Hydrogen production from natural organic matter via cascading oxic-anoxic photocatalytic processes: An energy recovering water purification technology

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A B S T R A C T
Photocatalysis provides a “green” strategy to produce the clean energy of H2. However, the realization of efficient H2 production is usually accomplished by the consumption of electron donors, which are costly energy carriers themselves. Here, we attempted to utilize the naturally abundant humic acid (HA), a representative natural organic matter (NOM), as the source of electron donor in a cascading oxic-anoxic photocatalytic system. Results showed that degradation of HA and remarkable H2 yield (1660.9 mol g−1 h−1 at optimal condition) were obtained successively, whereas the anoxic photocatalytic treatment of pristine HA did not improve H2 yield but substantially eliminated the H2 production and HA degradation efficiency. These phenomena suggested the preoxidation process played a vital role in counteracting the detrimental effect of HA on photocatalytic H2 production. Electrochemical measurement indicated that the preoxidized HA harbored more redox-active moieties than the untreated HA and thus leading to a higher photo-induced charge carrier separation efficiency. A variety of advanced spectroscopic analyses revealed that the photocatalytic oxic pre-treatment resulted in breakdown of chemically inert, electron mediating and chromophoric aromatic macrostructure of HA to form smaller sized oxygenated organic intermediates. These intermediates were more nucleophilic than the pristine HA and acted as sacrificial reagent in the subsequent anoxic process for boosting H2 production. This study showcases an energy recovering water remediation process and paves the way for the design of novel photocatalytic technologies for environmental application.

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1. Introduction

Hydrogen (H2) is being intensively investigated as an environmentally benign energy carrier for industry and daily life (Dunn, 2002). To date, however, H2 is mainly derived from gas steam reforming from fossil fuels and natural gas at high temperature, which in turn consume huge energy and emit large amount of greenhouse gas of CO2, making the effective implementation of H2 economically and environmentally unsustainable (Hosseini and Wahid, 2016). Thus, cost-effective and “green” H2 production methods are being actively sought to mitigate the environmental and energy issues. An appealing method is solar H2 production from water splitting driven by photocatalysis (Ni et al., 2007).

The principles of photocatalytic water splitting are well documented and typically employs semiconductors, e.g., TiO2, as the photocatalyst. Upon irradiation, the photogenerated electrons of the photocatalysts migrate to the conduction band or a cocatalyst, e.g., Pt, which then reduce protons (H+) or water molecules to generate H2 (Ni et al., 2007; Puga, 2016). However, the process employing pure water is usually rather inefficient or is not even...
operative for application (Schneider and Bahnemann, 2013). To improve the H2 yield, numerous researches have been carried out in the presence of an excess of electron donors (e.g., alcohols), namely, the sacrificial reagents. As photogenerated holes are irreversibly scavenged by these sacrificial molecules and electron/hole recombination can be greatly reduced, resulting in higher conversion efficiency. Furthermore, as O2 is not produced, the thermodynamically favored backward reaction of H2 with O2 to form H2O is suppressed (Puga, 2016). Various organic substances such as alcohols (Fu et al., 2011), organic acids (Zielinska et al., 2008), and hydrocarbons (Hashimoto et al., 1984) have been tested as sacrificial donors with different photocatalysts for H2 production in recent years. However, it is worth noting that these commonly used sacrificial reagents are valuable energy carriers themselves and obtained costly, which hinders the application of such photocatalytic system in industry.

To address this challenge, efforts ought to be devoted to replacing the expensive electron donors with naturally abundant materials or waste that must be disposed of (Puga, 2016). Indeed, the effectiveness of photocatalysis has been intensively studied in water remediation and found to be successful in achieving degradation of numerous organic compounds in water (Tanaka et al., 2000; Gaja and Abdullah, 2008; Ahmed et al., 2011). It is therefore very attractive to develop photocatalytic technologies that combine water treatment with H2 production. This approach is economically and environmentally sensible since H2 can be recovered as a fuel to reduce the total costs associated with water treatment. The key for establishing such “single-step” system lies in the synergy between the photocatalysts and the pollutants, in which the electrons reduce the water/protons and the hole or hole- derived ROS oxidize the pollutants selectively, analogous to the situation when using standard sacrificial reagent (Kim et al., 2012). However, it should be noted that the characteristics of organic contaminants are very different from those of standard sacrificial reagents (Schneider and Bahnemann, 2013). For example, typical sacrificial reagents (e.g. alcohol, aldehydes and carbonyl acids) are small molecules with a tendency to donate electron, whereas organic contaminants (e.g. dyes, hormones, and pesticides) are commonly both chemically inert and biologically recalcitrant (Baban et al., 2010; Ghattas et al., 2017). Therefore, organic contaminants are commonly found to be inefficiently oxidized by photocatalysis in the absence of O2 (anoxic condition) (Kim and Choi, 2010). Most reported values for the efficiencies of photocatalytic pollutant degradation and simultaneous H2 production were relatively low, and even this technique was reported to be infeasible when using TiO2 as the photocatalyst (Puga, 2016; Romao et al., 2016). A few literature has reported that the realization of water remediation with simultaneous H2 production can be attained by surface modification of TiO2, hybrid photocatalysts or using novel photocatalysts such as metal-organic frameworks (Kim et al., 2012; Jiang et al., 2018; Kampouri et al., 2018). Despite their dual function in such “single-step” system, it is not known yet the key factors that determine their success in such system and how these photocatalysts distinguish from the other photocatalysts that did not perform well in such system. Moreover, the fabrication of the dual function photocatalysts is generally a challenging process. Therefore, it would be of great merit to develop new strategies to achieve energy recovering water treatment process that is applicable to universal photocatalysts such as TiO2, which can be commercially available in large scale.

