This item was submitted to [Loughborough's Research Repository](#) by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

Dye-sensitized photoelectrochemical cell on plasmonic Ag/AgCl @ chiral TiO₂ nanofibers for treatment of urban wastewater effluents, with simultaneous production of hydrogen and electricity

PLEASE CITE THE PUBLISHED VERSION

<http://dx.doi.org/10.1016/j.apcatb.2014.11.012>

PUBLISHER

© Elsevier

VERSION

AM (Accepted Manuscript)

PUBLISHER STATEMENT

This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: <https://creativecommons.org/licenses/by-nc-nd/4.0/>

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Wang, Dawei, Yi Li, Gianluca Li-Puma, Chao Wang, Peifang Wang, Wenlong Zhang, and Qing Wang. 2014. "Dye-sensitized Photoelectrochemical Cell on Plasmonic Ag/agcl @ Chiral Tio₂ Nanofibers for Treatment of Urban Wastewater Effluents, with Simultaneous Production of Hydrogen and Electricity". Loughborough University. <https://hdl.handle.net/2134/19052>.

Manuscript Number: APCATB-D-14-01160R2

Title: Dye-sensitized photoelectrochemical cell on plasmonic Ag/AgCl @ chiral TiO₂ nanofibers for treatment of urban wastewater effluents, with simultaneous production of hydrogen and electricity

Article Type: Research Paper

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

Corresponding Author: Prof. Gianluca LI Puma, PhD

Corresponding Author's Institution: Loughborough University

First Author: Dawei Wang

Order of Authors: Dawei Wang; Yi Li, PhD; Gianluca LI Puma, PhD; Chao Wang; Peifang Wang; Wenlong Zhang; Qing Wang

1 **Dye-sensitized photoelectrochemical cell on plasmonic**
2 **Ag/AgCl @ chiral TiO₂ nanofibers for treatment of urban**
3 **wastewater effluents, with simultaneous production of**
4 **hydrogen and electricity**

5 Dawei Wang ^a, Yi Li^{a*}, Gianluca Li Puma^{b*}, Chao Wang ^a, Peifang Wang ^a, Wenlong
6 Zhang ^a and Qing Wang ^a

7
8 ^a *Key Laboratory of Integrated Regulation and Resource Development of Shallow*
9 *Lakes, Ministry of Education, College of Environment, Hohai University. Xi Kang*
10 *Road #1, Nanjing 210098, PR China; E-mail: envly@hhu.edu.cn (Corresponding*
11 *Author 1)*

12 ^b *Environmental Nanocatalysis & Photoreaction Engineering, Department of Chemical*
13 *Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom;*
14 *E-mail: g.lipuma@lboro.ac.uk (Corresponding Author 2)*

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 TiO₂ nanofibers (Ag and AgCl nanoparticles supported on chiral TiO₂ nanofibers). The electrolyte in the DSPC was actual wastewater to which an estrogen (17- β -ethynylestradiol, EE2) and a heavy metal (Cu²⁺) were added. The contaminants in the wastewater rather than I⁻/I₃⁻ (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), Cu²⁺, 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 H₂ after the consumption of dissolved oxygen (DO), Cu²⁺ and TN. This performance was attributed to the “symbiotic” relationship between the TiO₂ 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 TiO₂ 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 (TiO₂) is an effective method for the removal of chemically stable contaminants, it requires no chemicals input or output and TiO₂ is inexpensive and non-toxic [4-8]. The photocatalytic oxidation of contaminants is initiated by the excitation of TiO₂, 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 TiO₂ [9]. The photogenerated electrons and holes produce highly reactive oxygen species (ROS) (*i.e.* H₂O₂, HO[·], O₂^{·-}) 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

1 advancement in wastewater treatment should be the development of a new process that
2 can simultaneously capture the chemical energy of the oxidized contaminants while
3 meeting the effluent quality standards [1]. Although the appeal of the direct conversion
4 of solar into chemical energy during a wastewater treatment process has been
5 recognized for a long time, effective efforts are still rare. Recently, a series of studies
6 have succeeded in using some organic fractions in wastewater (*i.e.* phenolic
7 compounds and dyes) to act as electron donors for producing H₂ [11, 12] and for
8 electricity generation [13], and our group has reported the feasibility of hydrogen
9 generation during the removal of emerging contaminants [14, 15]. Very few studies
10 have focused on the harvesting of energy during the removal of both organic and
11 inorganic compounds (*e.g.* nutrients) in contaminated water and wastewater, making
12 this the main scientific and technological challenge for the water industry. In this study,
13 inspired by the PhotoFuelCell system proposed by Lianos and coworkers [16-19], we
14 demonstrate that dye-sensitized photoelectrochemical cells (DSPCs) may be valuable
15 to address this technological issue.

16 The concept of DSPCs was similar with that of dye-sensitized solar cells (DSSCs). In a
17 DSSC, the sensitizer, which is usually a dye, absorbs the incident photons resulting in
18 the excitation of electrons from the highest occupied molecular orbital (HOMO) to the
19 lowest unoccupied molecular orbital (LUMO) of the dye. The excited electrons are then
20 injected to the conduction band (CB) of the photoanode material (usually TiO₂), they
21 further transfer to the photoanode fluorine-doped tin oxide (FTO) supporting the TiO₂
22 and through the external load, travel to the cathode FTO and to the cathode material

1 (usually a Pt layer). They then transfer to the HOMO of the redox couples (usually
2 I/I_3^-), and finally back to the HOMO of the dye [20, 21] to close the cycle. In this
3 process, the redox couples play a very important role as electrons bridges for the
4 stabilization of charges in the DSSCs. One major innovating aspect of the present study
5 is the replacement of the redox couples (such as I/I_3^-) in DSSCs with organic and
6 inorganic compounds naturally occurring in urban wastewater, which collectively can
7 act as an effective electrolyte and also reduced the dye in excited state to stable state.
8 Although dyes have been reported to be unstable in water, they may have a temporary
9 sensitization effect. Under an ideal situation, organic contaminants may be oxidized by
10 an excited dye in the photoanode, while nitrate and heavy metal could be reduced in the
11 cathode (Fig. 1) including the reduction of protons into H_2 .
12 The DSPC with Ag/AgCl @ chiral TiO_2 nanofibers as photoanode material, a
13 platinized FTO sheet as a counter electrode and actual urban wastewater as electrolyte
14 was investigated for the first time for the simultaneous generation of electricity,
15 hydrogen gas and for simultaneous removal of contaminants from wastewater,
16 including 17- β -ethynylestradiol (EE2) as a representative of chemically stable and
17 emerging contaminants which was added to the wastewater. The performance and the
18 underlying mechanisms of this highly innovating concept for environmental
19 remediation with simultaneous generation of renewable energy are presented in this
20 study.

2. Materials and Methods

2.1 Synthesis of Ag/AgCl @ chiral TiO₂ nanofibers photoanode

Chiral TiO₂ nanofibers were synthesized with N-(1-oxooctadecyl)-D-glutamic acid (C₁₈-D-Glu) as template and details can be found in our previous study [22]. In a typical synthesis, C18-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 TiO₂ nanofibers were used to fabricate Ag/AgCl @ chiral TiO₂ nanofibers. In a typical synthesis of Ag/AgCl @ chiral TiO₂ nanofibers, pure chiral TiO₂ 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

1 with the application of pressure at 10 MPa using FTIR tablet press (to avoid changes of
2 the TiO₂ morphological structures) prior to the deposition of Ag/AgCl, to prepare
3 Ag/AgCl @ broken chiral TiO₂ nanofibers. The synthesis of Ag/AgCl @ broken chiral
4 TiO₂ nanofibers was carried out under the same conditions used to prepare the Ag/AgCl
5 @ chiral TiO₂ nanofibers, to ensure that an equal amount of Ag/AgCl was deposited on
6 the same amount of chiral TiO₂ nanofibers and broken chiral nanofibers.

