Dye-sensitized photoelectrochemical cell on plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers for treatment of urban wastewater effluents, with simultaneous production of hydrogen and electricity

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Citation: WANG, D. ...et al., 2015. Dye-sensitized photoelectrochemical cell on plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers for treatment of urban wastewater effluents, with simultaneous production of hydrogen and electricity. Applied Catalysis B-Environmental, 168 pp. 25-32.

Additional Information:

- This paper was accepted for publication in the journal Applied Catalysis B-Environmental and the definitive published version is available at: http://dx.doi.org/10.1016/j.apcatb.2014.11.012

Metadata Record: https://dspace.lboro.ac.uk/2134/19052

Version: Accepted for publication

Publisher: © Elsevier

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Article Type: Research Paper

Keywords: Wastewater treatment; Dye-sensitized photoelectrochemical cell; Hydrogen production; Electricity generation; Ag/AgCl @ chiral TiO2 nanofibers

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Dye-sensitized photoelectrochemical cell on plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers for treatment of urban wastewater effluents, with simultaneous production of hydrogen and electricity

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Abstract

The feasibility of simultaneous production of hydrogen and electricity with simultaneous contaminants removal from “actual” urban wastewater within a dye-sensitized photoelectrochemical cell (DSPC) is demonstrated for the first time. The photoanode in the DSPC was a novel nanostructured plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers (Ag and AgCl nanoparticles supported on chiral TiO$_2$ nanofibers). The electrolyte in the DSPC was actual wastewater to which an estrogen (17-β-ethynylestradiol, EE2) and a heavy metal (Cu$^{2+}$) were added. The contaminants in the wastewater rather than I/I$_3^-$ (usual electrolyte in conventional DSPCs) acted as electrons bridges for the stabilization of charges in this DSPC. Almost total removal of total organic carbon (TOC), Cu$^{2+}$, EE2, and 70% removal of total nitrogen (TN) were achieved under visible-light irradiation. A relatively high solar energy conversion efficiency (PCE 3.09%) was recorded and approximately 98% of the electricity was converted to H$_2$ after the consumption of dissolved oxygen (DO), Cu$^{2+}$ and TN. This performance was attributed to the “symbiotic” relationship between the TiO$_2$ chiral nanofibers and the plasmonic effect of Ag nanoparticles at the photoanode although Ag acting as a recombination site may hinder the generation of electricity. The dye N719 in this study exhibited a temporary sensitization effect, and a more efficient sensitizer is expected to be studied in the future. This study opens up new opportunities for producing renewable energy from wastewater treatment processes including organic and inorganic matter as viable resources.
Keywords:

Wastewater treatment; Dye-sensitized photoelectrochemical cell; Hydrogen production; Electricity generation; Ag/AgCl @ chiral TiO$_2$ nanofibers

1. Introduction

Energy crisis and increasing environmental pollution are two of the greatest threats to human population sustainability at a global scale. Within this wide contest, wastewater previously considered as a waste is increasingly being used as a valuable resource for producing fresh water, energy and fertilizing nutrients (N and P). For instance, the wastewater's organic content can be converted into methane gas through the anaerobic process [1], and microbial fuel cell (MFC) [2,3] may also be a viable route for the production of energy from wastewater treatment. Photocatalytic oxidation using titanium dioxide (TiO$_2$) is an effective method for the removal of chemically stable contaminants, it requires no chemicals input or output and TiO$_2$ is inexpensive and non-toxic [4-8]. The photocatalytic oxidation of contaminants is initiated by the excitation of TiO$_2$, which results in the promotion of an electron (e-) to the conduction band (CB) and creation of a hole (h+) in the valence band (VB) of TiO$_2$ [9]. The photogenerated electrons and holes produce highly reactive oxygen species (ROS) (i.e. H$_2$O$_2$, HO$^-$, O$_{2^-}$) which can attack and oxidize organic contaminants, ultimately leading to complete mineralization. The utilization of freely available solar energy as the only energy input makes photocatalysis a sustainable and green process. However, one of the most important
advancement in wastewater treatment should be the development of a new process that can simultaneously capture the chemical energy of the oxidized contaminants while meeting the effluent quality standards [1]. Although the appeal of the direct conversion of solar into chemical energy during a wastewater treatment process has been recognized for a long time, effective efforts are still rare. Recently, a series of studies have succeeded in using some organic fractions in wastewater (i.e. phenolic compounds and dyes) to act as electron donors for producing H$_2$ [11, 12] and for electricity generation [13], and our group has reported the feasibility of hydrogen generation during the removal of emerging contaminants [14, 15]. Very few studies have focused on the harvesting of energy during the removal of both organic and inorganic compounds (e.g. nutrients) in contaminated water and wastewater, making this the main scientific and technological challenge for the water industry. In this study, inspired by the PhotoFuelCell system proposed by Lianos and coworkers [16-19], we demonstrate that dye-sensitized photoelectrochemical cells (DSPCs) may be valuable to address this technological issue.

The concept of DSPCs was similar with that of dye-sensitized solar cells (DSSCs). In a DSSC, the sensitizer, which is usually a dye, absorbs the incident photons resulting in the excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye. The excited electrons are then injected to the conduction band (CB) of the photoanode material (usually TiO$_2$), they further transfer to the photoanode fluorine-doped tin oxide (FTO) supporting the TiO$_2$ and through the external load, travel to the cathode FTO and to the cathode material
(usually a Pt layer). They then transfer to the HOMO of the redox couples (usually I/I₃), and finally back to the HOMO of the dye [20, 21] to close the cycle. In this process, the redox couples play a very important role as electrons bridges for the stabilization of charges in the DSSCs. One major innovating aspect of the present study is the replacement of the redox couples (such as I/I₃) in DSSCs with organic and inorganic compounds naturally occurring in urban wastewater, which collectively can act as an effective electrolyte and also reduced the dye in excited state to stable state. Although dyes have been reported to be unstable in water, they may have a temporary sensitization effect. Under an ideal situation, organic contaminants may be oxidized by an excited dye in the photoanode, while nitrate and heavy metal could be reduced in the cathode (Fig. 1) including the reduction of protons into H₂. The DSPC with Ag/AgCl @ chiral TiO₂ nanofibers as photoanode material, a platinized FTO sheet as a counter electrode and actual urban wastewater as electrolyte was investigated for the first time for the simultaneous generation of electricity, hydrogen gas and for simultaneous removal of contaminants from wastewater, including 17-β-ethynylestradiol (EE2) as a representative of chemically stable and emerging contaminants which was added to the wastewater. The performance and the underlying mechanisms of this highly innovating concept for environmental remediation with simultaneous generation of renewable energy are presented in this study.
2. Materials and Methods

2.1 Synthesis of Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode

Chiral TiO$_2$ nanofibers were synthesized with N-(1-oxooctadecyl)-D-glutamic acid (C$_{18}$-D-Glu) as template and details can be found in our previous study [22]. In a typical synthesis, C$_{18}$-D-Glu (0.06 g, 0.16 mmol) was dissolved in a mixture of methanol (27.2 g) and deionized water (160 ml) while stirring at room temperature. After the mixture was stirred for 10 min, TDA (0.58 g, 75% in isopropanol, purchased from TCI) was added to the mixture with stirring at 55°C. The mixture was allowed to react at 55 °C with stirring for 2 h. The products were collected by centrifugal separation and dried by freeze drying at -60 °C, which resulted in a pale yellow powder. All organics in this product were removed by calcination at 550 °C, and crystalline anatase was obtained.

Then, the as-prepared pure chiral TiO$_2$ nanofibers were used to fabricate Ag/AgCl @ chiral TiO$_2$ nanofibers. In a typical synthesis of Ag/AgCl @ chiral TiO$_2$ nanofibers, pure chiral TiO$_2$ nanofibers (0.2 g) and cetyltrimethylammonium chloride (0.3 g, purchased from TCI) were added into deionized water (100 mL) while stirring at room temperature. After the mixture was stirred for 60 min, AgNO$_3$ (2.0 mL, 0.1 M) was quickly added into the mixture. The resulting solution was stirred at room temperature for further 60 min and irradiated with an 8W UVC light for 40 min. The suspension was collected by centrifugal separation and then dried at 80 °C for 8 h, which resulted in a brown powder. Finally, the powder was calcined at 300 °C in air and Ag/AgCl @ chiral TiO$_2$ nanofibers were obtained. Chiral TiO$_2$ nanofibers were also physically broken.
with the application of pressure at 10 MPa using FTIR tablet press (to avoid changes of the TiO$_2$ morphological structures) prior to the deposition of Ag/AgCl, to prepare Ag/AgCl @ broken chiral TiO$_2$ nanofibers. The synthesis of Ag/AgCl @ broken chiral TiO$_2$ nanofibers was carried out under the same conditions used to prepare the Ag/AgCl @ chiral TiO$_2$ nanofibers, to ensure that an equal amount of Ag/AgCl was deposited on the same amount of chiral TiO$_2$ nanofibers and broken chiral nanofibers.