Previously, a research conducted by Kim and Choi (2010) has highlighted the possible benefits of combining the photocatalytic anoxic and oxic treatment in sequence, which resembles the biological wastewater treatment process that comprised of cascading anaerobic and aerobic phases. They demonstrated that the photocatalytic energy-recovering water treatment process can be accomplished in two steps: (1) anoxic degradation organic pollution in which H2 is produced and (2) the post-phase of oxic degradation where the organic intermediates were mineralized. As a matter of fact, sequential adaptation of anoxic and oxic treatment is a commonly applied strategy in biological treatment of municipal wastewater treatment plants to achieve a combination of goals including organic degradation, nitrification, denitrification as well as energy production (Baeza et al., 2004; Zhao et al., 2009). Despite the advantage of simultaneous production of H2 and degradation of organic pollutants, this photocatalytic anoxic-oxic approach may not be applicable to photocatalysts that cannot achieve simultaneous pollutant degradation and H2 production in the first phase. Furthermore, the organic intermediates were wasted without profitable output in the post-phase of oxic degradation. A recent study by our research group indicated that the organic intermediates, other than the pristine organic pollutant, could contribute to enhanced H2 production (Chu et al., 2017). Drawing inspiration from these studies, it would be of great interest to switch the sequential treatment process to an alignment of photocatalytic oxic-anoxic treatment, in which the organic intermediates from the oxic treatment can be used as sacrificial reagent in the post-anoxic phase for H2 production.

In addition, organic pollutants are often encountered as multicomponent mixtures (Dao et al., 2010). For example, the natural organic matter (NOM) are complex organic macromolecules that ubiquitously present in various environment including soils, waters, sediments (Matilainen et al., 2011). NOM is objectionable to water supplier and water end users because NOM is resistant to biological oxidation and present a hazard as a precursor of potential harmful disinfection byproduct (DBP), e.g. trihalomethanes, formed by water chlorination (Kitis et al., 2001). In a typical water treatment plant, the removal of NOM is achieved in the coagulation process, where the NOM is transferred from the liquid to the solid phase (as flocs) using coagulants. However, it is often difficult to achieve reliable and effective coagulation, particularly for water conditions that are highly variable (Sharp et al., 2006). Moreover, there is always a significant fraction of NOM recalcitrant to removal by coagulation processes (Fabris et al., 2004). Previous studies have proven that photocatalysis can be used as an effective method to degrade NOM because of its potential to use sunlight to drive the process using a reusable catalyst (Bekbølet, 1996; Valencia et al., 2013). Besides, NOM is naturally abundant and plays a significant role in the global carbon cycle as one of the largest reservoirs of reduced carbon on the earth surface (Kujawinski et al., 2009). For example, the carbon in soil NOM is estimated from $700 \times 10^{15}$ to $3000 \times 10^{15}$ g C, which is in magnitude comparable to the atmospheric carbon (Aiken, 1995). Therefore, NOM is attractive as an easily available electron source for photocatalytic H2 production because of its high carbon content, low cost and large availability. Previously, Klauson et al. (2014) has used humic acid (HA), a representative NOM, as the substrate for photocatalytic H2 production under simulated solar light. However, the HA they used is a pure chemical with a specific characteristic structure, which cannot reflect the complex nature of the multicomponent HA. Despite the wide presence of HA in the environment, no literature has employed naturally-derived and multicomponent HA as the substrate for photocatalytic H2 production.

In this work, we explore an innovative cascading oxic-anoxic photocatalytic system for the oxic degradation of HA, and the successful anoxic H2 production using the intermediates from the post oxic phases. Model photocatalyst, TiO2, was used as the catalyst under UVA-LED irradiation. Results show that the oxic pretreatment could counteract the inhibitory effect of HA on photocatalytic H2 production. The corresponding mechanism was
systematically probed by electrochemical measurements and a variety of advanced spectroscopic analyses. This study may provide useful information to guide the future design and optimization of photocatalytic energy recovering water treatment processes and is intended to encourage more thinking and research on photocatalyticoxic and anoxic treatment technologies.

2. Materials and methods

2.1. Reagents and solution preparation

All solutions were prepared using reagent-grade chemicals and Milli-Q water (18.2 MQ cm). The TiO2 benchmark (Degussa P25, $S_BET = 50 \text{ m}^2/\text{g}$) was used as model photocatalyst. HA (Sigma-Aldrich Co., USA) was used as a model for NOM in all experiments. HA were purified prior to use. In brief, HA were dissolved in ultrapure water at a concentration of 100 mg/L and centrifuged at 15,000g for 15 min to remove any insoluble particles. The total organic carbon (TOC) of the purified HA solution was determined as 15.4 mg/L. The solution was stored in a refrigerator at ~4°C prior to use.