7 **2.2. Assembly of DSPCs**

8 The Ag/AgCl @ chiral TiO₂ nanofibers photoanode was prepared by adding 6 g of PVA
9 (MW 22000, purchased from TCI) into 14 mL of boiled distilled water with powerful
10 stirring, producing a highly viscous liquid that was further diluted by adding to a
11 solvent made of 18 mL distilled water and 25 mL ethanol at 70 °C. Then, 1.62 g of the
12 as-prepared Ag/AgCl @ chiral TiO₂ nanofibers were added into the PVA/water/ethanol
13 solution to produce a suspension which was then left to cooled to room temperature.
14 The photoanode films were produced on FTO glass (2.3 mm thickness, 25 cm² area, 8
15 Ω /sq, Dyesol Glass, previously cleaned with 2-propanol in an ultrasonic bath for 30
16 min, and then thoroughly rinsed with distilled water, followed by drying on nitrogen)
17 by coating a paste of the suspension using the doctor-blade technique [23]. After
18 coating the films were kept in a clean box for 15 min to relax surface irregularities and
19 the residual mechanical stress of the coating. Finally, the photoanode was gradually
20 heated at 80 °C for 15 min and then at 500 °C for 30 min. The thickness of the film (11
21 μm) was increased by repeating this doctor-blade technique [24]. For the preparation of
22 the counter electrode, a drop of 5 mM H₂PtCl₆·H₂O in 2-propanol was placed on the

1 FTO glass substrate (25 cm² area), following by drying and annealing at 450 °C for 30
2 min.

3 The photoanode was impregnated with the dye by immersion into a 1:1 (v/v) mixture of
4 acetonitrile (CR, Sigma-Aldrich) and tert-butanol (CR, Sigma-Aldrich) containing a
5 0.5 mM N719 (Dyesol) dye solution for 6 h. Then, the dye-loaded photoanode was
6 washed with acetonitrile and dried with nitrogen.

7 The DSPCs were assembled into a sandwich design using the dye loaded photoanode
8 and the cathode. The distance between the two electrodes was 5 mm. The gap between
9 the electrodes was filled with actual wastewater collected from the effluent of a
10 municipal wastewater treatment plant in Suzhou (China) with further addition (0.56
11 mg/L) of 17-β-ethynylestradiol (EE2) (HPLC grade, Merck) and CuSO₄ (1.03 mg/L).
12 The chemical properties of the wastewater effluent are presented in Table S1
13 (Supplementary Material). The pH of the wastewater in the DSPCs was adjusted using
14 1 mol/L H₂SO₄.

15 **2.3. Instruments and experimental conditions**

16 Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7041F
17 at an accelerating voltage of 1 kV. Large scope EDX analysis was conducted on an
18 energy dispersive X-ray spectrometer (ZAF Quantification) attached to the SEM of
19 JEOL JSM-7041F. Transmission electron microscopy (TEM) was performed on a
20 JEOL 2011 operation at 200 kV. X-ray diffraction (XRD) patterns were recorded on a
21 Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu Kα radiation (40 kV,
22 20 mA). X-ray photoelectron spectroscopy (XPS) results were obtained with PHI

1 5000C ESCA with Mg $K\alpha$ source operating at 14 kV and 25 mA. UV-vis diffuse
2 reflectance spectroscopy was performed in triplicate on similar samples to ensure
3 reproducibility, on a SHIMADZU UV-2450 with a collection speed of 40 nm min⁻¹
4 BaSO₄ as the reference. All samples were obtained by scratching films off the FTO
5 substrates and degassing at 200 °C overnight.

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

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 TiO₂ nanofibers

SEM pictures of the Ag/AgCl @ chiral TiO₂ 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 TiO₂ 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 TiO₂ nanofibers, preferentially at the outer edges of the TiO₂ 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 TiO₂ 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 Ag⁰ and Ag⁺¹ could be verified by further peaks divisions [24]. Consequently, the XPS analyses suggested that the nanoparticles

1 deposited on chiral TiO₂ nanofibers were made of Ag/AgCl composites. The
2 elemental composition determined by EDX (Fig. S2, Supplementary Material),
3 resulted in a Ag content of 5.49 mol % and a Cl content of 2.86 mol %, which
4 indicated that the Ag/AgCl was virtually at a 1:1 molar ratio. XRD results also
5 suggested the co-existence of Ag and AgCl (Fig. S3 and detailed descriptions in
6 Supplementary Material). Further details on material characterization have been
7 reported [22]. Moreover, the chiral nanostructure was preserved after the doctor-blade
8 process although some aggregation of the nanofibers was observed (Fig. 3).

9 **3.2. Contaminants removal in the DSPC**

10 EE2 representing for chemically stable organic compounds Cu²⁺ representing for
11 heavy metal ions were spiked into the wastewater at specific concentrations to
12 investigate the removal of contaminants (TOC, TN, EE2 and Cu²⁺) in the cell were
13 spiked into the wastewater at specific concentrations to investigate the removal of
14 contaminants (TOC, TN, EE2) in the cell (Fig. 4). TOC, Cu²⁺ and EE2 were totally
15 removed after 80 min, while only approximately 70% of TN was removed within 120
16 min. Meanwhile, a decrease of DO over time was observed, indicating the
17 mineralization of TOC and EE2 is aerobic [15]. The fast photodegradation of the TOC
18 including EE2 should be attributed to the combined effect of (i) the strong
19 photocatalytic activity of irradiated Ag/AgCl @ chiral TiO₂ nanofibers and of (ii) the
20 oxidization ability of sensitized dyes. Regarding the first effect, Ag/AgCl @ chiral
21 TiO₂ nanofibers under visible-light irradiation produces photogenerated electron-hole
22 pairs in the Ag nanoparticles due to surface plasmon resonance (SPR) [26]. In this

1 process, SPR generates the electron-hole pairs in the semiconductor (AgCl and TiO₂)
 2 by the dipole-dipole interaction between the donor (Ag) and the acceptors (AgCl and
 3 TiO₂). The photocatalytic activity of Ag/AgCl @ chiral TiO₂ nanofibers should
 4 mainly be attributed to two simultaneous processes. The strong electronic coupling
 5 between Ag and AgCl conduction bands which injects photoinduced electrons from
 6 the Ag nanoparticles, quickly and efficiently, into the AgCl [27] and into the TiO₂
 7 helical structure, probably yielding superoxide radicals and finally HO· radicals from
 8 the reductive pathway, as reported with other dyes [28]. However, this effect seems
 9 negligible for the removal of the contaminants since the direct charge transfer from
 10 noble nanoparticles or the internal photoemission from TiO₂ and AgCl [29] only play
 11 a supporting role in the photoelectrical performance. This was verified of the *J-V*
 12 characteristics of the solar cells not sensitized without dye N719 (see Fig S5).
 13 Regarding the effect of the sensitized dye on the removal of TOC and EE2, the redox
 14 potential of N719/sensitized N719 is ~ 1.1 V (vs. normal hydrogen electrode (NHE))
 15 [21] and sensitized N719/oxidized N719 is ~ -0.6 V (vs. NHE) [30] which is sufficient
 16 to oxidize most organic compounds in wastewater, since their redox potentials were
 17 mostly less than 0.6 V vs. NHE [31]. As a result, the reduction of the sensitized dye to
 18 its ground state maintained the cell cycle until all organic contaminants were removed
 19 from the wastewater. Since the synthesized wastewater was acid, the decrease in the
 20 TN should be attributed to the reduction of NO₃⁻ of the wastewater by the electrons
 21 transferred to the photocathode:

2 This significant mass deficit in the TN balance also confirms some gaseous product
3 such as NO and N₂O are generated as a result of NO₃⁻ reduction. The 30% of TN
4 survived from the photoelectrical degradation should be NH₃-N as they cannot be
5 reduced in acid or neutral conditions [32].