2.2. Assembly of DSPCs

The Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode was prepared by adding 6 g of PVA (MW 22000, purchased from TCI) into 14 mL of boiled distilled water with powerful stirring, producing a highly viscous liquid that was further diluted by adding to a solvent made of 18 mL distilled water and 25 mL ethanol at 70 °C. Then, 1.62 g of the as-prepared Ag/AgCl @ chiral TiO$_2$ nanofibers were added into the PVA/water/ethanol solution to produce a suspension which was then left to cooled to room temperature. The photoanode films were produced on FTO glass (2.3 mm thickness, 25 cm$^2$ area, 8 Ω/sq, Dyesol Glass, previously cleaned with 2-propanol in an ultrasonic bath for 30 min, and then thoroughly rinsed with distilled water, followed by drying on nitrogen) by coating a paste of the suspension using the doctor-blade technique [23]. After coating the films were kept in a clean box for 15 min to relax surface irregularities and the residual mechanical stress of the coating. Finally, the photoanode was gradually heated at 80 °C for 15 min and then at 500 °C for 30 min. The thickness of the film (11 μm) was increased by repeating this doctor-blade technique [24]. For the preparation of the counter electrode, a drop of 5 mM H$_2$PtCl$_6$·H$_2$O in 2-propanol was placed on the
FTO glass substrate (25 cm$^2$ area), following by drying and annealing at 450 °C for 30 min.

The photoanode was impregnated with the dye by immersion into a 1:1 (v/v) mixture of acetonitrile (CR, Sigma-Aldrich) and tert-butanol (CR, Sigma-Aldrich) containing a 0.5 mM N719 (Dyesol) dye solution for 6 h. Then, the dye-loaded photoanode was washed with acetonitrile and dried with nitrogen.

The DSPCs were assembled into a sandwich design using the dye loaded photoanode and the cathode. The distance between the two electrodes was 5 mm. The gap between the electrodes was filled with actual wastewater collected from the effluent of a municipal wastewater treatment plant in Suzhou (China) with further addition (0.56 mg/L) of 17-β-ethynylestradiol (EE2) (HPLC grade, Merck) and CuSO$_4$ (1.03 mg/L).

The chemical properties of the wastewater effluent are presented in Table S1 (Supplementary Material). The pH of the wastewater in the DSPCs was adjusted using 1 mol/L H$_2$SO$_4$.

2.3. Instruments and experimental conditions

Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7041F at an accelerating voltage of 1 kV. Large scope EDX analysis was conducted on an energy dispersive X-ray spectrometer (ZAF Quantification) attached to the SEM of JEOL JSM-7041F. Transmission electron microscopy (TEM) was performed on a JEOL 2011 operation at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu $K\alpha$ radiation (40 kV, 20 mA). X-ray photoelectron spectroscopy (XPS) results were obtained with PHI
5000C ESCA with Mg Ka source operating at 14 kV and 25 mA. UV-vis diffuse reflectance spectroscopy was performed in triplicate on similar samples to ensure reproducibility, on a SHIMADZU UV-2450 with a collection speed of 40 nm min\(^{-1}\) BaSO\(_4\) as the reference. All samples were obtained by scratching films off the FTO substrates and degassing at 200 °C overnight.

Prior to irradiation, twelve fabricated DSPC cells (the volume of each cell was 12.5 mL) were vertically fixed into an oscillation box, and were all shaken in the dark, for 40 min to establish adsorption-desorption equilibrium of the solution species with the electrodes. Then water samples for analysis were taken when all 12 cells were irradiated for two hours using an AM 1.5 solar simulator (Oriel) equipped with a 150 W xenon light and AM 1.5G type filter (Newport, 81094). It should be noted that for analyses were collected at 10-min interval sequentially from ordered DSPCs (e.g. sample #1 was collected from cell #1 at t = 0, sample #2 was collected from cell #2 at t = 10 min, etc.) since the liquid volume in each cell was small and repeated sampling only from one cell would interfere with the cell performance. The current-voltage (J-V) characteristics of the 12 cells were measured as described elsewhere [24]. The amount of hydrogen, the concentrations of EE2, TOC, TN and DO were measured as shown our previous studies [4, 14, 25]. Briefly, the concentration of EE2 was detected by High Performance Liquid Chromatography (HPLC, Agilent 1100). TOC was measured by means of a Shimadzu TOC-V\(_{VPN}\) with an ANSI-V auto sampler. TN was measured using multi N/C 2100 TOC analyzer (Analytikjena, Germany). DO was monitored with electrode for DO sensor (UC-12-SOL, Central Kagaku Co.).
produced was collected by water displacement method using sulfuric acid (2%) and NaCl (10%) containing solution and then measured using a gas chromatograph (HP Agilent, 6890) equipped with a thermal conductivity detector and a molecular sieve 5A column.

3. Results and Discussion

3.1. Characterization of Ag/AgCl @ chiral TiO$_2$ nanofibers

SEM pictures of the Ag/AgCl @ chiral TiO$_2$ nanofibers (Fig. 2a) revealed that the left-handed, double-helical morphology was preserved after the deposition of the Ag and AgCl nanoparticles. The average length of undamaged TiO$_2$ nanofibers was ~ 500 nm and diameter was ~ 20 nm. TEM analyses (Fig. 2b-c) revealed that Ag/AgCl nanoparticles with the average diameters of 5-8 nm were deposited on the surface of the chiral TiO$_2$ nanofibers, preferentially at the outer edges of the TiO$_2$ crystals of the helical structure, following the conceptual structure shown in Fig. 2d.

The elemental and chemical compositions of the samples were further determined by XPS. The results (Fig. S1a, Supplementary Material) suggest that Ag/AgCl @ chiral TiO$_2$ nanofibers contain Ti, O, C, Ag and Cl elements. The C1s was attributed to the adventitious hydrocarbon released from the XPS instrument [23]. In Fig. S1b (Supplementary Material), the Ag 3d spectra consists of two individual peaks approximately at 373 and 367 eV, which are due to Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ binding energy, respectively. The existence of Ag$^0$ and Ag$^{+1}$ could be verified by further peaks divisions [24]. Consequently, the XPS analyses suggested that the nanoparticles
deposited on chiral TiO$_2$ nanofibers were made of Ag/AgCl composites. The elemental composition determined by EDX (Fig. S2, Supplementary Material), resulted in a Ag content of 5.49 mol % and a Cl content of 2.86 mol %, which indicated that the Ag/AgCl was virtually at a 1:1 molar ratio. XRD results also suggested the co-existence of Ag and AgCl (Fig. S3 and detailed descriptions in Supplementary Material). Further details on material characterization have been reported [22]. Moreover, the chiral nanostructure was preserved after the doctor-blade process although some aggregation of the nanofibers was observed (Fig. 3).

3.2. Contaminants removal in the DSPC

EE2 representing for chemically stable organic compounds Cu$^{2+}$ representing for heavy metal ions were spiked into the wastewater at specific concentrations to investigate the removal of contaminants (TOC, TN, EE2 and Cu$^{2+}$) in the cell were spiked into the wastewater at specific concentrations to investigate the removal of contaminants (TOC, TN, EE2) in the cell (Fig. 4). TOC, Cu$^{2+}$ and EE2 were totally removed after 80 min, while only approximately 70% of TN was removed within 120 min. Meanwhile, a decrease of DO over time was observed, indicating the mineralization of TOC and EE2 is aerobic [15]. The fast photodegradation of the TOC including EE2 should be attributed to the combined effect of (i) the strong photocatalytic activity of irradiated Ag/AgCl @ chiral TiO$_2$ nanofibers and of (ii) the oxidization ability of sensitized dyes. Regarding the first effect, Ag/AgCl @ chiral TiO$_2$ nanofibers under visible-light irradiation produces photogenerated electron-hole pairs in the Ag nanoparticles due to surface plasmon resonance (SPR) [26]. In this
process, SPR generates the electron-hole pairs in the semiconductor (AgCl and TiO$_2$) by the dipole-dipole interaction between the donor (Ag) and the acceptors (AgCl and TiO$_2$). The photocatalytic activity of Ag/AgCl @ chiral TiO$_2$ nanofibers should mainly be attributed to two simultaneous processes. The strong electronic coupling between Ag and AgCl conduction bands which injects photoinduced electrons from the Ag nanoparticles, quickly and efficiently, into the AgCl [27] and into the TiO$_2$ helical structure, probably yielding superoxide radicals and finally HO$\cdot$ radicals from the reductive pathway, as reported with other dyes [28]. However, this effect seems negligible for the removal of the contaminants since the direct charge transfer from noble nanoparticles or the internal photoemission from TiO$_2$ and AgCl [29] only play a supporting role in the photoelectrical performance. This was verified of the J-V characteristics of the solar cells not sensitized without dye N719 (see Fig S5).