2.2. Photocatalytic experiments

The oxic photocatalytic degradation of HA was carried out in a 350 mL reactor. For each experiment, fifty mL of the purified HA and 50 mg TiO2 P25 (1 g/L) were added into the reactor. The final solution pH was adjusted to circumneutral condition (pH 7.0) using 0.01 M HCl and 0.01 M NaOH to ensure environmental relevance. The light source was provided by a UVA (peak at 365 nm) LED point light source (LAMPLIC, China). The LED point light source was mounted 20 cm above the surface of the reaction mixture and UV light intensity was measured by a UVX digital radiometer (UVP, Upland, California, USA). The light intensity on the surface of the reaction mixture was measured as ~6.04 mW/cm². The fluorescence (UV dose) along with reaction time was also determined and shown in Table S1 (Bolton and Linden, 2003). Prior to irradiation, the reaction mixture was magnetically stirred in the dark for 1h to reach adsorption/desorption equilibrium. The reaction mixture was under continuously stirring to obtain sufficient mixing and dissolved oxygen for each oxic photocatalytic treatment. At different time intervals, aliquots of the reaction mixture were sampled and filtered through a 0.45 µm nitrocellulose membrane to remove the TiO2 nanoparticles for further analysis.

The anoxic photocatalytic H2 production was carried in the same reactor and connected to a Labsolar-III AG closed gas system (Beijing Perfect Light Technology Co., Ltd China). 50 mg of photocatalysts was suspended in 50 mL solution containing the treated or untreated HA as an electron donor. Prior to irradiation, the air in the closed system was evacuated using a vacuum pump until a vacuum degree of ~0.1 MPa was reached to ensure an anoxic condition. The vacuum degree was monitored via a vacuum gauge mounted in the closed system. At different time intervals, a volume of 1.5 mL of gas was sampled and the H2 was measured by gas chromatography (GC 7806, Beijing Shiweiexi analysis instrument co., LTD China) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column, where N2 was used as the carrier gas. Unless otherwise stated, the H2 production experiments were carried using TiO2 loaded with Pt (wt 1%) as cocatalyst (Leung et al., 2010). The TiO2/Pt was prepared according to our previous study (Ye et al., 2016).

For a typical cascading oxic-anoxic photocatalytic treatment process, HA were firstly treated in the oxic phase and then transferred to the successive anoxic treatment. The preoxidized HA samples were filtered through a 0.45 µm nitrocellulose membrane to remove the TiO2 nanoparticles since TiO2/Pt was used as photocatalysts in the anoxic phase.

In addition, the time profiles of H2 production in the presence or absence of preoxidized HA (6h) were measured through repeated cycles of photocatalytic anoxic treatment. The suspension was purged with nitrogen prior to between each cycle to remove accumulated H2.

2.3. Bulk parameters

The concentration of HA were indexed by absorbance at 254 nm (UV254) and TOC (Yi et al., 2019). The UV254 of the collected samples were determined using a UV-VIS spectrophotometer (LabTech Ltd, USA) with a 1 cm pathlength quartz cuvette. Specific UV absorbance at 254 nm (SUVA254) was calculated by dividing the UV254 by the corresponding DOC value of each sample. SUVA254 can be used as a surrogate assessment of organic matter aromaticity in water samples (Weishaar et al., 2003). The TOC were obtained from the photocatalytic experiments were analyzed using a TOC analyzer (TOC-V, Shimadzu, Japan). The formic acid and oxalic acid concentrations were measured using ion Chromatograph (IC, CIC-D100, SHINE IC Solution Experts, China).

2.4. Apparent quantum yield

The apparent quantum yield, i.e. the ratio between the moles of H2 produced and the moles of photons absorbed in the presence of preoxidized HA and model compounds (i.e. glucose, methanol, phenol and EDTA) were evaluated and compared according to the following equation:

\[
\text{Apparent quantum yield} = \frac{N_H_2}{N_p} = \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{the number of incident photons}} \times 100% = \frac{2 \times N_0 \times M_{H_2}}{P_{St} \lambda \times h c}
\]

where $N_0$ is the Avogadro constant, $6.02214076 \times 10^{23} \text{ 1/mol}$; $M_{H_2}$ is the $H_2$ yield; $P$ is the light intensity of the LED light source, 6.04 mW/cm²; $S$ is the active irradiation area, 32.5 cm²; $\lambda$ is the irradiation time, 1 h; $\lambda$ is the wavelength of the LED light, 365 nm; $h$ is the planck constant, $6.62607015 \times 10^{-34}$ J s; $c$ is the speed of light in vacuum, $3 \times 10^8$ m/s.

2.5. Electrochemical measurement

All the photoelectrochemical measurements were performed in a CHI 760E electrochemical workstation equipped with a three-
electrode cell that consists of a Ag/AgCl (saturated KCl) reference electrode, a platinum counter electrode, and the TiO₂ P25 as working electrode. TiO₂ P25 powder (100 mg) was suspended in 1 mL of absolute ethanol and dip-coated onto an area of 1.5 × 2 cm² fluorinated-tin-oxide (FTO) conducting glass as the working electrode. The electrodes were then heated at 60 °C in air for 2 h. The photocurrent and cyclic voltammetry curves were recorded in the 0.1 M Na₂SO₄ solution with the as-prepared HA, preoxidized HA or without any organic substrates (Zhang and Katayama, 2012; Zhang et al., 2014). Cyclic voltammetry measurements were carried out with a scan rate of 10 mV s⁻¹ and the potential of the peaks were calibrated to be against standard hydrogen electrode (SHE) based on an equation of \( \phi \) (vs. SHE) = \( \phi \) (vs. Ag/AgCl) + 0.199 V (Mizuta et al., 2009; Zhang et al., 2014). All test solutions were purged with N₂ for 10 min prior to each set of scans to remove oxygen.

