



Photocatalytic and photoelectrocatalytic degradation of small biological compounds: A case study of uridine

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ABSTRACT

Photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of small hazardous biological compounds was accomplished by using uridine as a model compound. The net charge transfer (Q_{net}) originated from PEC degradation of uridine and blank charge transfer (Q_{blank}) due to photocatalytic oxidation of water remained constant when the light intensity increased from 20 to 40 mW/cm². The effect of solution pH on Q_{net} and Q_{blank} showed that the suitable pH range for this proposed analytical application is between 4 and 9. For both PC and PEC, an increase in the uridine concentration within low concentration range led to a rapid decrease in the mineralization percentage for converting organic nitrogens to both NH₃/NH₄⁺ and NO₃⁻. With further increase of uridine concentration to 320 μM, the PEC mineralization percentages maintained at about 85% and 56% for N oxidized to NH₃ and NO₃⁻, respectively. While for PC treatment, the mineralization percentages decreased steadily. Finally, PC and PEC degradation mechanism of uridine was also clarified on the basis of intermediates identified by HPLC/MS/MS and frontier electron densities calculation. Uridine as well as the intermediates can be eventually mineralized into CO₂, H₂O and NH₃ or NO₃⁻ (or both) during PC and PEC degradation with enough reaction time.

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1. Introduction

Besides heavy metals and organic contaminants, the pathogenic biohazard is another important group of contaminants present in aquatic environment. Microbial pathogens in drinking water and wastewater impose a serious threat on public health and safety, responsible for over 80% of disease outbreaks [1]. The removal of biohazards has therefore drawn an increasing attention to researchers in the field. In this regard, the recently reported water disinfection technique based on photocatalysis processes at illuminated nanostructured titanium dioxide (TiO₂) has attracted considerable research interests [2–6]. The major attraction of such type photocatalysis-based disinfection techniques is that the inactivation and decomposition of biohazards can be achieved in a single process without the use of toxic chemicals and producing hazardous byproducts [6,7]. Various bacterial inactivation mechanisms have been proposed by different research groups. For instance, Lu et al. [8] proposed that •OH attacks to intracellular macromolecules such as nucleic acids could lead to the cell

death. A two-step inactivation mechanism involving photocatalytic (PC) decomposition of the outer membrane and disordering the cytoplasmic membrane were suggested by Sunada et al. [9]. However, the oxidative damage and decomposition of genetic material such as DNA and RNA has been recognized as a major cause of mutations and cell death in all aerobic microorganisms [10,11]. It is well known that a microbial cell is built by different classes of large biomolecules (e.g., protein, DNA and RNA). These large biomolecules consist of large numbers of basic building blocks (e.g., amino acids and nucleotides). A conjectural view of microbial cell decomposition is that the process is highly complicated as it involves an initial breaking down of the microbial cell to large biomolecules, which is further decomposed to small biological species (basic building blocks) before the mineralization is achieved. PC degradation of nucleotides is of interest due to a sensible bottom-up approach that could aid in interpreting such complex disinfection processes by investigating the degradation behaviors of basic building blocks such as uridine. Nevertheless, little has been known regarding the mechanistic steps of PC degradation of microbial cells at the molecular level. Another reason for interesting on PC degradation of uridine is because the uridine exists not only as one of the four naturally occurring nucleosides found in cellular RNA in biological species, but also as a

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pollutant in environment resulted from sewage effluents, hospital waste, human excrements, and improper disposal of unused drugs. Such type of contaminations mainly come from the use of uridine as a versatile therapeutic agent for patients with hereditary orotic aciduria, cystic fibrosis, liver dysfunction, chemotherapy toxicity, pervasive developmental delay, schizophrenia, epilepsy, and diabetes-induced peripheral neuropathy [12,13]. Hence, it is very necessary to understand the fates, as well as the degradation patterns in the aquatic environment. However, the PC degradation of uridine has yet not been studied.

In this account, we emphasize our recent efforts to aid in the understanding the PC degradation of nucleotides using uridine as the model compound. It has been widely accepted that the application of an appropriate potential bias to a TiO₂ nanoparticulate photoanode during the PC oxidation can significantly improve the degradation efficiency of organic compounds [14–16]. The applied potential bias to timely remove the photogenerated electrons and physical separation of photoanode from the cathode are generally regarded as the major attributions for the enhanced efficiency [17,18]. For this reason, the photoelectrocatalytic (PEC) degradation of uridine was also studied. The PC and PEC degradation characteristics were compared and degradation pathways were tentatively proposed based on the degradation intermediates detected by HPLC/MS/MS and the frontier electron densities (FEDs) calculation results.