Regarding the effect of the sensitized dye on the removal of TOC and EE2, the redox potential of N719/sensitized N719 is $\sim 1.1$ V (vs. normal hydrogen electrode (NHE)) [21] and sensitized N719/oxidized N719 is $\sim -0.6$ V (vs. NHE) [30] which is sufficient to oxidize most organic compounds in wastewater, since their redox potentials were mostly less than 0.6 V vs. NHE [31]. As a result, the reduction of the sensitized dye to its ground state maintained the cell cycle until all organic contaminants were removed from the wastewater. Since the synthesized wastewater was acid, the decrease in the TN should be attributed to the reduction of NO$_3^-$ of the wastewater by the electrons transferred to the photocathode:

$$\text{NO}_3^- + 2H^+ + e^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad E^0 = 0.7989\text{V}$$

(1)
\[ \text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O} \quad E^0 = 0.9637\text{V} \quad (2) \]

This significant mass deficit in the TN balance also confirms some gaseous products such as NO and N\textsubscript{2}O are generated as a result of NO\textsubscript{3}\textsuperscript{-} reduction. The 30\% of TN survived from the photoelectrical degradation should be NH\textsubscript{3} as they cannot be reduced in acid or neutral conditions [32].

3.3. Photoelectrical performance and hydrogen generation of the DSPC

SPR is characterized by a build-up of intense, spatially non-homogeneous oscillating electric fields in the neighbourhood of the nanostructure [22]. The SPR effect at the photoanode improves the efficiency of the DSPCs by (1) increased light absorption due to surface plasmons and light-trapping effects, (2) improved charge separation as a result of the localized electro-magnetic field, (3) the promotion of electron transfer to adsorbed species, and (4) the electron storage effect that can shifts the Fermi level to more negative potentials [33-36]. Although the direct charge transfer from Ag nanoparticles to the semiconductor may also prove useful for the electricity generation as mentioned above, the main mechanism of photo-excitation of the photoanode with visible light implies the sensitization of the N719 dye, and the transfer of excited electrons to the Ag/AgCl @ chiral TiO\textsubscript{2} nanofibers, the external load, the counter cathode and lastly the simultaneous reductions of NO\textsubscript{3}\textsuperscript{-}, H\textsuperscript{+} and Cu\textsuperscript{2+}. The presence of metallic Cu on the surface of the counter electrode after the process was further substantiated by two XPS peaks at 932.6 eV and 952.5 eV (Fig. S4, Supplementary Material). In parallel to the above mechanism, the sensitized N719 dye is reduced back to its ground state by the adsorbed organic matter and nitrogen,
which were present in the wastewater, therefore, sacrificial organic and inorganic matter are essential to sustain the mechanism of the DSPCs. This mechanism is further exemplified by the current-voltage (J-V) and current-power densities (J-P) plots, which were recorded to investigate the electrical performance of the cell (Fig. 5). The short-circuit current densities ($J_{sc}$), open-circuit voltage ($V_{oc}$) and power densities varied with time during the irradiation of DSPCs. $J_{sc}$ decreased significantly over time and it even turned to be 0.02 mA/cm$^2$ after 80 min and then remained stable, while $V_{oc}$ just showed slight decrease (Table S2). These should be attributed to the removal of contaminants in the cell as they functioned as electrons bridges. Moreover, $J_{sc}$ is determined by electron injection [20,35] which depends on the concentration of contaminants, hence, $J_{sc}$ decreased eventually to a relatively low level as the contaminants were totally removed, after 80 min. However, $J_{sc}$ did not decrease to 0 as expected, this may be due to Ag can also be excited by visible-light irradiation while TiO$_2$ can be excited by the small fraction of UV accessible under AM 1.5 irradiation, and also produced electron-hole pairs [33]. Then the produced electrons transferred through external load to counter photocathode while the holes may react with H$_2$O. This is consistent with the photoelectrical performances of the solar cells not sensitized with N719 (Fig. S5, Supplementary Material). Meanwhile, these produced holes may also oxidize some N719 molecules and disable this DSPC (this will be discussed in following section). In contrast, $V_{oc}$ is largely affected by the properties of the photoanode, i.e., the conductive band potential of the photoanode and the dye absorption number [36], thus $V_{oc}$ decreased.
The characterization of the cell under dark conditions is shown in Fig. S6 (Supplementary Material). The dark currents observed due to the presence of CuSO$_4$ ($J_{sc}$ of 0.016 mA/cm$^2$) were insignificant in comparison with the currents observed under irradiation (Fig. 5). Cu$^{2+}$ is practically removed from the aqueous solution in 40 min (Fig. 4) to which corresponds a $J_{sc}$ of 4.59 mA/cm$^2$.

The fill factors (Table 1) were calculated according to [16,37]:

$$ff = \frac{P_{max}}{J_{sc}V_{oc}}$$ (3)

where $P_{max}$ is the maximum power density.

Fig. 6 shows the photogeneration of H$_2$ over time in the DSPCs. The electrons transferred to the counter electrodes reduced protons to H$_2$, although some H$_2$ could also be formed during the degradation of organic matter [11, 38]. The H$_2$ production was not observed until 40 min ca., when DO and Cu$^{2+}$ were almost totally consumed (Fig. 4) as the redox potentials of Cu$^{2+}$/Cu (0.3394 V vs. NHE) and the redox potentials of O$_2$/H$_2$O (1.229 V vs. NHE) were higher than that of H$^+/H_2$ (0 vs. NHE) [39]. In agreement with the electrical performance, the rate of H$_2$ production gradually decreased as the concentration of contaminants decreased and reached approximately zero, after 80 min, when the electricity was only generated due to the excitation of TiO$_2$ and Ag under irradiation.

The photo-electricity conversion efficiency (PCE) was calculated (Table S2) to evaluate the photoelectrical performance of the DSPC. An efficiency of 3.09% was recorded at 0 min, indicating 3.09% of the incident light energy was converted into electricity. Moreover, the electricity-hydrogen conversion efficiency (ECE) was
calculated:
\[ ECE(\%) = \frac{E_{\text{H}_2}}{E_{\text{el}}} = \frac{2n_iU}{\int P_{\text{max}}A dt} \times 100 \]  
(4)

where \( E_{\text{H}_2} \) is the \( \text{H}_2 \) energy (J) produced by the cell, \( E_{\text{el}} \) is generated electricity energy on the photoanode (J), \( P_{\text{max}} \) is the maximum power density (W/cm\(^2\)), \( A \) is the irradiated surface area of photoanode (cm\(^2\)), \( n \) is the total amount of hydrogen produced (mol), \( U \) is the hydrogen energy content (122 kJ/g) and \( t \) is time (s). As shown in Table S2, 78.1% of the electricity generated from 40 to 50 min was converted to hydrogen energy. While after 60 min, approximately 98% of the electricity was converted due to the total removal of \( \text{NO}_3^- \) in the wastewater.