2.6. Spectroscopic characterization of HA

To better understand the observed effects of HA and preoxidized HA on photocatalytic H₂ production, an array of advanced instrumental tools including UV-VIS spectrometer, fluorescence EEM, FTIR and XPS, with an attempt to probe the potential characteristics of the HA and its transformation during the treatment process. The UV-VIS light absorption spectra was determined using a UV-VIS spectrophotometer (LabTech Ltd, USA). Spectral slope ratio (\( S_n \)) was calculated as the slope in 275—295 nm divided by slope in 350—400 nm (Helms et al., 2008).

A fluorescence spectrometer (F-4500, Hitachi, Japan) was used to obtain the three-dimensional excitation-emission-matrix (EEM) spectra of the samples with excitation wavelengths in the range of 200—400 nm in 5 nm intervals and with emission wavelengths in the range of 290—500 nm in 5 nm intervals. The emission and excitation slits were fixed at 10 nm, and the scanning speed was 12000 nm/min. Second-order Raleigh scattering in the EEM measurements was eliminated using a 290 nm emission cutoff filter. According to suggested protocols of the manufacturer, the instrument was corrected for excitation and emission prior to use. The inner filter effect was minimized by diluting the samples to their UV absorbance at 254 nm less than 20 m⁻¹. The contour plots of the EEM dataset were visualized using Matlab 12.0. Parallel factor analysis (PARAFAC) was performed for the obtained EEM dataset according to our previous publication (Huang et al., 2017).

An FTS-4000 Varian Excalibur series FT-IR spectrometer with attenuated total reflection (ATR) (Varian, Palo Alto, CA) was used to collect the infrared spectra. The samples were freeze-dried and then ground, homogenized and pressed with 100 mg of potassium bromide (KBr, IR grade). The band from 4000 to 400 cm⁻¹ were predominantly involved in the degradation of HA. Considering the relatively low reactivity of \( \cdot \)OH derived from it (Long et al., 2017). In short, these results indicated that the aromatic structure can be substantially degraded under anoxic environment was also conducted for comparison (Fig. S2). As shown in Fig. S3, the SUVA₂₅⁴ value of the untreated HA (6.2 L mg⁻¹ m⁻¹) underwent a significant decline to 0.4 L mg⁻¹ m⁻¹, an indication of NOM of low aromaticity (SUVA < 2 mg⁻¹ m⁻¹), after 6 h photocatalytic oxic treatment. After 8 h, the SUVA₂₅⁴ further decreased to 0.1 mg⁻¹ m⁻¹. This value is much lower than the reported SUVA₂₅⁴ values (1.5 and 1.2 mg⁻¹ m⁻¹) of the finished water in two drinking water treatment trains that applied coagulation and filtration to remove NOM (Baghoth et al., 2011). This finding suggested the photocatalytic oxic treatment can significantly reduce the aromatic character of the HA in the treated water. It was found that no obvious decrease in both UV₂₅⁴ and TOC occurred in the deaerated suspension, suggesting that oxygen is required for efficient degradation of HA. This conclusion was further corroborated by the results of scavenger studies (Fig. S4), which indicated that the \( \cdot \)O₂⁻ were predominantly involved in the degradation of HA. Considering the relatively low reactivity of \( \cdot \)O₂⁻, the contributing role of \( \cdot \)O₂⁻ in the degradation of HA could be attributed to the generation of highly oxidative \( \cdot \)OH derived from it (Long et al., 2017). In short, these results indicated that the oxo photocatalytic pretreatment was effective in the decomposition of HA, but not the mineralization of HA. This is of particular importance since the decomposed HA is assumed to serve as electron donors in the subsequent H₂ production.
Next, the cascading photocatalytic H₂ production experiments were conducted in the presence of the various pre-oxidized HA under anoxic environment (Fig. 2). The H₂ production experiments using pure water and untreated HA were also carried out as references. Firstly, the H₂ evolution profiles for all the samples follow a linear trend as a function of irradiation time. Secondly, the photocatalytic production of H₂ in the absence of organic substrates (i.e., in pure water) was observed with a H₂ generation rate of 116.0 μmol g⁻¹ h⁻¹, whereas no H₂ was detected in the presence of untreated HA. This indicated that the untreated HA could not serve as sacrificial reagent for boosting photocatalytic H₂ production, but substantially impeding the generation of H₂. This could be ascribed to the fact that the untreated HA would compete with the photocatalysts for the UVA light (peak at 365 nm) source (Fig. S5), as the untreated HA (t = 0 h) had strong absorbance in the region of 200–400 nm (Fig. S1). As such, the light attenuation by the untreated HA could be a reason for the inhibited H₂ production. Thirdly, in comparison with the control case without any organic substrate, the photocatalytic H₂ production was enhanced to different extent in the presence of preoxidized substrates, and the H₂ generation rates improved with increased preoxidation time and peaked at 1660.9 μmol g⁻¹ h⁻¹ during the initial 6 h. However, a marked decayed of H₂ yield with the preoxidation time prolonged to 8 h (452.8 μmol g⁻¹ h⁻¹). This decrease of the H₂ yield could be ascribed to decrease of preoxidized organic intermediates contents, as reflected by the corresponding decrease in TOC at 8 h (Fig. 1). Hence, the preoxidation time of 6 h is the optimal condition for the subsequent H₂ production, in which the intermediates can be further mineralized as revealed by the TOC evolution under anoxic condition (Fig. S6). This H₂ production profile highlighted the significance of preoxidation process and the preoxidized organic intermediates in enhancing the photocatalytic H₂ production from HA.