6 **3.3. Photoelectrical performance and hydrogen generation of the DSPC**

7 SPR is characterized by a build-up of intense, spatially non-homogeneous oscillating
8 electric fields in the neighbourhood of the nanostructure [22]. The SPR effect at the
9 photoanode improves the efficiency of the DSPCs by (1) increased light absorption
10 due to surface plasmons and light-trapping effects, (2) improved charge separation as
11 a result of the localized electro-magnetic field, (3) the promotion of electron transfer
12 to adsorbed species, and (4) the electron storage effect that can shifts the Fermi level
13 to more negative potentials [33-36]. Although the direct charge transfer from Ag
14 nanoparticles to the semiconductor may also prove useful for the electricity
15 generation as mentioned above, the main mechanism of photo-excitation of the
16 photoanode with visible light implies the sensitization of the N719 dye, and the
17 transfer of excited electrons to the Ag/AgCl @ chiral TiO₂ nanofibers, the external
18 load, the counter cathode and lastly the simultaneous reductions of NO₃⁻, H⁺ and Cu²⁺.
19 The presence of metallic Cu on the surface of the counter electrode after the process
20 was further substantiated by two XPS peaks at 932.6 eV and 952.5 eV (Fig. S4,
21 Supplementary Material). In parallel to the above mechanism, the sensitized N719
22 dye is reduced back to its ground state by the adsorbed organic matter and nitrogen,

1 which were present in the wastewater, therefore, sacrificial organic and inorganic
 2 matter are essential to sustain the mechanism of the DSPCs. This mechanism is
 3 further exemplified by the current-voltage (J - V) and current-power densities (J - P)
 4 plots, which were recorded to investigate the electrical performance of the cell (Fig.
 5 5). The short-circuit current densities (J_{sc}), open-circuit voltage (V_{oc}) and power
 6 densities varied with time during the irradiation of DSPCs. J_{sc} decreased significantly
 7 over time and it even turned to be 0.02 mA/cm² after 80 min and then remained stable,
 8 while V_{oc} just showed slight decrease (Table S2). These should be attributed to the
 9 removal of contaminants in the cell as they functioned as electrons bridges. Moreover,
 10 J_{sc} is determined by electron injection [20,35] which depends on the concentration of
 11 contaminants, hence, J_{sc} decreased eventually to a relatively low level as the
 12 contaminants were totally removed, after 80 min. However, J_{sc} did not decrease to 0
 13 as expected, this may be due to Ag can also be excited by visible-light irradiation
 14 while TiO₂ can be excited by the small fraction of UV accessible under AM 1.5
 15 irradiation, and also produced electron-hole pairs [33]. Then the produced electrons
 16 transferred through external load to counter photocathode while the holes may react
 17 with H₂O. This is consistent with the photoelectrical performances of the solar cells
 18 not sensitized with N719 (Fig. S5, Supplementary Material). Meanwhile, these
 19 produced holes may also oxidize some N719 molecules and disable this DSPC (this
 20 will be discussed in following section). In contrast, V_{oc} is largely affected by the
 21 properties of the photoanode, *i.e.*, the conductive band potential of the photoanode
 22 and the dye absorption number [36], thus V_{oc} decreased.

1 The characterization of the cell under dark conditions is shown in Fig. S6
 2 (Supplementary Material). The dark currents observed due to the presence of CuSO₄
 3 (J_{sc} of 0.016 mA/cm²) were insignificant in comparison with the currents observed
 4 under irradiation (Fig. 5). Cu²⁺ is practically removed from the aqueous solution in
 5 40 min (Fig. 4) to which corresponds a J_{sc} of 4.59 mA/cm².

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

$$7 \quad ff = \frac{P_{\max}}{J_{sc} V_{oc}} \quad (3)$$

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

9 Fig. 6 shows the photogeneration of H₂ over time in the DSPCs. The electrons
 10 transferred to the counter electrodes reduced protons to H₂, although some H₂ could
 11 also be formed during the degradation of organic matter [11, 38]. The H₂ production
 12 was not observed until 40 min *ca.*, when DO and Cu²⁺ were almost totally consumed
 13 (Fig. 4) as the redox potentials of Cu²⁺/Cu (0.3394 V *vs.* NHE) and the redox
 14 potentials of O₂/H₂O (1.229 V *vs.* NHE) were higher than that of H⁺/H₂ (0 *vs.* NHE)
 15 [39]. In agreement with the electrical performance, the rate of H₂ production gradually
 16 decreased as the concentration of contaminants decreased and reached approximately
 17 zero, after 80 min, when the electricity was only generated due to the excitation of
 18 TiO₂ and Ag under irradiation.

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

1 calculated:

$$2 \quad ECE(\%) = \frac{E_{H_2}}{E_{el}} = \frac{2n_t U}{\int P_{max} A dt} \times 100 \quad (4)$$

3 where E_{H_2} is the H_2 energy (J) produced by the cell, E_{el} is generated electricity
4 energy on the photoanode (J), P_{max} is the maximum power density (W/cm^2), A is the
5 irradiated surface area of photoanode (cm^2), n is the total amount of hydrogen
6 produced (mol), U is the hydrogen energy content (122 kJ/g) and t is time (s). As
7 shown in Table S2, 78.1% of the electricity generated from 40 to 50 min was
8 converted to hydrogen energy. While after 60 min, approximately 98% of the
9 electricity was converted due to the total removal of NO_3^- in the wastewater.

10 **3.4. Chirality and plasmonic effect in the DSPC**

11 The highest PCE in this study was 3.09% which is relatively high considering the
12 electrolyte was actual wastewater rather than I^-/I_3^- solution. This supports the superior
13 performance of Ag/AgCl @ chiral TiO_2 nanofibers as photoanode in the DSPC.
14 Herein, the photoanodes prepared with chiral TiO_2 nanofibers, Ag/AgCl@broken
15 chiral TiO_2 nanofibers served as references, to exemplify the chiral plasmonic effect
16 on the performance of the DSPC. The SEM and TEM pictures of these reference
17 photoanode are shown in Fig. S7 (Supplementary Material). The absorption spectrums
18 of Ag/AgCl @ chiral TiO_2 nanofibers thin film and other reference photoanode thin
19 films are shown in Fig. S8 (Supplementary Material). The stronger absorption of
20 Ag/AgCl @ chiral TiO_2 nanofibers at 200-350 nm compared to pure chiral TiO_2
21 nanofibers can be attributed to the characteristic absorption of the AgCl
22 semiconductor [40], besides, Ag NPs can absorb photons from an area much larger