3.4. Chirality and plasmonic effect in the DSPC

The highest PCE in this study was 3.09% which is relatively high considering the electrolyte was actual wastewater rather than \( \Gamma/\text{I}_3^- \) solution. This supports the superior performance of Ag/AgCl @ chiral TiO\(_2\) nanofibers as photoanode in the DSPC. Herein, the photoanodes prepared with chiral TiO\(_2\) nanofibers, Ag/AgCl@broken chiral TiO\(_2\) nanofibers served as references, to exemplify the chiral plasmonic effect on the performance of the DSPC. The SEM and TEM pictures of these reference photoanode are shown in Fig. S7 (Supplementary Material). The absorption spectrums of Ag/AgCl @ chiral TiO\(_2\) nanofibers thin film and other reference photoanode thin films are shown in Fig. S8 (Supplementary Material). The stronger absorption of Ag/AgCl @ chiral TiO\(_2\) nanofibers at 200-350 nm compared to pure chiral TiO\(_2\) nanofibers can be attributed to the characteristic absorption of the AgCl semiconductor [40], besides, Ag NPs can absorb photons from an area much larger
than their geometric cross section. Resonance energy transfer (RET), the transfer of energy from a plasmon to a nearby semiconductor, enhances the intensity of the electric field thereby increasing optical absorption [41]. In contrast, the increased response in the visible-light region (400-800 nm) results from the creation of SPR [42]. The significant red shift of the absorption edge observed in the Ag/AgCl @ chiral TiO$_2$ nanofibers (trace c) when compared with Ag/AgCl @ broken chiral TiO$_2$ nanofibers (trace b), demonstrates that controlled chirality at the nanoscale level and the periodic distribution of the plasmonic Ag/AgCl in the chiral TiO$_2$ nanofiber, induces a greater SPR effect. The nanostructured ordered helical arrangement of the Ag/AgCl nanoparticles induces coupled plasmon waves propagating along the helical path, causing increased absorption of the incident light components that are in tune with the handedness of the helices. The collective plasmons that oscillate along the plasmonic chiral structure of certain handedness lead to different absorptions in response to right- and left- circularly polarized light [42]. Therefore, the acceleration of SPR excitation results from the nanostructured architecture of ordered and periodically positioned Ag/AgCl nanoparticles (Fig. 2), which are irradiated at specific incident polarization angles. Thus, it could be concluded that the more intense SPR created by Ag nanoparticles of Ag/AgCl @ chiral TiO$_2$ nanofibers can cause a stronger local field enhancement around Ag nanoparticles, which can increase light absorption of surrounding dye molecules in a dye-loaded film (Fig. S8, Supplementary Material). The higher rate of light absorption by the dye can result in an enhancement of the rate of electron injection to the photoanode [43].
The production of energy of the DSCP with the Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode and with other reference photoanodes were also studied (Fig. S9, Supplementary Material) to exemplify the advantages associated with the use of a chiral plasmonic structure. The PCE values of the cell with Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode were higher than those of reference cell with Ag/AgCl @ broken chiral TiO$_2$ nanofibers, which should be partly attributed to the higher light harvesting efficiency of these materials. Furthermore, in these materials Ag nanoparticles act as an effective ‘antenna’ for the incident visible light that stores the incident energy and create an intense electromagnetic field in the immediate vicinity \cite{33}, which in turn increases the rate of electron-hole formation in some localized regions of the semiconductor by a few orders of magnitude \cite{43}. Concurrently, nanofibers owns faster electron transport, slower recombination rate \cite{44, 45} and can serve as light-scattering centers to increase the optical light extinction length in the film, thus also enhancing the light harvesting efficiency \cite{24}. Hence, in the photoanode of this cell, chiral TiO$_2$ nanofibers and Ag nanoparticles act in a symbiotic relationship that improves the electrical performance of Ag/AgCl @ chiral TiO$_2$ nanofibers film. Firstly, the SPR effect of Ag nanoparticles is accelerated by the chiral structure due to its capacity of tuning the angle of the incident light and the scattering of light. Secondly, the lifetime of the large amount of electrons generated is extended, owning to the faster electron transport and slower recombination rate in the chiral TiO$_2$ nanofibers. Thirdly, the surface plasmons and light scattering (Ag also acts as a scattering centre) can increase the intensity of the local field and light pathways,
which enlarges the optical cross-section of dye sensitizer coated on the photoanode [46]. However, it was unexpected that only slight higher PCE of the cell with Ag/AgCl @ chiral TiO$_2$ nanofibers than that of pure chiral TiO$_2$ nanofibers was observed (Fig. S9, Supplementary Material). We reason that this is due to the Ag nanoparticles acting as recombination centers, in essence creating internal short-circuits throughout the bulk of the photoactive layer [47]. Hence, the slight PCE improvement should be ascribed to the trade-off between the chiral plasmonic effect and electron recombination role of Ag nanoparticles.

3.5. Cell stability and reuse

The stability and reuse of the DSPEC was investigated to establish the effect of inactivation caused by leaching of dye from the photoanode or deposition of by-products. Fig. 7 shows the absorbance of N719 dye deposited on the photoanode as a function of time $t$ relative to the absorbance of a freshly prepared photoanode (i.e., $A_t/A_0$) [48]. 45% of the dye was found to desorb after 24h immersion in wastewater, while only 20% of the dye still remained after 120h. Therefore, with such long timescale the reduction of photoelectrical performance shown in Fig. 5 cannot be attributed to dye detachment alone.

In general, water is believed to cause a loss of activity in the DSPECs [49, 50]. For the particular case of N719 dye, since the redox potential of ROS/H$_2$O (~ 2.85 V vs. NHE) [28] is higher than that of N719/sensitized N719 (~1.0 V vs. NHE) [33] it is conceivable that the leached dye could be oxidized by ROS after the total
consumption of TOC from the wastewater. Such effect was demonstrated by examining the photoanode absorbance and photoelectrical performance of the cell with the wastewater sealed in the cell replaced by fresh wastewater every hour or every two hours (referred as 1h cell and 2h cell). The rate of leached dye (Fig. 7) for the 1h cell was as that with the photoanode immersed in wastewater since the TOC of the wastewater was never totally consumed. In contrast, the rate of leached dye for the 2h cell was much more rapid, implying N719 molecules were oxidized by the excited ROS after the total removal of TOC. Similarly, the photoelectrical performance of the 1h cell (Fig. 8) showed PCE values of the 1h cell decreasing by approximately 50% (mainly due to the lower $J_{sc}$), and lower $V_{oc}$ after 24 h, which can be ascribed to dye desorption [20]. However, the loss of photoelectrical performance was significantly higher for the 2h cell with a 90% decrease of the PCE after 12 hours, which should be attributed to the oxidization of N719 after the removal of TOC of the wastewater. Therefore, a more stable performance of the photoanodes can be anticipated if the cell is operated with a continuous flow of fresh wastewater. Further research efforts should be directed towards the production of more stable dyes for use in water-based DSPCs including the use of electrolyte additives (such as ionic surfactants) [51-55] and the use of hydrophobic dye sensitizers [49].
4. Conclusion

In summary, a DSPC with Ag/AgCl @ chiral TiO$_2$ nanofibers as photoanode material, platinized conducting glass as cathode material and actual wastewater as the bridging electrolyte was proposed for simultaneous generation of electricity, hydrogen and contaminants removal. Excellent photoelectrical performance, fast hydrogen generation and contaminants removal were observed due to the symbiotic relationship between Ag nanoparticles and chiral nanofibers, which was exemplified by comparing the photoelectrical performance of Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode with that of Ag/AgCl @ broken chiral TiO$_2$ nanofibers. This configuration opens up new opportunities for producing renewable energy from wastewater treatment processes including organic and inorganic matter as viable resources. Chiral nanofibers doped with SPR metal nanoparticles photoanode have great potential in boosting the performance of DSPC. Although the novel DSPC shown here is far from optimum performance, there are huge opportunities for further development. The introduction of a semiconductor insulator could hinder Ag from capturing electrons and the operation of the cell in continuous flow of wastewater may reduce dye leaching. With continued advances in DSPCs for water-based applications, it may therefore be possible to increase the efficiency of energy generation and contaminants removal and finally achieve its successful implementation in domestic and industrial wastewater treatment processes.
Acknowledgement

The study was financially supported by the National Natural Science Foundation of China (No. 51322901) and the Fundamental Research Funds for the Central Universities (No. 2014B02914), the research fund was provided by the National Basic Research Program of China (‘973’ program, No. 2010CB429006).

Supplementary Material Available

The characteristics of the wastewater used in this study, detailed photoelectrical performances, XPS, XRD, SEM, UV-vis spectroscopy and EDX results of Ag/AgCl @ chiral TiO$_2$ nanofibers.

References


**Figure Captions**

**Fig. 1.** Schematic diagram of the cell.
Fig. 2. Microscopy and schematic drawing of Ag/AgCl @ chiral TiO$_2$ nanofibers. (A) SEM image of Ag/AgCl @ chiral TiO$_2$ nanofibers. (B, C) TEM images of Ag/AgCl @ chiral TiO$_2$ nanofibers, which shows there are some nanoparticles deposited on the surfaces of Ag/AgCl @ chiral TiO$_2$ nanofibers. (D) Structural model showing Ag/AgCl nanoparticles deposited on the double helixes. The scale bars in A, B and C represent 40, 10 and 20 nm, respectively.

Fig. 3. SEM image of the photoanode film after deposition by the doctor-blade process and calcination.

Fig. 4. The removal of contaminants in the cell. The initial concentrations of TOC, EE2, DO and TN were 44 mg/L, 0.56 mg/L, 6.7 mg/L and 13 mg/L, respectively. The pH of wastewater was adjusted to 6.0.

Fig. 5. The electrical performances of the cell: 0 min (black dash trace), 40 min (red dot trace) and 70 min (blue solid trace). The pH of wastewater was adjusted to 6.0.

Fig. 6. The accumulation of H$_2$ in the cell (■) and rate of H$_2$ production (●). The pH of wastewater was adjusted to 6.0.