To appreciate the significance of the photocatalytic H₂ production from HA in the cascading oxic-anoxic process, photocatalytic H₂ production experiments using other substrates were carried out (Table 1) for comparison. Standard aqueous solutions of methanol, glucose, phenol and EDTA were prepared at TOC concentrations equivalent to that of the preoxidized HA for 6 h (~12 mg/mL). Results show that the H₂ yields and the apparent quantum yields by the preoxidized HA are comparable to those of the typical sacrificial agents (i.e. methanol, glucose and EDTA). When phenol was used as substrate, the H₂ yield and apparent quantum yield was similar to that of the pure water, suggesting that aromatic organic contaminants could not play a role of sacrificial reagent. In addition, the H₂ production under optimal condition was repeated up for 5 cycles as shown in Fig. S7. The H₂ production in the initial four cycles were obviously higher than the control experiment without organic substrates, but the difference decreased with increasing number of cycles. After the 5th cycle, the H₂ production was similar to that of the control, suggesting negligible H₂ was produced owing to the consumption of the intermediates.

### 3.2. Enhanced electron transfer by preoxidized HA

In this study, we demonstrate the degradation of HA and efficient photocatalytic H₂ production on HA can be achieved in cascading two steps: (1) the pre-phase of oxic degradation and partial mineralization of HA; (2) the post-phase of anoxic photocatalytic reaction where H₂ is produced using the organic intermediates. On the contrast, the untreated HA cannot improve H₂ yield but substantially eliminate the photocatalytic H₂ production activity, suggesting the preoxidation process play a vital role in counteracting the detrimental effect of HA on the photocatalytic H₂ production. The underneath mechanism accounting for these observed effects are of great merit for the potential application of photocatalysis in H₂ production. Generally, the photocatalytic H₂ production is related to the electron transfer from the conduction band (CB) of semiconductor photocatalysts to protons or water molecules, which is usually denoted as “water splitting”. Therefore, one possible mechanism for the improved H₂ yield could be ascribed to the effect of the modification on the electron transfer process. It is very plausible that the preoxidized HA played a role of sacrificial electron donors to promote the charge separation. On the contrary, in addition to light attenuation, the untreated HA would likely adsorb onto the TiO₂ surface and react directly with the photon-generated e⁻, thus quenching the reactivity before water could be split (Brame et al., 2015; Zhao et al., 2019).

The abilities of the untreated and preoxidized HA to mediate electron transfer were probed by measuring the photocurrent

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**Table 1**

<table>
<thead>
<tr>
<th>Substrates</th>
<th>H₂ yield (μmol)</th>
<th>Apparent quantum yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>76.02</td>
<td>7.0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>93.71</td>
<td>8.6%</td>
</tr>
<tr>
<td>Phenol</td>
<td>7.265</td>
<td>0.67%</td>
</tr>
<tr>
<td>EDTA</td>
<td>122.81</td>
<td>11.3%</td>
</tr>
<tr>
<td>HA</td>
<td>83.045</td>
<td>7.6%</td>
</tr>
</tbody>
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Fig. 2. (A) Cascading photocatalytic anoxic hydrogen evolution in the presence of the different preoxidized HA and (B) the corresponding H₂ evolution rates.

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metric analysis (Fig. 3B). Pure water produced CVs with no useful scavenger that enhance the reduction of water. This can be ascribed to the negative effect of light-blocking by untreated HA. In the preoxidized HA solution, two peaks were observed with the corrected redox potential of 599 mV and 524 mV vs SHE, respectively. The increased peak number signified the increased types of electron donors in the preoxidized HA samples. Moreover, the lower redox potential implied that the intermediates in the preoxidized HA were more easily oxidized than that of the untreated HA. We therefore can postulate that the redox-active moieties in preoxidized HA as well as the elimination of the light-blocking effect contribute to the improved H₂ production in the successive anoxic phase.