1 than their geometric cross section. Resonance energy transfer (RET), the transfer of
2 energy from a plasmon to a nearby semiconductor, enhances the intensity of the
3 electric field thereby increasing optical absorption [41]. In contrast, the increased
4 response in the visible-light region (400-800 nm) results from the creation of SPR
5 [42]. The significant red shift of the absorption edge observed in the Ag/AgCl @
6 chiral TiO₂ nanofibers (trace c) when compared with Ag/AgCl @ broken chiral TiO₂
7 nanofibers (trace b), demonstrates that controlled chirality at the nanoscale level and
8 the periodic distribution of the plasmonic Ag/AgCl in the chiral TiO₂ nanofiber,
9 induces a greater SPR effect. The nanostructured ordered helical arrangement of the
10 Ag/AgCl nanoparticles induces coupled plasmon waves propagating along the helical
11 path, causing increased absorption of the incident light components that are in tune
12 with the handedness of the helices. The collective plasmons that oscillate along the
13 plasmonic chiral structure of certain handedness lead to different absorptions in
14 response to right- and left- circularly polarized light [42]. Therefore, the acceleration
15 of SPR excitation results from the nanostructured architecture of ordered and
16 periodically positioned Ag/AgCl nanoparticles (Fig. 2), which are irradiated at
17 specific incident polarization angles. Thus, it could be concluded that the more intense
18 SPR created by Ag nanoparticles of Ag/AgCl @ chiral TiO₂ nanofibers can cause a
19 stronger local field enhancement around Ag nanoparticles, which can increase light
20 absorption of surrounding dye molecules in a dye-loaded film (Fig. S8,
21 Supplementary Material). The higher rate of light absorption by the dye can result in
22 an enhancement of the rate of electron injection to the photoanode [43].

1 The production of energy of the [DSPC](#) with the Ag/AgCl @ chiral TiO₂ nanofibers
2 photoanode and with other reference photoanodes were also studied (Fig. S9,
3 Supplementary Material) to exemplify the advantages associated with the use of a
4 chiral plasmonic structure. The PCE values of the cell with Ag/AgCl @ chiral TiO₂
5 nanofibers photoanode were higher than those of reference cell with Ag/AgCl @
6 broken chiral TiO₂ nanofibers, which should be partly attributed to the higher light
7 harvesting efficiency of these materials. Furthermore, in these materials Ag
8 nanoparticles act as an effective ‘antenna’ for the incident visible light that stores the
9 incident energy and create an intense electromagnetic field in the immediate vicinity
10 [33], which in turn increases the rate of electron-hole formation in some localized
11 regions of the semiconductor by a few orders of magnitude [43]. Concurrently,
12 nanofibers owns faster electron transport, slower recombination rate [44,45] and can
13 serve as light-scattering centers to increase the optical [light extinction](#) length in the
14 film, thus also enhancing the light harvesting efficiency [24]. Hence, in the
15 photoanode of this cell, chiral TiO₂ nanofibers and Ag nanoparticles act in a symbiotic
16 relationship that improves the electrical performance of Ag/AgCl @ chiral TiO₂
17 nanofibers film. Firstly, the SPR effect of Ag nanoparticles is accelerated by the chiral
18 structure due to its capacity of tuning the angle of the incident light and the scattering
19 of light. Secondly, the lifetime of the large amount of electrons generated is extended,
20 owing to the faster electron transport and slower recombination rate in the chiral
21 TiO₂ nanofibers. [Thirdly, the surface plasmons and light scattering \(Ag also acts as a](#)
22 [scattering centre\) 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 TiO₂ nanofibers than that of pure chiral TiO₂ 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 DSPC 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 DSPCs [49, 50]. For the particular case of N719 dye, since the redox potential of ROS/H₂O (~ 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

1 consumption of TOC from the wastewater.

2 Such effect was demonstrated by examining the photoanode absorbance and

3 photoelectrical performance of the cell with the wastewater sealed in the cell replaced

4 by fresh wastewater every hour or every two hours (referred as 1h cell and 2h cell).

5 The rate of leached dye (Fig. 7) for the 1h cell was as that with the photoanode

6 immersed in wastewater since the TOC of the wastewater was never totally consumed.

7 In contrast, the rate of leached dye for the 2h cell was much more rapid, implying

8 N719 molecules were oxidized by the excited ROS after the total removal of TOC.

9 Similarly, the photoelectrical performance of the 1h cell (Fig. 8) showed PCE values

10 of the 1h cell decreasing by approximately 50% (mainly due to the lower J_{sc}), and

11 lower V_{oc} after 24 h, which can be ascribed to dye desorption [20]. However, the loss

12 of photoelectrical performance was significantly higher for the 2h cell with a 90%

13 decrease of the PCE after 12 hours, which should be attributed to the oxidization of

14 N719 after the removal of TOC of the wastewater. Therefore, a more stable

15 performance of the photoanodes can be anticipated if the cell is operated with a

16 continuous flow of fresh wastewater. Further research efforts should be directed

17 towards the production of more stable dyes for use in water-based DSPCs including

18 the use of electrolyte additives (such as ionic surfactants) [51-55] and the use of

19 hydrophobic dye sensitizers [49].

1

2

4. Conclusion

In summary, a **DSPC** with Ag/AgCl @ chiral TiO₂ 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 TiO₂ nanofibers photoanode with that of Ag/AgCl @ broken chiral TiO₂ 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 TiO₂ nanofibers.

References

- [1] P.L. Mcarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer - Can this be achieved? *Environ. Sci. Technol.* 45 (2011) 7100-7106.
- [2] H. Liu, B.E. Logan, Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ. Sci. Technol.* 38 (2004) 4040-4046.
- [3] S.K. Chaudhuri, D.R. Lovley, Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. *Nature Biotechnol.* 21 (2003) 1229-1232.
- [4] D. Wang, Y. Li, W. Zhang, Q. Wang, C. Wang, P. Wang, Development and modeling of a flat plate serpentine reactor for photocatalytic degradation of 17-ethinylestradiol. *Environ. Sci. Poll. Res.* 20 (2013) 2321-2329.

- 1 [5] M. Narumiya, N. Nakada, N. Yamashita, H. Tanaka, H., Phase distribution and
2 removal of pharmaceuticals and personal care products during anaerobic sludge
3 digestion. *J. Hazard. Mater.* 260 (2013) 305-312.
- 4 [6] J. Shen, C. Ou, Z. Zhou, J. Chen, H. Fang, X. Sun, J. Li, L. Zhou, L. Wang,
5 pretreatment of 2,4-dinitroanisole (DNAN) producing wastewater using a combined
6 zero-valent iron (ZVI) reduction and Fenton oxidation process. *J. Hazard. Mater.* 260
7 (2013) 993-1000.
- 8 [7] S. Papadimitriou, S. Armyanov, E. Valova, A. Hubin, O. Steenhat, E. Pavlidou, G.
9 Kokkinidis, S. Sotiropoulos, Methanol oxidation at Pt-Cu, Pt-Ni, and Pt-Co electrode
10 coatings prepared by a galvanic replacement process. *J. Phys. Chem. C* 114 (2010)
11 5217-5223.
- 12 [8] V.K. Gupta, R. Jain, A. Mittal, T.A. Saleh, A. Nayak, S. Agarwal, S. Sikarwar,
13 Photocatalytic degradation of toxic dye amaranth on TiO₂/UV in aqueous suspensions.
14 *Mater. Sci. Eng.: C* 32 (2012) 12–17.
- 15 [9] D.M.A. Alrousan, M.I. Polo-Lopez, P.S.M., Dunlop, P. Fernandez-Ibanez, J.A.
16 Byrne, Solar photocatalytic disinfection of water with immobilised titanium dioxide in
17 re-circulating flow CPC reactors. *Appl. Catal. B: Environ.* 128 (2012) 126-134.
- 18 [10] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent development in
19 photocatalytic water treatment technology: A review. *Water Res.* 44 (2010)
20 2997–3027.
- 21 [11] J. Kim, W. Choi, W. Hydrogen producing water treatment through solar
22 photocatalysis. *Energy Environ. Sci.* 3 (2010) 1042-1045.