Fig. 7. Relative $A_d/A_0$ absorbance of dye molecules (at 510 nm) detached from the photoanode immersed in wastewater (■), from the photoanode in the cell with wastewater replaced every hour (●) and every two hours (▲).

Fig. 8. Time evolution of PCE (●), $J_{sc}$ (■) and $V_{oc}$ (▲) for the cell with the wastewater was replaced (A) every hour (referred as 1h cell) and (B) every two hours (referred as 2h cell). All data were recorded immediately when the wastewater was replaced with fresh wastewater.
Figures

Fig. 1.
Fig. 2.

Fig. 3.
Fig. 4.

Fig. 5.
Fig. 6.
Fig. 7.
Fig. 8.
Dye-sensitized solar cells on plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers for treatment of urban wastewater effluents, with simultaneous production of hydrogen and electricity

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Abstract

The feasibility of simultaneous production of hydrogen and electricity with simultaneous contaminants removal from “actual” urban wastewater within a dye-sensitized solar cell (DSSC) is demonstrated for the first time. The photoanode in the modified DSSC was a novel nanostructured plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers (Ag and AgCl nanoparticles supported on chiral TiO$_2$ nanofibers). The electrolyte in the DSSC was actual wastewater spiked with an estrogen (17-β-ethynylestradiol, EE2) and a heavy metal (Cu$^{2+}$). The contaminants in the wastewater rather than I$_3^-$ (usual electrolyte in conventional DSSCs) acted as electrons bridges for the stabilization of charges in this DSSC. Almost total removal of total organic carbon, Cu$^{2+}$ and EE2, and 70% removal of total nitrogen were achieved under visible-light irradiation. A relatively high solar energy conversion efficiency (PCE 3.09%) was recorded and approximately 98% of the electricity was converted to H$_2$ after the consumption of dissolved oxygen, Cu$^{2+}$ and TN. This performance was attributed to the “symbiotic” relationship between the TiO$_2$ chiral nanofibers and the plasmonic effect of Ag nanoparticles at the photoanode although Ag acting as a recombination site may hinder the generation of electricity. This study opens up new opportunities for producing renewable energy from wastewater treatment processes including organic and inorganic matter as viable resources.

Keywords:
Wastewater treatment, Dye-sensitized solar cell, Hydrogen production, Electricity generation, Ag/AgCl @ chiral TiO$_2$ nanofibers
1. Introduction

Energy crisis and increasing environmental pollution are two of the greatest threats to human population sustainability at a global scale. Within this wide contest, wastewater previously considered as a waste is increasingly being used as a valuable resource for producing fresh water, energy and fertilizing nutrients (N and P). For instance, the wastewater’s organic content can be converted into methane gas through the anaerobic process [1], and microbial fuel cell (MFC) [2,3] may also be a viable route for the production of energy from wastewater treatment. Conventional municipal wastewater treatment plants (MWWPs), typically based on biological processes, are unable of removing some emerging contaminants such as endocrine disrupting chemicals [4] pharmaceuticals and personal care products [5]. Furthermore, residual TOC, TN, TP and heavy metals could still remain at the effluent of MWWPs [6]. All these residual contaminants in the effluent represent an increasing threat to human health, the ecological environment and global sustainability, in addition to representing an avoidable loss of valuable energy. Photocatalytic oxidation using TiO$_2$ is an effective method for the removal of these contaminants, it requires no chemicals input or output and TiO$_2$ is inexpensive and non-toxic [7, 8]. The photocatalytic oxidation of contaminants is initiated by the excitation of TiO$_2$, which results in the promotion of an electron (e$^-$) from the conduction band (CB) and creation of a hole (h$^+$) in the valence band (VB) of TiO$_2$ [9]. The photogenerated electrons and holes produce highly reactive
oxygen species (ROS) \( i.e. \) H\(_2\)O\(_2\), HO\(^-\), O\(_2\)\(^-\) which can attack and oxidize ECs [10], ultimately leading to complete mineralization.

The utilization of freely available solar energy as the only energy input allows photocatalysis to meet the requirements for being a sustainable and green process. However, the most important energy-saving goal in wastewater treatment should be to use a process that can simultaneously capture the chemical energy of the contaminants and that can also meet the effluent quality standards [1]. Although the appeal of the direct conversion of solar into chemical energy during a wastewater treatment process has been recognized for a long time, effective efforts are still scare. Recently, a series of studies have succeeded in using some organic fractions in wastewater \( i.e. \) phenolic compounds and dyes) to act as electron donors for producing H\(_2\) [11, 12] and for electricity generation [13], and our group has reported the feasibility of hydrogen generation during the removal of emerging contaminants [14, 15]. Very few studies have focused on the harvesting of energy during the removal of both organic and inorganic compounds (including nutrients and heavy metals \textit{etc.}) in contaminated water and wastewater, making this the main scientific and technological challenge for the water industry. The recent advances on the development of dye-sensitized solar cells (DSSCs) in recent years may be valuable to address this technological issue.

In a DSSC, the sensitizer, which is usually a dye, absorbs the incident photons resulting in the excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye. The excited electrons are then injected to the conduction band (CB) of the photoanode material (usually TiO\(_2\)),
they further transfer to the photoanode fluorine-doped tin oxide (FTO) supporting the TiO$_2$ and through the external load, travel to the cathode FTO and to the cathode material (usually a Pt layer). They then transfer to the HOMO of the redox couples (usually I$^-$/I$_3^-$), and finally back to the HOMO of the dye [16, 17] to close the cycle. In this process, the redox couples play a very important role as electrons bridges for the stabilization of charges in the DSSCs. One innovating aspect of the present study is the replacement of the redox couples (such as I$^-$/I$_3^-$) in DSCCs with organic and inorganic compounds naturally occurring in urban wastewater, which collectively can act as an effective electrolyte. The simultaneous production of hydrogen from wastewater may also be achieved according to pioneering works on photoelectrochemical cells [18-21]. Under an ideal situation, organic contaminants may be oxidized by an excited dye in the photoanode, while nitrate and heavy metal could be reduced in the cathode (Fig. 1) including the reduction of protons into H$_2$. Among many aspects the nanostructuring of the photoanode material is key to improving the efficiency of DSSCs.

Our recent study has demonstrated that ordered deposition of Ag/AgCl on chiral TiO$_2$ nanofibers enhances the absorption of the incident light in such plasmonic nanostructured composites [22]. One aspect for this enhancement is related to the ability of chiral TiO$_2$ nanofibers to rotate the incident light in a helical pattern [23-26] resulting in the removal of the polarization sensitivity effect of plasmonic materials. This new generation of immobilized plasmonic materials that increases the harvesting of solar light, is incorporated in the photoanode of the DSSC developed in this study which was prepared with plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers.
The modified DSSC with Ag/AgCl @ chiral TiO$_2$ nanofibers as photoanode material, a platinized FTO sheet as a counter electrode and actual urban wastewater as electrolyte was investigated for the first time for the simultaneous generation of electricity, hydrogen gas and for simultaneous removal of contaminants from wastewater. The performance and the underlying mechanisms of this highly innovating concept for environmental remediation with simultaneous generation of renewable energy are presented in this study.

2. Materials and Methods

2.1 Synthesis of Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode.

C$_{18}$-D-Glu was chosen as template for the synthesis of chiral TiO$_2$ nanofibers [22]. In a typical synthesis, C$_{18}$-D-Glu (0.06 g, 0.16 mmol) was dissolved in a mixture of methanol (27.2 g) and deionized water (160 ml) while stirring at room temperature. After the mixture was stirred for 10 min, TDA (0.58 g, 75% in isopropanol, purchased from TCI) was added to the mixture with stirring at 55°C. The mixture was allowed to react at 55°C with stirring for 2 h. The products were collected by centrifugal separation and dried by freeze drying at -60°C, which resulted in a pale yellow powder. All organics in this product were removed by calcination at 550°C, and crystalline anatase was obtained. Then, the as-prepared pure chiral TiO$_2$ nanofibers were used to fabricate Ag/AgCl @ chiral TiO$_2$ nanofibers. In a typical synthesis of Ag/AgCl @ chiral TiO$_2$ nanofibers, pure chiral TiO$_2$ nanofibers (0.2 g) and cetyltrimethylammonium chloride (0.3 g, purchased from TCI) were added into
deionized water (100 mL) while stirring at room temperature. After the mixture was stirred for 60 min, AgNO₃ (2.0 mL, 0.1 M) was quickly added into the mixture. The resulting solution was stirred at room temperature for further 60 min and irradiated with an 8W UVC light for 40 min. The suspension was collected by centrifugal separation and then dried at 80 °C for 8 h, which resulted in a brown powder. Finally, the powder was calcined at 300 °C in air and Ag/AgCl @ chiral TiO₂ nanofibers were obtained. Chiral TiO₂ nanofibers were also physically broken with the application of pressure at 10 MPa using FTIR tablet press (to avoid changes of the TiO₂ morphological structures) prior to the deposition of Ag/AgCl, to prepare Ag/AgCl @ broken chiral TiO₂ nanofibers. The synthesis of Ag/AgCl @ broken chiral TiO₂ nanofibers was carried out under the same conditions used to prepare the Ag/AgCl @ chiral TiO₂ nanofibers, to ensure that an equal amount of Ag/AgCl was deposited on the same amount of chiral TiO₂ nanofibers and broken chiral nanofibers.