3.3. Spectroscopic analyses

3.3.1. Spectral slope ratio

Ultra violet–visible absorption spectral slope ratios ($S_0$) is an index reversely correlated with average molecular weight and is routinely used as a proxy for NOM samples (Helms et al., 2008). HA is widely accepted as a high molecular weight macromonomer. Though HA do not have one specific characteristic structure, a theoretical structure has been proposed by scientists to comprehend the complex structure of HA as illustrated in Fig. S8 (Hudson et al., 2007). As shown in Fig. S8, under oxic condition, the $S_0$ value of the untreated HA ($t = 0 h$) increased progressively during the initial reaction time and underwent drastic drop from 5 h onward, suggesting the reaction of high molecular weight compounds breaking into lower molecular weight compounds mainly occurred after 5 h, corresponding to a UV fluence of 108.72 mJ/cm². This result is consistent with previous report that photocatalytic oxic treatment was found to preferentially break down molecules with high molecular weights to form lower molecular weights molecules (Valencia et al., 2014; Phong and Hur, 2015). This phenomena also coincides with the photocatalytic H₂ production results in the anoxic phase, in which the preoxidized HA for 6 h yielding the maximum H₂. It is very plausible that the transformation of molecular size play a role in boosting the H₂ yield because smaller size molecules are considered to have more chance to interact with the photocatalysts under soluble, diffusion-limited conditions, and thus leading to higher reactivity (Sun et al., 2013). Although a variety of organic substrates have been tested to replace the standard sacrificial reagent, the effect of their molecular sizes have seldom been considered. Our results suggest that one advantage of pre-oxidation is to break down the macro structure of the pollutant to form smaller sized molecules that can be easily used in the subsequent H₂ production phase.

3.3.2. Fluorescence EEM

Fluorescence EEM is a well-established tool to get insights into the nature of the HA. Fig. 4 illustrates the changes in EEM spectra of HA during the oxic and anoxic photocatalytic treatment. For the untreated HA ($t = 0 h$), a prominent peak with Ex/Em centered at 250–270/430–490 nm and a shoulder peak at 320–350/430–480 nm were identified, which was corresponded to the Peak A and Peak C, respectively, in the literature (Hudson et al., 2007). Both the peak intensities decreased along with the oxic photocatalytic treatment, indicating the decomposition of the structure of fluorophore in HA. In the successive anoxic treatment (using preoxidized HA for 6h as sacrificial reagent), the EEM fingerprints continued to disappear, suggesting the remaining fluorophores were degraded in the anoxic phase. The PARAFAC modeling results in Fig. S10, Supporting Information, resolve two independent components peaked at Ex/Em = 280/460 (C1) and 230/320/435 (C2) nm, respectively. C1 and C2 could be ascribed to the phenolic-like and carboxylic-like fluorophores. Under oxic photocatalytic treatment, the maximum fluorescence intensity ($F_{max}$) of C1

Fig. 3. Comparison of the (A) transient photocurrent response curves and (B) cyclic voltammograms in the presence of the untreated HA, preoxidized HA (6h) and pure water as background; the inset shows the peaks in the region from 0.2 to 0.6 V for clarity.
increased in the initial 1 h and then decreased, whereas the $F_{\text{max}}$ of C2 decreased drastically in the initial 1 h and then fluctuated (Fig. S11). The increase of C1 in the initial 1 h can be attributed to the oxidation of the macro aromatic structure of HA to form phenolic-like intermediates. Nevertheless, both the $F_{\text{max}}$ of C1 and C2 drop close to zero after 6 h. This result together with the H2 production profile (Fig. 2) suggested the fluorophore (aromatic structure) are not favorable for H2 production. Indeed, HA are well documented to be excellent electron acceptors (Keller et al., 2009), the decomposition of the aromatic structure in HA would likely improve the transfer of photo-generated electron to proton instead of HA and contributed to the improved H2 yield.

3.3.3. FTIR and XPS

To examine the changes in the functional aspects of HA during the oxic-anoxic photocatalytic treatment, the structural and functional aspects of HA were analyzed by FTIR and XPS. Fig. 5 presents the FTIR spectra of HA samples. The vibrations were mostly in the regions of 1750-950 cm$^{-1}$ and assignment of major peaks are listed in Table S2. We found that photocatalytic oxic pretreatment resulted in considerably decreased in the major peaks in 1570, 1380 and 1085 cm$^{-1}$, which were attributed to aromatic C=C, C=O in phenolic OH and aromatic C=C=C deformation (Hay and Myneni, 2007; Yang et al., 2009; Chen et al., 2014b; Wu et al., 2017). Meanwhile, the peak intensities in 1700, 1647, 1155 and 1070 cm$^{-1}$, corresponding to C=O in protonated carboxylic acid (COOH), C=O stretching in carboxylate (COO$^{-}$), C=O (alcohols, carboxylic acids, esters, or ethers) and aliphatic OH, respectively, were found to increase. This is in line with previous reports that photocatalytic oxidation resulted in the oxygenation of the humic substances (Birben et al., 2017; Wu et al., 2017). After the cascading photocatalytic anoxic treatment, the peak intensities in 1700, 1647 and 1115 cm$^{-1}$ decreased, indicating that the carboxyl and hydroxyl intermediates in the preoxidized HA were consumed in the anoxic photocatalytic H2 production process. Thus, it can be speculated that hydroxyl and carboxylic groups were vital in facilitating the cascading photocatalytic H2 production process.