- 1 [12] J. Kim, D. Monllor-Satoca, W. Choi, Simultaneous production of hydrogen with
2 the degradation of organic pollutants using TiO₂ Photocatalyst modified with dual
3 surface components. *Energy Environ. Sci.* 5 (2012) 7647-7656.
- 4 [13] K. Li, Y. Xu, Y. He, C. Yang, Y. Wang, J. Jia, J. Photocatalytic fuel cell (PFC)
5 and dye self-photosensitization photocatalytic fuel cell (DSPFC) with BiOCl/Ti
6 photoanode under UV and visible light irradiation. *Environ. Sci. Technol.* 47 (2013)
7 3490-3497.
- 8 [14] W. Zhang, Y. Li, C. Wang, P. Wang, Q. Wang, Energy recovery during
9 advanced wastewater treatment: Simultaneous estrogenic activity removal and
10 hydrogen production through solar photocatalysis. *Water Res.* 47 (2013) 1480-1490.
- 11 [15] W. Zhang, Y. Li, C. Wang, P. Wang, Q. Wang, D. Wang, Mechanisms of
12 simultaneous hydrogen production and estrogenic activity removal from secondary
13 effluent through solar photocatalysis. *Water Res.* 47 (2013) 3173-3182.
- 14 [16] P. Lianos, Production of electricity and hydrogen by photocatalytic degradation
15 of organic wastes in a photoelectrochemical cell. The concept of the Photofuelcell: A
16 review of a re-emerging research field. *J. Hazard. Mater.* 185 (2011) 575-590
- 17 [17] E. Stathatos and P. Lianos, S.M. Zakeeruddin, P. Liska, M. Grätzel. A
18 Quasi-solid-state dye-sensitized solar cell based on a Sol-Gel nanocomposite
19 electrolyte containing ionic liquid. *Chem. Mater.* 15 (2003) 1825-1829.
- 20 [18] E. Stathatos, P. Lianos, U. Lavrencic-Stangar, B. Orel, A High-Performance
21 Solid-State Dye-Sensitized Photoelectrochemical Cell Employing a Nanocomposite
22 Gel Electrolyte Made by the Sol-Gel Route. *Adv. Mater.* 14 (2002) 354-357

- 1 [19] M. Antoniadou and P. Lianos, Production of electricity by photoelectrochemical
2 oxidation of ethanol in a PhotoFuelCell. *Appl. Catal. B. Environ.* 99 (2010) 307-313.
- 3 [20] Z. Ning, Y. Fu, H. Tian, Improvement of dye-sensitized solar cells: What we
4 know and what we need to know. *Energy Environ. Sci.* 3 (2010) 1170-1181.
- 5 [21] F. Hao, P. Dong, Q. Luo, J. Li, J. Lou, H. Lin, Recent advances in alternative
6 cathode materials for iodine-free dye-sensitized solar cell. *Energy Environ. Sci.* 6
7 (2013) 2003-2019
- 8 [22] D. Wang, Y. Li, G. Li Puma, C. Wang, P. Wang, W. Zhang, Q. Wang,
9 Visible-light driven plasmon photocatalyst Ag/AgCl @ helical chiral TiO₂ nanofibers.
10 *Chem. Commun.* 49 (2013) 10367-10369.
- 11 [23] A. Mills, N. Elliott, G. Hill, D. Fallis, J.R. Durrant, R.L. Willis, Preparation and
12 characterization of novel thick sol-gel titania film photocatalysts. *Photochem.*
13 *Photobiol. Sci.* 2 (2003) 591-596.
- 14 [24] Y. Bai, H. Yu, Z. Li, R. Amal, G.Q. Lu, L. Wang, In situ growth of a ZnO
15 nanowire network within a TiO₂ nanoparticles film for enhanced dye-sensitized solar
16 cells. *Advan. Mater.* 24 (2012) 5850-5856.
- 17 [25] D. Wang, Y. Li, G. Li, C. Wang, W. Zhang, Q. Wang, Modeling of quantitative
18 effects of water components on the photocatalytic degradation of 17
19 α -ethynylestradiol in a modified flat plate serpentine reactor. *J. Hazard. Mater.*
20 254-255 (2013) 64-71.
- 21 [26] J. Yu, G. Dai, B. Huang, Fabrication and characterization of visible-light driven
22 plasmonic photocatalyst Ag/AgCl/TiO₂ nanotube arrays. *J. Phys. Chem. C* 113 (2009)

1 16394-16401.

2 [27] Y. Tang, Z. Jiang, G. Xing, A. Li, P.D. Kanhere, Y. Zhang, T.C. Sum, S. Li, X.

3 Chen, Z. Dong, Z. Chen, Efficient Ag@AgCl cubic cage photocatalysts profit from

4 ultrafast plasmon-induced electron transfer processes. *Adv. Functional Mater.* 23

5 (2013) 2932-2940.

6 [28] T.X. Wu, G.M. Liu, J.C. Zhao, H. Hidaka, N. Serpone, Photoassisted degradation

7 of dye pollutants. V. Self-photosensitized oxidative transformation of rhodamine B

8 under visible light irradiation in aqueous TiO₂ dispersions. *J. Phys. Chem. B* 102

9 (1998) 5845-5851.

10 [29] C. Hagglund, M. Zach, B. Kasemo, Enhanced charge carrier generation in dye

11 sensitized solar cells by nanoparticles plasmons. *Appl. Phys. Lett.* 92 (2008) 013113.

12 [30] T. Daeneke, T-H. Kwon, A.B. Holmes, N.W. Duffy, U. Bach, L. Spiccia,

13 High-efficiency dye-sensitized solar cells with ferrocene-base electrolytes. *Nature*

14 *Chem.* 3 (2011) 211-215.

15 [31] D.T. Scott, D.M. McKnight, E.L. Blunt-Harris, S. E. Kolesar, D.R. Lovely

16 Quinone moieties act as electron acceptors in the reduction of humic substances by

17 humics-reducing microorganisms. *Environ. Sci. Technol.* 32 (1998) 2984-2989.

18 [32] J. Lee, H. Park, W. Choi, Selective Photocatalytic oxidation of NH₃ to N₂ on

19 platinized TiO₂ in water. *Environ. Sci. Technol.* 36 (2002) 5462-5468.

20 [33] H. Choi, W.T. Chen, P.V. Kamat, Know thy nano neighbor. Plasmonic versus

21 electron charging effects of metal nanoparticles in dye-sensitized solar cell. *ACS*

22 *Nano* 6 (2012) 4418-4427.