2. Materials and methods

2.1. Reagents and apparatus

Uridine ($\geq 99\%$) was supplied by Sigma–Aldrich Inc. and used as received. Titanium butoxide (97%), acetonitrile (for HPLC, $\geq 99.9\%$) and sodium perchlorate ($\geq 98.0\%$) were also obtained from Sigma–Aldrich Inc. All other reagents were of analytical grade and purchased from Guangzhou Chemical Reagent Co., Inc., China. Indium tin oxide conducting glass slides (ITO, 8 Ω /square) were purchased from Delta Technologies Ltd. (USA). All solutions were prepared using high purity deionized water (Millipore Corp., 18 M Ω cm).

2.2. Apparatus and methods

Both PC and PEC degradation experiments were performed under identical UV intensity using the same UV-LED/TiO₂ photoelectrochemical thin-layer cell [15]. The TiO₂ photoanode was prepared by hydrolysis of titanium butoxide according to the method described in our previous study [19]. A UV-LED (NCCU033 (T), Nichia Corporation) was used as the illumination source. The specified peak wavelength of the LED was 365 nm with a spectrum half width of 8 nm. The UV intensity was adjusted by a power supply and measured with an UV-irradiance meter (UV-A, Beijing Normal University).

As for PEC degradation experiments, a microelectrochemical system (μ ECS, PLAB, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, China) powered and controlled by a laptop was used for application of potential bias and current signal recording. For the exhaustive degradation experiment, a sample containing various concentrations of uridine and 2.0 M NaClO₄ supporting electrolyte was injected into the thin-layer cell via a precision pump before the degradation process and then subjected to PEC oxidation. For samples need HPLC analysis after PEC oxidation, a continuous sample injection mode via a precision pump during the degradation process was used. Under such conditions, the reaction time of a sample was controlled by adjusting the flow rate. A sufficient volume of the reacted sample was collected for further

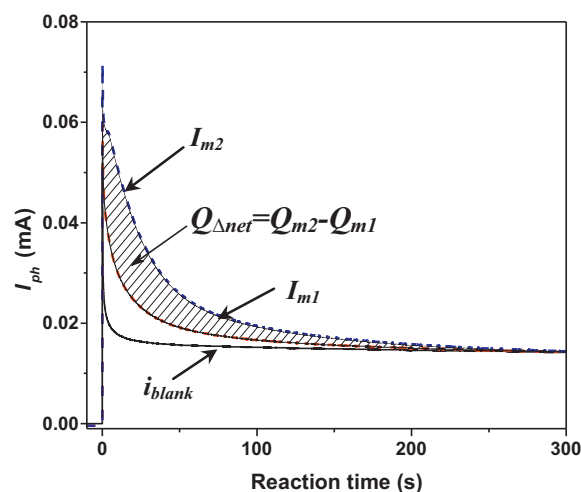


Fig. 1. Schematic illustration of charge quantification using a series of typical photocurrent profiles of the TiO₂ photoanode in the thin-layer photoelectrochemical cell of photocatalytic degradation of organic compounds.

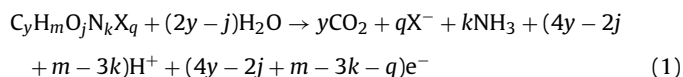
analyses after the system reaching its steady-state. A 2.0 M NaClO₄ solution was used to clean the cell between the two sample injections. PC degradation experiments were conducted under identical conditions as PEC system, except the electrochemical system was disconnected.

2.3. Analysis

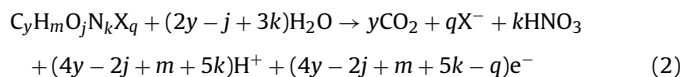
For PEC experiments, the extent of the mineralization was determined by measuring the charge originated from the oxidation of uridine using PeCOD™ technique [17,19]. The measured net charge transfer (Q_{net}) during the degradation was used to calculate the percentage of mineralization in accordance to:

$$\text{Mineralization (\%)} = \frac{Q_{net}}{Q_{th}} \times 100\%$$

where Q_{th} is the theoretically required charge transfer for complete mineralization calculated using Faraday's law, according to Eqs. (1) and (2) [15,17].



$$n_{\text{NH}_3} = 4y - 2j + m - 3k - q \quad (1a)$$



$$n_{\text{NO}_3^-} = 4y - 2j + m + 5k - q \quad (2a)$$

where N and X represents nitrogen and halogen atom, respectively. The numbers of carbon, hydrogen, oxygen, nitrogen and halogen atoms in the organic compound are represented by y , m , j , k and q . n_{NH_3} and $n_{\text{NO}_3^-}$ are the required number of electron transfer for converting N to NH₃/NH₄⁺ and NO₃⁻, respectively.

For PC experiments, the extent of the mineralization was also determined by measuring the charge transfer originated from the PC oxidation of organic pollutants using PeCOD™ technique [17,19]. Fig. 1 shows a set of typical photocurrent–time profiles obtained during exhaustive PC degradation of organic pollutants in

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