Fig. S12 of the Supporting Information presents the XPS spectra recorded in the energy range 0–1100 eV for the HA samples. The core-level peaks of the XPS spectra were C 1s (284.8 eV), O 1s (532.0 eV), and N 1s (400.0 eV). High resolution scans of C 1s were performed to obtain the functional groups associated with these core-level peaks (Fig. 6). The C 1s peak can be decomposed into four individual peaks: (1) the peak at 284.8 eV is an indicator of the presence of C=C=C=H and aromatic C; (2) the peak at 286.2 eV is attributed to C=O, from ether, or alcohol; (3) the peak at 287.8 eV is attributed to C=O or O=C=O, as can be found in carboxylate, amide, carbonyl, and acetal; and (4) the peak at 289.0 eV results from the O=C=OH or O=C-OR, such as in ester or carboxyl groups. The individually resolved peaks were numerically integrated to calculate concentration ratios and summarized in Table S3. Over an oxic photocatalytic degradation period of 6 h, the C 1s peaks at 284.8 eV experienced reductions of 12%. However, the area of the C

![Fig. 4. Variation of the fluorescence EEM spectra of the HA under (A) photocatalytic oxic treatment and (B) anoxic treatment (using the preoxidized HA for 6 h as sacrificing reagent) in the cascading treatment process.](image)

![Fig. 5. Comparison of the FTIR spectra of the untreated HA, preoxidized HA for 6 h and photocatalytic anoxic treated HA for 1 h (using the preoxidized HA for 6 h as sacrificing reagent) in the cascading treatment process.](image)
1s peak at 286.2, 287.8 and 289.0, eV increased by 7%, 3% and 2%, respectively. The C 1s data indicated that oxygen was enriched significantly in the functional groups of the HA during the pre-oxidation period, which might be due to the aerobic transformation of some functional groups; for example, aromatic C was transformed to C=O or C–O. After 1 h cascading anoxic photocatalytic treatment, oxygenated C 1s peaks at 286.2 and 287.8 eV decreased in peak area (approximately 7% and 5%, respectively), and peak at the 289.0 eV remained unchanged. Additionally, the concentrations of two typical oxygenated organics (i.e. formic acid and oxalic acid) were measured during the process (Fig. 7). Results indicated that the preoxidation process gave rise to both formic acid and oxalic acid concentration, while these oxygenated compounds were significantly reduced after photocatalytic anoxic treatment. These results were consistent with the FTIR data and suggested that the photocatalytic oxic pre-treatment lead to the oxidation of aromatic fractions in the HA to form carboxyl and hydroxyl containing intermediates; and these oxygen-rich intermediates possibly serve as sacrificial reagent in the subsequent anoxic photocatalytic process, which promotes interfacial electron transfer and thus contributing to the enhanced H2 production.

Indeed, the oxygenated organic compounds with carboxyl or hydroxyl moieties, such as methanol and carboxylic acids were widely used as sacrificial reagents in the photocatalytic systems, due to their high propensity to donate electron, while the alkyl or aromatic structures are weakly electron donating moieties due to their relatively low electrostatic potential (Remya and Suresh, 2016). In addition, the aromatic structure in HA had been reported to have lower affinity to TiO2 nanoparticles than carboxyl and hydroxyl groups as revealed by FTIR analysis (Chen et al., 2014a; Wu et al., 2017). More specifically, the high affinity of the TiO2 surface for carboxylic acids is well studied and can be attributed to their bidentate binding (Balajka et al., 2018). An illustration of typical carboxylic acids (formic acid and oxalic acid) can be found in Fig. S13 in the Supporting Information (Li et al., 2003). The direct adsorption of sacrificial reagents on the TiO2 surfaces is undoubtedly important for H2 production by photocatalysis because the scavenging of photo-generated hole need direct interaction between the organic substrates and photocatalyst. The formation of the oxygenated compounds such as formic acid and oxalic acid in the photocatalytic oxic process may enhance interaction between organic substrates and TiO2 surface and thus enhanced the subsequent their oxidation and corresponding H2 production under anoxic condition. Although HA contains oxygenated side chains, the macro structure of aromatic backbone in HA would decrease the nucleophiles of the electron donating moieties because of the large size and the corresponding steric hindrance effect (Hoffman, 2004), which renders the approach of electron donating moieties to the photogenerated hole difficult. Moreover, HA are redox-active organic compounds that can be either oxidized or reduced by photocatalysis (Minero et al., 1999). It is also possible that the adsorbed HA on the TiO2 surface can block active sites for H2 evolution by scavenging the photo-generated electrons. As such, it is
very unlikely that the HA can be served as an efficient sacrificial reagent for photocatalytic H₂ production. Our results herein showcase the advantages of preoxidation phase, in which the HA were transformed to nucleophilic (electron donating) oxygenated intermediates.

