recombination [30]. The combination of all these factors allows the photo-generated electron-holes to have longer lifespans, which, in turn, leads to the increased production of hydroxyl free radicals which are very reactive towards the degradation of organics. Significant enhancement in the PEC activity of pristine TiNTs was demonstrated in our case even at low Cu/S-loading. This is important in reducing the overall cost of the material for PEC applications.

4. Conclusions

Copper and sulfur were successfully co-doped in titanium dioxide nanotubes with a highly-ordered surface morphology in a one-pot approach. The Cu/S-TiNTs were shown to be catalytically active in degrading conventional textile dyes such as C.I. Basic Blue 9 under both ultraviolet and visible light photoelectrocatalysis. Co-doping pristine TiNTs significantly improved the degradation rate of the model dye even at a low dopant loading. Most importantly, it remained catalytically-active in degrading textile dyes even after several usages, showing its excellent reusability. This makes Cu/S-TiNTs a promising material for the photoelectrocatalytic degradation of recalcitrant organic compounds in wastewater.

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