- 1 [34] D. Bui, J. Mu, L. Wang, S. Kang, X. Li, Preparation of Cu-loaded SrTiO₃
2 nanoparticles and their photocatalytic activity for hydrogen evolution from methanol
3 aqueous solution. Appl. Surf. Sci. 274 (2013) 328-333.
- 4 [35] T. Marinado, K. Nonomura, J. Nissfolk, M.K. Karlsson, D.P. Hagberg, L. Sun, S.
5 Mori, A. Hagfeldt, How the nature of triphenylamine-polyene dyes in dye-sensitized
6 solar cells affects the open-circuit voltage and electron lifetimes. Langmuir 26 (2009)
7 2592-2598.
- 8 [36] B.C. O'Regan, J.R. Durrant. Kinetic and energetic paradigms for dye-sensitized
9 solar cells: moving from the ideal to the real. Accounts of Chem. Res. 42, (2009)
10 1799-1808.
- 11 [37] B.C. O'Regan, M. Gratzel, Low-cost, High-efficiency solar cell based on dye
12 sensitized colloidal TiO₂ films. Nature 345 (1991) 737-740.
- 13 [38] H.C. Park, D. Vecitis, W. Choi, O. Weres, M.R. Hoffmann, Solar-powered
14 production of molecular hydrogen from water. J. Phys. Chem. C 112 (2008) 885-889.
- 15 [39] Dean, J.A., 1998. Lange's handbook of chemistry 15th ed. McGraw-Hill
16 Professional
- 17 [40] P. Wang, B. Huang, Z. Lou, X. Zhang, X. Qin, Y. Dai, Z. Zheng, X. Wang,
18 Synthesis of highly efficient Ag@AgCl plasmonic photocatalysts with various
19 structures. Chem.-An European J. 16 (2010) 538-544.
- 20 [41] S.C. Warren, E. Thimsen, Plasmonic solar water splitting. Energy Environ. Sci. 5
21 (2012) 5133-5146.
- 22 [42] X. Shen, C. Shen, J. Wang, D. Shi, Z. Wang, N. Liu, B. Ding, Rolling up gold

1 nanoparticle-dressed DNA origami into three-dimensional plasmonic chiral
2 nanostructures. *J. Am. Chem. Soc.* 134 (2012) 146-149.

3 [43] J. Lee, T. Javed, T. Skeini, A.O. Govorov, G.W. Bryant, N.A. Kotov,
4 Bioconjugated Ag nanoparticles and CdTe nanowires: Metamaterials with
5 field-enhanced light absorption. *Angewandte Chemie Int. Ed.* 45 (2006) 4819-4823.

6 [44] J. Liao, B. Lei, D. Kuang, C. Su, Tri-functional hierarchical TiO₂ spheres
7 consisting of anatase nanorods and nanoparticles for high efficiency dye-sensitized
8 solar cells. *Energy Environ. Sci.* 4 (2011) 4079-4085.

9 [45] Y. Ohsaki, N. Masaki, T. Kitamura, Y. Wada, T. Okamoto, T. Sekino, K. Niihara,
10 S. Yanagida, Dye-sensitized TiO₂ nanotube solar cells: fabrication and electronic
11 characterization. *Phys. Chem. Chem. Phys.* 7 (2005) 4157-4163.

12 [46] B. Ding, B.J. Lee, M. Yang, H.S. Jung, J-K. Lee, Surface-plasmon assisted
13 energy conversion in dye-sensitized solar cells. *Adv. Energy Mater.* 1 (2011) 415-421.

14 [47] M.D. Brown, T. Suteewong, R.S.S. Kumar, V. d’Innocenzo, A. Petrozza, M.M.
15 Lee, U. Wiesner, H.J. Snaith, Plasmonic dye-sensitized solar cells using core-shell
16 metal-insulator nanoparticles. *Nano Lett.* 11 (2011) 438-445.

17 [48] H.J. Son, C. Prasittichai, J.E. Mondloch, L. Luo, J.K.D.W. Wu, O.K., Farha, J.T.
18 Hupp, Dye stabilization and enhanced photoelectrode wettability in water-based
19 dye-sensitized solar cells through post-assembly atomic layer deposition of TiO₂. *J.*
20 *Am. Chem. Soc.* 135 (2013) 11529-11532.

21 [49] C. Law, S.C. Pathirana, X. Li, A.Y. Anderson, P.R.F. Barnes, A. Listorti, T.H.
22 Ghaddar, B.C. O’Regan, Water-based electrolytes for dye-sensitized solar cell. *Adv.*

1 Mater. 22 (2010) 4505-4509.

2 [50] Y. Liu, Y., A. Hagfeldt, X.R. Xiao, S.E. Lindquist, Investigation of influence of
3 redox species on the interfacial energetics of a dye-sensitized nanoporous TiO₂ solar
4 cell. Solar Energy Materials Solar Cells 55 (1998) 267-281.

5 [51] H. Zhang, L. Qiu, X. Dan, W. Zhang, F. Yan, Performance enhancement of water
6 based dye-sensitized solar cells via addition of ionic surfactants. J. Mater. Chem. 2
7 (2014) 2221-2226.

8 [52] T. Daeneke, Y. Uemura, N.W. Duffy, A.J. Mozer, N. Koumura, U. Bach L.
9 Spiccia, Aqueous dye-sensitized solar cell electrolytes based on the
10 ferricyanide-ferrocyanide redox couple. Advan. Mater. 14 (2012) 1222-1225.

11 [53] Y. Jung, B. Yoo, M.K. Lim, S.Y. Lee, K.J. Kim, Effect of triton-X in water-added
12 electrolytes on the performance of dye-sensitized solar cells. Electrochimica Acta 54
13 (2009) 6286-6291.

14 [54] C.Lian, D.Zhi, S. Xu, H. Liu, and Y. Hu. "A lattice model for thermally-sensitive
15 core-shell hydrogels." J. Colloid Interface Sci. 406 (2013) 148-153.

16 [55] C. Lian, L. Wang, X. Chen, X. Han, S. Zhao, H. Liu, Y. Hu, Modeling Swelling
17 Behavior of Thermoresponsive Polymer Brush with Lattice Density Functional
18 Theory, Langmuir 30 (2014) 4040-4048.

19 **Figure Captions**

20 **Fig. 1.** Schematic diagram of the cell.

1 **Fig. 2.** Microscopy and schematic drawing of Ag/AgCl @ chiral TiO₂ nanofibers. (A)
2 SEM image of Ag/AgCl @ chiral TiO₂ nanofibers. (B, C) TEM images of Ag/AgCl
3 @ chiral TiO₂ nanofibers, which shows there are some nanoparticles deposited on the
4 surfaces of Ag/AgCl @ chiral TiO₂ nanofibers. (D) Structural model showing
5 Ag/AgCl nanoparticles deposited on the double helices. The scale bars in A, B and C
6 represent 40, 10 and 20 nm, respectively.

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

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

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

14 **Fig. 6.** The accumulation of H₂ in the cell (■) and rate of H₂ production (●). The pH
15 of wastewater was adjusted to 6.0.

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

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

1 Figures

Fig. 1.

1

2

3

Fig. 2.

4

5

6

Fig. 3.

7

8

1

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

1
2
3
4
5
6
7
8
9

1

2

3

4

Fig. 8.

Dye-sensitized solar cells on plasmonic Ag/AgCl @ chiral TiO₂ nanofibers for treatment of urban wastewater effluents, with simultaneous production of hydrogen and electricity

Dawei Wang ^a, Yi Li^{a*}, Gianluca Li Puma^{b*}, Chao Wang ^a, Peifang Wang ^a, Wenlong Zhang ^a and Qing Wang ^a

^a *Key Laboratory of Integrated Regulation and Resource Development of Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Xi Kang Road #1, Nanjing 210098, PR China; E-mail: envly@hhu.edu.cn*

^b *Environmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom; E-mail: g.lipuma@lboro.ac.uk*

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 TiO₂ nanofibers (Ag and AgCl nanoparticles supported on chiral TiO₂ nanofibers). The electrolyte in the DSSC was actual wastewater spiked with an estrogen (17- β -ethynylestradiol, EE2) and a heavy metal (Cu²⁺). The contaminants in the wastewater rather than I⁻/I₃⁻ (usual electrolyte in conventional DSSCs) acted as electrons bridges for the stabilization of charges in this DSSC. Almost total removal of total organic carbon, Cu²⁺ 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 H₂ after the consumption of dissolved oxygen, Cu²⁺ and TN. This performance was attributed to the “symbiotic” relationship between the TiO₂ 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 TiO₂ 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_2O_2 , $\text{HO}\cdot$, $\text{O}_2\cdot^-$) 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 scarce. 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 *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 DSSCs 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 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. 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 TiO₂ nanofibers photoanode.