2.2. Assembly of DSSCs.

The Ag/AgCl @ chiral TiO₂ nanofibers photoanode was prepared by adding 6 g of PVA (MW 22000, purchased from TCI) into 14 mL of boiled distilled water with powerful stirring, producing a highly viscous liquid that was further diluted by adding to a solvent made of 18 mL distilled water and 25 mL ethanol at 70 °C. Then, 1.62 g of the as-prepared Ag/AgCl @ chiral TiO₂ nanofibers were added into the PVA/water/ethanol solution to produce a suspension which was then left to cooled to room temperature. The photoanode films were produced on FTO glass (2.3 mm thickness, 25 cm² area, 8 Ω /sq, Dyesol Glass, previously cleaned with 2-propanol in an ultrasonic bath for 30
min, and then thoroughly rinsed with distilled water, followed by drying on nitrogen) by coating a paste of the suspension using the doctor-blade technique [27]. After coating the films were kept in a clean box for 15 min to relax surface irregularities and the residual mechanical stress of the coating. Finally, the photoanode was gradually heated at 80 °C for 15 min and then at 500 °C for 30 min. The thickness of the film (11 μm) was increased by repeating this doctor-blade technique [28]. For the preparation of the counter electrode, a drop of 5 mM H₂PtCl₆·H₂O in 2-propanol was placed on the FTO glass substrate (25 cm² area), following by drying and annealing at 450 °C for 30 min.

The photoanode was impregnated with the dye by immersion into a 1:1 (v/v) mixture of acetonitrile (CR, Sigma-Aldrich) and tert-butanol (CR, Sigma-Aldrich) containing a 0.5 mM N719 (Dyesol) dye solution for 6 h. Then, the dye-loaded photoanode was washed with acetonitrile and dried with nitrogen.

The DSSCs were assembled into a sandwich design using the dye loaded photoanode and the cathode. The distance between the two electrodes was 5 mm. The gap between the electrodes was filled with actual wastewater collected from the effluent of a municipal wastewater treatment plant in Suzhou (China) with further addition of 17-β-ethynylestradiol (EE2) (HPLC grade, Merck) and CuSO₄. The chemical properties of the wastewater effluent are presented in Table S1 (SI). The pH of the wastewater in the DSSCs was adjusted using 1 mol/L H₂SO₄.

2.3. Instruments and experimental conditions.

Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7041F
at an accelerating voltage of 1 kV. Large scope EDX analysis was conducted on an energy dispersive X-ray spectrometer (ZAF Quantification) attached to the SEM of JEOL JSM-7041F. Transmission electron microscopy (TEM) was performed on a JEOL 2011 operation at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA). X-ray photoelectron spectroscopy (XPS) results were obtained with PHI 5000C ESCA with Mg Kα source operating at 14 kV and 25 mA. UV-vis diffuse reflectance spectroscopy was performed in triplicate on similar samples to ensure reproducibility, on a SHIMADZU UV-2450 with a collection speed of 40 nm min⁻¹ BaSO₄ as the reference. All samples were obtained by scratching films off the FTO substrates and degassing at 200 °C overnight.

Prior to irradiation, the fabricated DSSC cells were vertically fixed into 12 beakers, each one containing 12.5 mL of spiked wastewater, and were all shaken in an orbital shaker, in the dark, for 40 min, to establish adsorption-desorption equilibrium of the solution species with the electrodes. Then samples were taken from each beaker, and the beakers were irradiated for two hours using a AM 1.5 solar simulator (Oriel) equipped with a 150 W xenon light and AM 1.5G type filter (Newport, 81094). samples for analyses were collected at specific time intervals sequentially from each DSSC (one more sample per cell), since the liquid volume in each beaker was small. The current-voltage (J-V) characteristics of the 12 cells were measured as described elsewhere [28]. The amount of hydrogen, the concentrations of EE2, TOC, TN and were measured as shown in our previous studies [4,14,29]. Briefly, the concentration
of EE2 was detected by High Performance Liquid Chromatography (HPLC, Agilent 1100). TOC was measured by means of a Shimadzu TOC-VVPN with an ANSI-V auto sampler. TN was measured using multi N/C 2100 TOC analyzer (Analytikjena, Germany). DO was monitored with electrode for DO sensor (UC-12-SOL, Central Kagaku Co.). The amount of collected H$_2$ was measured by using a gas chromatograph (HP Agilent, 6890) equipped with a thermal conductivity detector and a molecular sieve 5A column.

3. Results and Discussion

3.1. Characterization of Ag/AgCl @ chiral TiO$_2$ nanofibers.

SEM pictures of the Ag/AgCl @ chiral TiO$_2$ nanofibers (Fig. 2a) revealed that the left-handed, double-helical morphology was preserved after the deposition of the Ag and AgCl nanoparticles. The average length of undamaged TiO$_2$ nanofibers was ~ 500 nm and diameter was ~ 20 nm. TEM analyses (Fig. 2b-c) revealed that Ag/AgCl nanoparticles with the average diameters of 5-8 nm were deposited on the surface of the chiral TiO$_2$ nanofibers, preferentially at the outer edges of the TiO$_2$ crystals of the helical structure, following the conceptual structure shown in Fig. 2d.

The elemental and chemical compositions of the samples were further determined by XPS. The results (Fig. S1a, SI) suggest that Ag/AgCl @ chiral TiO$_2$ nanofibers contain Ti, O, C, Ag and Cl elements. The C1s was attributed to the adventitious hydrocarbon released from the XPS instrument [27]. In Fig. S1b, the Ag 3d spectra consists of two individual peaks approximately at 373 and 367 eV, which are due to
Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ binding energy, respectively. The existence of Ag$^0$ and Ag$^{+1}$ could be verified by further peaks divisions [28]. Consequently, the XPS analyses suggested that the nanoparticles deposited on chiral TiO$_2$ nanofibers were made of Ag/AgCl composites. The elemental composition determined by EDX (Fig. S2), resulted in a Ag content of 5.49 mol % and a Cl content of 2.86 mol %, which indicated that the Ag/AgCl was virtually at a 1:1 molar ratio. XRD results also suggested the co-existence of Ag and AgCl (Fig. S3 and detailed descriptions in SI). Further details on material characterization have been reported [22].

3.2. Contaminants removal in the DSSC.

EE2 representing for chemically stable organic compounds and Cu$^{2+}$ representing for heavy metal ions were spiked into the wastewater at specific concentrations to investigate the removal of contaminants (TOC, TN, EE2 and Cu$^{2+}$) in the cell (Fig. 3). TOC, EE2 and Cu$^{2+}$ were totally removed after 80 min, 80 min and 55 min respectively, while only approximately 70% of TN was removed within 120 min. Meanwhile, a decrease of DO over time was observed, indicating the mineralization of TOC and EE2 is aerobic [15]. The fast photodegradation of the TOC including EE2 should be attributed to the combined effect of (i) the strong photocatalytic activity of irradiated Ag/AgCl @ chiral TiO$_2$ nanofibers and of (ii) the oxidization ability of sensitized dyes. Regarding the first effect, Ag/AgCl @ chiral TiO$_2$ nanofibers under visible-light irradiation produces photogenerated electron-hole pairs in the Ag nanoparticles due to surface plasmon resonance (SPR) [30]. In this process, SPR generates the electron-hole pairs in the semiconductor (AgCl and TiO$_2$) by the
dipole-dipole interaction between the donor (Ag) and the acceptors (AgCl and TiO$_2$). The photocatalytic activity of Ag/AgCl @ chiral TiO$_2$ nanofibers should mainly be attributed to two simultaneous processes. The strong electronic coupling between Ag and AgCl conduction bands which injects photoinduced electrons from the Ag nanoparticles, quickly and efficiently, into the AgCl [31] and into the TiO$_2$ helical structure, yielding superoxide radicals and finally HO- radicals from the reductive pathway [32]. However, this effect seems negligible for the removal of the contaminants since the direct charge transfer from noble nanoparticles (Hagglund et al., 2008) or the internal photoemission from TiO$_2$ and AgCl [33] only play a supporting role in the photoelectrical performance. This was verified of the $J$-$V$ characteristics of the solar cells not sensitized with dye N719 (see Fig S4).