Notably, there is also possibility that photocatalytic H₂ production was proceeded by the partial conversion of the preoxidized organic substrates to produce molecular H₂ as a result of the dehydrogenation of organic substrates. In this case, the generated H₂ gas was originated from the hydrogen atoms on the organic substrates other than the water. Generally, the discrimination between the two reaction routes can be achieved through isotopic labelling (deuteration) of either the organic substrates or water. For instance, Kandiel et al. (2014) employed deuterated water or deuterated methanol to study the photocatalytic H₂ production on platinitized TiO₂ photocatalysts. They found that the H₂ was mainly produced by the reduction of protons originating from water and the methanol only acted as a sacrificial reagent in such system. However, due to the lack of deuterated HA samples and the preoxidation process can generate water from the HA, which may interfere the isotopic study in the anoxic phase, the discrimination between the two routes is challenging in this study. Nevertheless, whatever the H₂ production routes was proceeded, the enhanced molecular H₂ can be regarded as the reforming of the preoxidized organic substrates and the overall equation for the two pathways were identical, which can be depicted as follow:

\[
\text{Preoxidized C}_x\text{H}_y\text{O}_z + (2x - z)\text{H}_2\text{O} \rightarrow x\text{CO}_2 + (2x + 0.5y - z)\text{H}_2 \quad (2)
\]

Collectively, the mechanisms by which the preoxidation counteracts the inhibitory effect of HA on photocatalytic H₂ production can be rationalized by formation of smaller sized oxygenated organic intermediates, which served as the sacrificial reagent to promote H₂ production.

3.4. Technological implication

The undesired role of sacrificial reagent has limited the application of photocatalysis for H₂ production. Considerable efforts have also been devoted to replacing the valued sacrificial reagent with the organic pollutant in water to accomplish sustainable development. In this study, we envision a sustainable water remediation strategy, based on a cascading oxic and anoxic photocatalytic treatment of HA. Specifically, the photocatalytic oxic treatment (preoxidation) counteract the detrimental effect of HA by transforming the inert macrostructure of HA into electron donating intermediates, whereas the TOC content was slightly decreased. The post-phase of anoxic photocatalytic reaction generated H₂ effectively using the preoxidized intermediates. Despite its notorious role in water industry, HA is naturally obtained and abundant, and thus can be regarded as a renewable resource for H₂ production. This means that the utilization of HA as electron donor feedstock for photocatalytic H₂ production is a carbon neutral process, in which the carbon dioxide produced from the oxidation of HA can be again recycled back to nature via plant photosynthesis within the time shorter than our lifetime (Shimura and Yoshida, 2011).

While we acknowledge that the application of this photocatalytic oxic-anoxic technology is still far from real practical application owing to the involvement of energy-intensive UV facilities and the difficulty to capturing H₂ at this relatively low pressure. However, this study showcased a perspective photocatalytic technology to achieve water treatment with H₂ as a byproduct, which can be capture through novel membrane technology (Perry et al., 2006; Ockwig and Nenoff, 2007), and dictate a new direction of future efforts to realize a sustainable photocatalytic water treatment technology. Yet TiO₂ is definitely not the best active photocatalyst to harvest the solar energy, rational design and application of proper photocatalysts, especially visible-light-driven photocatalysts, will be of great value to assess their applicability for such system in the future. Furthermore, 6 h of preoxidation treatment is also unrealistic in practical application. However, it should be noted that the light source used in this study is the long wavelength UV (UVA, 315–400 nm). While shorter wavelength (UVC, 100–280 nm) is preferred and has been widely used in practical water treatment train (Phong and Hur, 2016). Photocatalytic water treatment under UVC irradiation has been reported to be shown superior oxidation ability than under UVA irradiation (Pigeot-Remy et al., 2012). Meanwhile, it has been reported that UVC irradiation alone can greatly oxidize the NOM as a result of photolysis (Parkinson et al., 2003). Therefore, the time for preoxidation step is expected to be greatly reduced in practical application given that UVC facility is easily available in the water treatment plant and used as the light source.

On the other hand, the findings are likely to be dependent on type of organics in various water environment. For example, dissolved effluent organic matter (DEOM) and textile dye waste are two common organic waste produced by human. The DEOM typically comprises a heterogeneous mixture of refractory organic compounds such as soluble microbial products (SMP), which are biologically derived and consists of mainly high molecular weight organics (Michael-Kordatou et al., 2015). The textile dye waste are usually colored aromatic organics that have low biodegradability (Yu and Viraraghavan, 2001). Provided that the low molecular weight oxygenated organics are better electron donor as demonstrated in this study, it is very unlikely that these organic wastes can be directly used as effective sacrificial reagent for photocatalytic H₂ production. Fortunately, photocatalysis is well-documented to be effective in degrading organics such as dyes (Houas et al., 2001) and SMP (Yu and Huang, 2020) to low molecular weight oxygenated intermediates in the presence of oxygen. Therefore, the photocatalytic oxic-anoxic treatment processes are also expected to shed light on the photocatalytic energy-recovering treatment of wastewater such as textile wastewater and sewage wastewater effluent.

4. Conclusions

This study envisions a sustainable water remediation strategy, based on a cascading oxic and anoxic photocatalytic treatment of the naturally abundant HA, a representative NOM. The major conclusions can be drawn as follows:

- The untreated HA cannot serve as effective sacrificial reagent for photocatalytic H₂ production, but substantially inhibited H₂ production. The inhibitory effect can be ascribed to light attenuation and electron-accepting by HA.
- Photocatalytic oxic pre-treatment counteract the detrimental effect of HA due to the formation of low molecular weight oxygenated organic intermediates. These intermediates acts as effective sacrificial reagent in the subsequent anoxic process.
- The suitable alignment of photocatalytic oxic and anoxic processes, which resemble the biological waste water treatment process, pave a new way for energy recovering water purification process and have significant implication for future design of photocatalytic technologies.

Declaration of competing interest

The authors declare that they have no known competing
financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References