C₁₈-D-Glu was chosen as template for the synthesis of chiral TiO₂ nanofibers [22]. In a typical synthesis, C₁₈-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 TiO₂ nanofibers were used to fabricate Ag/AgCl @ chiral TiO₂ nanofibers. In a typical synthesis of Ag/AgCl @ chiral TiO₂ nanofibers, pure chiral TiO₂ 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 $K\alpha$ radiation (40 kV, 20 mA). X-ray photoelectron spectroscopy (XPS) results were obtained with PHI 5000C ESCA with Mg $K\alpha$ 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-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.). The amount of collected H₂ 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 TiO₂ nanofibers.

SEM pictures of the Ag/AgCl @ chiral TiO₂ 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 TiO₂ 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 TiO₂ nanofibers, preferentially at the outer edges of the TiO₂ 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 TiO₂ 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 Ag⁰ and Ag⁺¹ could be verified by further peaks divisions [28]. Consequently, the XPS analyses suggested that the nanoparticles deposited on chiral TiO₂ 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 Cu²⁺ representing for heavy metal ions were spiked into the wastewater at specific concentrations to investigate the removal of contaminants (TOC, TN, EE2 and Cu²⁺) in the cell (Fig. 3). TOC, EE2 and Cu²⁺ 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 TiO₂ nanofibers and of (ii) the oxidization ability of sensitized dyes. Regarding the first effect, Ag/AgCl @ chiral TiO₂ 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 TiO₂) by the

dipole-dipole interaction between the donor (Ag) and the acceptors (AgCl and TiO₂). The photocatalytic activity of Ag/AgCl @ chiral TiO₂ 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 TiO₂ 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 TiO₂ 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 NO₃⁻ by the electrons transferred to the photocathode:

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/cm² 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 TiO₂ 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 H₂O. 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]:

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

where $P_{\max}$ 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_2O (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:

$$ECE(\%) = \frac{E_{H_2}}{E_{el}} = \frac{2n_t U}{\int P_{\max} A dt} \times 100 \quad (4)$$

where E_{H_2} is the H_2 energy (J) produced by the cell, E_{el} is generated electricity energy on the photoanode (J), $P_{\max}$ 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^{2+} and NO_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_3^- solution. This supports the superior performance of Ag/AgCl @ chiral TiO_2 nanofibers as photoanode in the DSSC. 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 DSSC. The SEM and TEM pictures of these reference photoanode are shown in Fig. S6. The absorption spectrums of Ag/AgCl @ chiral TiO_2 nanofibers thin film and other reference photoanode thin films are shown in Fig. S7. 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 [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_2 nanofibers (trace c) when compared with Ag/AgCl @ broken chiral TiO_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 TiO₂ 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 TiO₂ 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 TiO₂ nanofibers photoanode were higher than those of reference cell with Ag/AgCl @ broken chiral TiO₂ 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 TiO₂ nanofibers and Ag nanoparticles act in a symbiotic relationship that improves the electrical performance of Ag/AgCl @ chiral TiO₂ 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, owing to the faster electron transport and slower recombination rate in the chiral TiO₂ nanofibers. However, it was unexpected that only slight higher PCE of the cell with Ag/AgCl @ chiral TiO₂ nanofibers than that of pure chiral TiO₂ 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.*,

A_t/A_0) [51]. 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 TiO₂ 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 TiO₂ nanofibers photoanode with that of Ag/AgCl @ broken chiral TiO₂ 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 TiO₂ nanofibers.

References

- [1] P.L. Mcarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer - Can this be achieved? *Environ. Sci. Technol.* 45 (2011) 7100-7106.
- [2] H. Liu, B.E. Logan, Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ. Sci. Technol.* 38 (2004) 4040-4046.
- [3] S.K. Chaudhuri, D.R. Lovley, Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. *Nature Biotechnol.* 21 (2003) 1229-1232.
- [4] D. Wang, Y. Li, W. Zhang, Q. Wang, C. Wang, P. Wang, Development and modeling of a flat plate serpentine reactor for photocatalytic degradation of 17-ethinylestradiol. *Environ, Sci. Poll. Res.* 20 (2013) 2321–2329.
- [5] M. Narumiya, N. Nakada, N. Yamashita, H. Tanaka, H., Phase distribution and

removal of pharmaceuticals and personal care products during anaerobic sludge digestion. *J. Hazard. Mater.* 260 (2013) 305-312.

[6] J. Shen, C. Ou, Z. Zhou, J. Chen, H. Fang, X. Sun, J. Li, L. Zhou, L. Wang, pretreatment of 2,4-dinitroanisole (DNAN) producing wastewater using a combined zero-valent iron (ZVI) reduction and Fenton oxidation process. *J. Hazard. Mater.* 260 (2013) 993-1000.

[7] S. Papadimitriou, S. Armyanov, E. Valova, A. Hubin, O. Steenhat, E. Pavlidou, G. Kokkinidis, S. Sotiropoulos, Methanol oxidation at Pt-Cu, Pt-Ni, and Pt-Co electrode coatings prepared by a galvanic replacement process. *J. Phys. Chem. C* 114 (2010) 5217-5223.

[8] V.K. Gupta, R. Jain, A. Mittal, T.A. Saleh, A. Nayak, S. Agarwal, S. Sikarwar, Photocatalytic degradation of toxic dye amaranth on TiO₂/UV in aqueous suspensions. *Mater. Sci. Eng.: C* 32 (2012) 12–17.

[9] D.M.A. Alrousan, M.I. Polo-Lopez, P.S.M., Dunlop, P. Fernandez-Ibanez, J.A. Byrne, Solar photocatalytic disinfection of water with immobilised titanium dioxide in re-circulating flow CPC reactors. *Appl. Catal. B: Environ.* 128 (2012) 126-134.

[10] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent development in photocatalytic water treatment technology: A review. *Water Res.* 44 (2010) 2997–3027.

[11] J. Kim, W. Choi, W. Hydrogen producing water treatment through solar photocatalysis. *Energy Environ. Sci.* 3 (2010) 1042-1045.

[12] J. Kim, D. Monllor-Satoca, W. Choi, Simultaneous production of hydrogen with

the degradation of organic pollutants using TiO_2 Photocatalyst modified with dual surface components. *Energy Environ. Sci.* 5 (2012) 7647-7656.

[13] K. Li, Y. Xu, Y. He, C. Yang, Y. Wang, J. Jia, J. Photocatalytic fuel cell (PFC) and dye self-photosensitization photocatalytic fuel cell (DSPFC) with BiOCl/Ti photoanode under UV and visible light irradiation. *Environ. Sci. Technol.* 47 (2013) 3490-3497.

[14] W. Zhang, Y. Li, C. Wang, P. Wang, Q. Wang, Energy recovery during advanced wastewater treatment: Simultaneous estrogenic activity removal and hydrogen production through solar photocatalysis. *Water Res.* 47 (2013) 1480-1490.

[15] W. Zhang, Y. Li, C. Wang, P. Wang, Q. Wang, D. Wang, Mechanisms of simultaneous hydrogen production and estrogenic activity removal from secondary effluent through solar photocatalysis. *Water Res.* 47 (2013) 3173-3182.