Regarding the effect of the sensitized dye on the removal of TOC and EE2, the redox potential of N719/sensitized N719 is ~ 1.0 V (vs. normal hydrogen electrode (NHE)) [17] which is sufficient to oxidize most organic compounds in wastewater, since their redox potentials were mostly less than 0.6 V vs. NHE [35] As a result, the reduction of the sensitized dye to its ground state maintained the cell cycle until all organic contaminants were removed from the wastewater. Since the synthesized wastewater was acid, the decrease in the TN should be attributed to the reduction of NO$_3^-$ by the electrons transferred to the photocathode:

\begin{align*}
\text{NO}_3^- + 2\text{H}^+ + e^- & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad E^0 = 0.7989\text{V} \\
\text{NO}_3^- + 4\text{H}^+ + 3e^- & \rightarrow \text{NO} + \text{H}_2\text{O} \quad E^0 = 0.9637\text{V}
\end{align*}

This significant mass deficit in the TN balance also confirms some gaseous product
such as NO and N₂O are generated as a result of NO₃⁻ reduction. The 30% of TN survived from the photoelectrical degradation should be NH₃-N as they cannot be reduced in acid or neutral conditions [36].

3.3. Photoelectrical performance and hydrogen generation of the DSSC.

SPR is characterized by a build-up of intense, spatially non-homogeneous oscillating electric fields in the neighbourhood of the nanostructure [22]. The SPR effect at the photoanode improves the efficiency of the DSSCs by (1) increased light absorption due to surface plasmons and light-trapping effects, (2) improved charge separation as a result of the localized electro-magnetic field, (3) the promotion of electron transfer to adsorbed species, and (4) the electron storage effect that can shifts the Fermi level to more negative potentials [37-40]. Although the direct charge transfer from Ag nanoparticles to the semiconductor may also prove useful for the electricity generation as mentioned above, the main mechanism of photo-excitation of the photoanode with visible light implies the sensitization of the N719 dye, and the transfer of excited electrons to the Ag/AgCl @ chiral TiO₂ nanofibers, the external load, the counter cathode and lastly the simultaneous reductions of NO₃⁻, H⁺ and of Cu²⁺. The presence of metallic Cu on the surface of the counter electrode after the process was further substantiated by two XPS peaks at 932.6 eV and 952.5 eV [38-41] (Fig. S5.). In parallel to the above mechanism, the sensitized N719 dye is reduced back to its ground state by the adsorbed organic matter and nitrogen, which were present in the wastewater, therefore, sacrificial organic and inorganic matter are essential to sustain the mechanism of the DSSCs. This mechanism is further
exemplified by the current-voltage \((J-V)\) and current-power densities \((J-P)\) plots, which were recorded to investigate the electrical performance of the cell (Fig. 4).

The short-circuit current densities \(J_{sc}\), open-circuit voltage \(V_{oc}\) and power densities varied with time during the irradiation of DSSCs. \(J_{sc}\) decreased significantly over time and it even turned to be 0.02 mA/cm\(^2\) after 80 min and then remained stable, while \(V_{oc}\) just showed slight decrease (Table S2). These should be attributed to the removal of contaminants in the cell as they functioned as electrons bridges. Moreover, \(J_{sc}\) is determined by electron injection \([16,39]\) which depends on the concentration of contaminants, hence, \(J_{sc}\) decreased eventually to a relatively low level as the contaminants were totally removed, after 80 min. However, \(J_{sc}\) did not decrease to 0 as expected, this may be due to Ag can also be excited by visible-light irradiation while TiO\(_2\) can be excited by the small fraction of UV accessible under AM 1.5 irradiation, and also produced electron-hole pairs \([37]\). Then the produced electrons transferred through external load to counter photocathode while the holes may react with H\(_2\)O. This is consistent with the photoelectrical performances of the solar cells not sensitized with N719 (Fig. S4). Meanwhile, these produced holes may also oxidize some N719 molecules and disable this DSSC (this will be discussed in following section). In contrast, \(V_{oc}\) is largely affected by the properties of the photoanode, \(i.e.,\) the conductive band potential of the photoanode and the dye absorption number \([40]\), thus \(V_{oc}\) decreased. The fill factors (Table 1) were calculated according to \([41]\):

\[
ff = \frac{P_{\text{max}}}{J_{sc} V_{oc}}
\]  
\[\text{(3)}\]
where $P_{\text{max}}$ is the maximum power density.

Fig. 5 shows the photogeneration of H$_2$ over time in the DSSCs. The electrons transferred to the counter electrodes reduced protons to H$_2$, although some H$_2$ could also be formed during the degradation of organic matter [11, 42]. The H$_2$ production was not observed until 40 min ca., when DO and Cu$^{2+}$ were almost totally consumed (Fig. 3) as the redox potentials of Cu$^{2+}$/Cu (0.3394 V vs. NHE) and O$_2$/H$_2$O (1.229 V vs. NHE) were higher than that of H$^+$/H$_2$ (0 vs. NHE) [43]. In agreement with the electrical performance, the rate of H$_2$ production gradually decreased as the concentration of contaminants decreased and reached approximately zero, after 80 min, when the electricity was only generated due to the excitation of TiO$_2$ and Ag under irradiation.

The photo-electricity conversion efficiency (PCE) was calculated (Table S2) to evaluate the photoelectrical performance of DSSC. An efficiency of 3.09% was recorded at 0 min, indicating 3.09% of the incident light energy was converted into electricity. Moreover, the electricity-hydrogen conversion efficiency (ECE) was calculated:

$$ECE(\%) = \frac{E_{H_2}}{E_{\text{el}}} = \frac{2nU}{\int P_{\text{max}}Adt} \times 100$$

(4)

where $E_{H_2}$ is the H$_2$ energy (J) produced by the cell, $E_{\text{el}}$ is generated electricity energy on the photoanode (J), $P_{\text{max}}$ is the maximum power density (W/cm$^2$), $A$ is the irradiated surface area of photoanode (cm$^2$), $n$ is the total amount of hydrogen produced (mol), $U$ is the hydrogen energy content (122 kJ/g) and $t$ is time (s). As shown in Table S2, 78.1% of the electricity generated from 40 to 50 min was
converted to hydrogen energy. While after 60 min, approximately 98% of the electricity was converted due to the total removal of Cu\textsuperscript{2+} and NO\textsubscript{3} in the wastewater.

3.4. Chirality and plasmonic effect in the DSSC.

The highest PCE in this study was 3.09% which is relatively high considering the electrolyte was actual wastewater rather than I/I\textsubscript{3} solution. This supports the superior performance of Ag/AgCl @ chiral TiO\textsubscript{2} nanofibers as photoanode in the DSSC. Herein, the photoanodes prepared with chiral TiO\textsubscript{2} nanofibers, Ag/AgCl@broken chiral TiO\textsubscript{2} nanofibers served as references, to exemplify the chiral plasmonic effect on the performance of the DSSC. The SEM and TEM pictures of these reference photoanode are shown in Fig. S6. The absorption spectrums of Ag/AgCl @ chiral TiO\textsubscript{2} nanofibers thin film and other reference photoanode thin films are shown in Fig. S7. The stronger absorption of Ag/AgCl @ chiral TiO\textsubscript{2} nanofibers at 200-350 nm compared to pure chiral TiO\textsubscript{2} nanofibers can be attributed to the characteristic absorption of the AgCl semiconductor [44], besides, Ag NPs can absorb photons from an area much larger than their geometric cross section. Resonance energy transfer (RET, the transfer of energy from a plasmon to a nearby semiconductor) enhances the electric field intensity thereby increasing the optical absorption [45]. In contrast, the increased response in the visible-light region (400-800 nm) results from the creation of SPR [46]. The significant red shift of the absorption edge observed in the Ag/AgCl @ chiral TiO\textsubscript{2} nanofibers (trace c) when compared with Ag/AgCl @ broken chiral TiO\textsubscript{2} nanofibers (trace b), demonstrates that controlled chirality at the nanoscale level induces a greater SPR effect. The nanostructured ordered helical arrangement of the
Ag/AgCl nanoparticles induces coupled plasmon waves propagating along the helical path, causing increased absorption of the incident light components that are in tune with the handedness of the helices. The collective plasmons that oscillate along the plasmonic chiral structure of certain handedness lead to different absorptions in response to right- and left- circularly polarized light [46]. Therefore, the acceleration of SPR excitation results from the nanostructured architecture of ordered Ag/AgCl nanoparticles, which are irradiated at specific incident polarization angles. Thus, it could be concluded that the more intense SPR created by Ag nanoparticles of Ag/AgCl @ chiral TiO$_2$ nanofibers can cause a stronger local field enhancement around Ag nanoparticles, which can increase light absorption of surrounding dye molecules in a dye-loaded film (Fig. S7). The higher rate of light absorption by the dye can result in an enhancement of the rate of electron injection to the photoanode [47].

The production of energy of the DSSC with the Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode and with other reference photoanodes were also studied (Fig. S8) to exemplify the advantages associated with the use of a chiral plasmonic structure. The PCE values of the cell with Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode were higher than those of reference cell with Ag/AgCl @ broken chiral TiO$_2$ nanofibers, which should be partly attributed to the higher light harvesting efficiency of these materials. Furthermore, in these materials Ag nanoparticles act as an effective ‘antenna’ for the incident visible light that stores the incident energy and create an intense electromagnetic field in the immediate vicinity [23, 37], which in turn
increases the rate of electron-hole formation in some localized regions of the semiconductor by a few orders of magnitude [47]. Concurrently, nanofibers owns faster electron transport, slower recombination rate [48,49] and can serve as light-scattering centers to increase the optical length in the film, thus also enhancing the light harvesting efficiency [28]. Hence, in the photoanode of this cell, chiral TiO$_2$ nanofibers and Ag nanoparticles act in a symbiotic relationship that improves the electrical performance of Ag/AgCl @ chiral TiO$_2$ nanofibers film. Firstly, the SPR effect of Ag nanoparticles is accelerated by the chiral structure due to its capacity of tuning the angle of the incident light and the scattering of light. Secondly, the lifetime of the large amount of electrons generated is extended, owning to the faster electron transport and slower recombination rate in the chiral TiO$_2$ nanofibers. However, it was unexpected that only slight higher PCE of the cell with Ag/AgCl @ chiral TiO$_2$ nanofibers than that of pure chiral TiO$_2$ nanofibers was observed (Fig. S4). We reason that this is due to the Ag nanoparticles acting as recombination centers, in essence creating internal short-circuits throughout the bulk of the photoactive layer [50]. Hence, the slight PCE improvement should be ascribed to the trade-off between the chiral plasmonic effect and electron recombination role of Ag nanoparticles.

3.5. Cell stability and reuse.

The stability and reuse of the DSSC was investigated to establish the effect of inactivation caused by leaching of dye from the photoanode or deposition of by-products. Fig. 6 shows the absorbance of N719 dye deposited on the photoanode as a function of time $t$ relative to the absorbance of a freshly prepared photoanode (i.e.,
45% of the dye was found to desorb after 24h immersion in wastewater, while only 20% of the dye still remained after 120h. Therefore, with such long timescale the reduction of photoelectrical performance shown in Fig. 4 cannot be attributed to dye detachment alone.

In general, water is believed to cause a loss of activity in the DSSCs [52, 53]. For the particular case of N719 dye, since the redox potential of ROS/H₂O (~ 2.85 V vs. NHE) [32] is higher than that of N719/sensitized N719 (~1.0 V vs. NHE) [37] it is conceivable that the leached dye could be oxidized by ROS after the total consumption of TOC from the wastewater.

Such effect was demonstrated by examining the photoanode absorbance and photoelectrical performance of the cell with the wastewater sealed in the cell replaced by fresh wastewater every hour or every two hours (referred as 1h cell and 2h cell). The rate of leached dye (Fig. 6) for the 1h cell was as that with the photoanode soaked in wastewater since the TOC of the wastewater was never totally consumed. In contrast, the rate of leached dye for the 2h cell was much more rapid, implying N719 molecules were oxidized by the excited ROS after the total removal of TOC.

Similarly, the photoelectrical performance of the 1h cell (Fig. 7) showed PCE values of the 1h cell decreasing by approximately 50% (mainly due to the lower $J_{sc}$), and lower $V_{oc}$ after 24 h, which can be ascribed to dye desorption [16]. However, the loss of photoelectrical performance was significantly higher for the 2h cell with a 90% decrease of the PCE after 12 hours, which should be attributed to the oxidization of N719 after the removal of TOC of the wastewater. Therefore, a more stable
performance of the photoanodes can be anticipated if the cell is operated with a continuous flow of fresh wastewater. Further research efforts should be directed towards the production of more stable dyes for use in water-based DSSCs including the use of electrolyte additives (such as ionic surfactants) [54-56] and the use of hydrophobic dye sensitizers [52].
4. Conclusion

In summary, a modified DSSC with Ag/AgCl @ chiral TiO$_2$ nanofibers as photoanode material, platinized conducting glass as cathode material and actual wastewater as the bridging electrolyte was proposed for simultaneous generation of electricity, hydrogen and contaminants removal. Excellent photoelectrical performance, fast hydrogen generation and contaminants removal were observed due to the symbiotic relationship between Ag nanoparticles and chiral nanofibers, which was exemplified by comparing the photoelectrical performance of Ag/AgCl @ chiral TiO$_2$ nanofibers photoanode with that of Ag/AgCl @ broken chiral TiO$_2$ nanofibers. This configuration opens up new opportunities for producing renewable energy from wastewater treatment processes including organic and inorganic matter as viable resources. Chiral nanofibers doped with SPR metal nanoparticles photoanode have great potential in boosting the performance of DSSCs. Although the novel DSSC shown here is far from optimum performance, there are huge opportunities for further development. The introduction of a semiconductor insulator could hinder Ag from capturing electrons and the operation of the cell in continuous flow of wastewater may reduce dye leaching. With continued advances in DSSCs for water-based applications, it may therefore be possible to increase the efficiency of energy generation, metal recycling and contaminants removal and finally achieve its successful implementation in domestic and industrial wastewater treatment processes.
Acknowledgement

The study was financially supported by the National Natural Science Foundation of China (No. 51322901) and the Fundamental Research Funds for the Central Universities (No. 2014B02914), the research fund was provided by the National Basic Research Program of China (‘973’ program, No. 2010CB429006).

Supporting Information Available

The characteristics of the wastewater used in this study, detailed photoelectrical performances, XPS, XRD and EDX results of Ag/AgCl @ chiral TiO$_2$ nanofibers.

References


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Figure Captions

Fig. 1. Schematic diagram of the cell.

Fig. 2. Microscopy and schematic drawing of Ag/AgCl @ chiral TiO$_2$ nanofibers. (A) SEM image of Ag/AgCl @ chiral TiO$_2$ nanofibers. (B, C) TEM images of Ag/AgCl @ chiral TiO$_2$ nanofibers, which shows there are some nanoparticles deposited on the surfaces of Ag/AgCl @ chiral TiO$_2$ nanofibers. (D) Structural model showing Ag/AgCl nanoparticles deposited on the double helixes. The scale bars in A, B and C represent 40, 10 and 20 nm, respectively.

Fig. 3. The removal of contaminants in the cell. The initial concentrations of TOC, EE2, DO, Cu$^{2+}$ and TN were 44 mg/L, 0.56 mg/L, 6.7 mg/L, 1.03 mg/L and 13 mg/L, respectively. The pH of wastewater was adjusted to 6.0.

Fig. 4. The electrical performances of the cell: 0 min (black dot trace), 40 min (red solid trace) and 70 min (blue dash trace). The pH of wastewater was adjusted to 6.0.

Fig. 5. The accumulation of H$_2$ in the cell (■) and rate of H$_2$ production (●). The pH of wastewater was adjusted to 6.0.

Fig. 6. (A) UV-vis absorption spectrums of (a) Pure chiral TiO$_2$ nanofibers. (b) Ag/AgCl @ broken chiral TiO$_2$ nanofibers. (c) Ag/AgCl @ chiral TiO$_2$ nanofibers. (B) Corresponding spectra of the dye adsorbed onto the photoanode films.

Fig. 7. Time evolution of PCE (●), $J_{sc}$ (■) and $V_{oc}$ (▲) for the cell with the wastewater was replaced (A) every hour (referred as 1h cell) and (B) every two hours (referred as 2h cell). All data were recorded immediately when the wastewater was replaced with fresh wastewater.
Fig. 1.
Fig. 2.
Fig. 3.

Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Graphical abstract
Highlights:

- Environmental remediation with simultaneous generation of renewable energy
- Renewable energy is produced from urban wastewater effluents
- Simultaneous water detoxification and hydrogen/electricity production
- Urban wastewater effluent provides the electrolyte in the dye sensitised solar cell
- Photoanode made by a novel plasmonic Ag/AgCl @ chiral TiO$_2$ nanofibers