[16] Z. Ning, Y. Fu, H. Tian, Improvement of dye-sensitized solar cells: What we know and what we need to know. *Energy Environ. Sci.* 3 (2010) 1170-1181.

[17] F. Hao, P. Dong, Q. Luo, J. Li, J. Lou, H. Lin, Recent advances in alternative cathode materials for iodine-free dye-sensitized solar cell. *Energy Environ. Sci.* 6 (2013) 2003-2019

[18] S.K. Mohapatra, M. Misra, V.K. Mahajan, K.S. Raja, Design of a highly efficient photoelectrolytic cell for hydrogen generation by water splitting: application of $\text{TiO}_{2-x}\text{C}_x$ nanotubes as a photoanode and Pt/TiO_2 nanotubes as a cathode. *J. Phys. Chem. C* 111 (2007) 8677-8685.

[19] N. Kondamudi, M. Misra, M., Banerjee, S. Subarna., S. Mohapatra, S.,

Mohapatra, Simultaneous production of glyceric acid and hydrogen from the photooxidation of crude glycerol using TiSi_2 . *Appl. Catal. B: Environ.* 126 (2012) 180-185.

[20] Z. Liu, B. Pesic, K.S. Raja, R.R. Rangaraju, M. Misra, Hydrogen generation under sunlight by self ordered TiO_2 nanotube arrays. *Int. J. Hydrogen Energy* 34 (2009) 3250-3257.

[21] M. Antoniadou, P. Bouras, N. Strataki, P. Lianos, Hydrogen and electricity generation by photoelectrochemical decomposition of ethanol over nanocrystalline titania. *Int. J. Hydrogen Energy* 33 (2008) 5045-5051.

[22] D. Wang, Y. Li, G. Li Puma, C. Wang, P. Wang, W. Zhang, Q. Wang, Visible-light driven plasmon photocatalyst Ag/AgCl @ helical chiral TiO_2 nanofibers. *Chem. Commun.* 49 (2013) 10367-10369.

[23] H.A. Atwater, A. Polman, A., Plasmonics for improved photovoltaic devices. *Nature Mater.* 9 (2010) 205-213.

[24] S.A. Maier, *Plasmonics—Fundamentals and Applications*; Springer: New York, 2007.

[25] K.E. Shopsowitz, H. Qi, W.Y. Hamad, M.J. Maclachlan, Free-standing mesoporous silica films with tunable chiral nematic structures. *Nature* 468 (2010) 422-425.

[26] J. Xie, S. Che, Chirality of anisotropic metal nanowires with distinct multihelix. *Chemistry-An European J.* 18 (2012) 15954-15959.

[27] A. Mills, N. Elliott, G. Hill, D. Fallis, J.R. Durrant, R.L. Willis, Preparation and

characterization of novel thick sol-gel titania film photocatalysts. *Photochem. Photobiol. Sci.* 2 (2003) 591-596.

[28] Y. Bai, H. Yu, Z. Li, R. Amal, G.Q. Lu, L. Wang, In situ growth of a ZnO nanowire network within a TiO₂ nanoparticles film for enhanced dye-sensitized solar cells. *Advan. Mater.* 24 (2012) 5850-5856.

[29] Wang, D., Li, Y., Li, G., Wang, C., Zhang, W., Wang, Q., 2013c. Modeling of Quantitative Effects of Water Components on the Photocatalytic Degradation of 17 α -ethynylestradiol in A Modified Flat Plate Serpentine Reactor. *Journal of Hazardous Materials* 254-255, 64-71.

[30] J. Yu, G. Dai, B. Huang, Fabrication and characterization of visible-light driven plasmonic photocatalyst Ag/AgCl/TiO₂ nanotube arrays. *J. Phys. Chem. C* 113 (2009) 16394-16401.

[31] Y. Tang, Z. Jiang, G. Xing, A. Li, P.D. Kanhere, Y. Zhang, T.C. Sum, S. Li, X. Chen, Z. Dong, Z. Chen, Efficient Ag@AgCl cubic cage photocatalysts profit from ultrafast plasmon-induced electron transfer processes. *Adv. Functional Mater.* 23 (2013) 2932-2940.

[32] T.X. Wu, G.M. Liu, J.C. Zhao, H. Hidaka, N. Serpone, Photoassisted degradation of dye pollutants. V. Self-photosensitized oxidative transformation of rhodamine B under visible light irradiation in aqueous TiO₂ dispersions. *J. Phys. Chem. B* 102 (1998) 5845-5851.

[33] C. Hagglund, M. Zach, B. Kasemo, Enhanced charge carrier generation in dye sensitized solar cells by nanoparticles plasmons. *Appl. Phys. Lett.* 92 (2008) 013113

- [34] K. Ishikawa, C.-J. Wen, K. Yamada, T. Okubo, The photocurrent of dye-sensitized solar cells enhanced by the surface plasmon resonance. *J. Chem. Eng. Japan.* 37 (2004) 645-649.
- [35] D.T. Scott, D.M. McKnight, E.L. Blunt-Harris, S. E. Kolesar, D.R. Lovely Quinone moieties act as electron acceptors in the reduction of humic substances by humics-reducing microorganisms. *Environ. Sci. Technol.* 32 (1998) 2984-2989.
- [36] J. Lee, H. Park, W. Choi, Selective Photocatalytic oxidation of NH_3 to N_2 on platinized TiO_2 in water. *Environ. Sci. Technol.* 36 (2002) 5462-5468.
- [37] H. Choi, W.T. Chen, P.V. Kamat, Know thy nano neighbor. Plasmonic versus electron charging effects of metal nanoparticles in dye-sensitized solar cell. *ACS Nano* 6 (2012) 4418-4427.
- [38] D. Bui, J. Mu, L. Wang, S. Kang, X. Li, Preparation of Cu-loaded SrTiO_3 nanoparticles and their photocatalytic activity for hydrogen evolution from methanol aqueous solution. *Appl. Surf. Sci.* 274 (2013) 328-333.
- [39] T. Marinado, K. Nonomura, J. Nissfolk, M.K. Karlsson, D.P. Hagberg, L. Sun, S. Mori, A. Hagfeldt, How the nature of triphenylamine-polyene dyes in dye-sensitized solar cells affects the open-circuit voltage and electron lifetimes. *Langmuir* 26 (2009) 2592-2598.
- [40] B.C. O'Regan, J.R. Durrant. Kinetic and energetic paradigms for dye-sensitized solar cells: moving from the ideal to the real. *Accounts of Chem. Res.* 42, (2009) 1799-1808.
- [41] B.C. O'Regan, M.A. Gratzel, Low-cost, High-efficiency solar cell based on dye

sensitized colloidal TiO₂ films. *Nature* 24 (1991) 737–740.

[42] H.C. Park, D. Vecitis, W. Choi, O. Weres, M.R. Hoffmann, Solar-powered production of molecular hydrogen from water. *J. Phys. Chem. C* 112 (2008) 885-889.

[43] Dean, J.A., 1998. *Lange's handbook of chemistry* 15th ed. McGraw-Hill Professional

[44] P. Wang, B. Huang, Z. Lou, X. Zhang, X. Qin, Y. Dai, Z. Zheng, X. Wang, Synthesis of highly efficient Ag@AgCl plasmonic photocatalysts with various structures. *Chem.-An European J.* 16 (2010) 538-544.

[45] S.C. Warren, E. Thimsen, Plasmonic solar water splitting. *Energy Environ. Sci.* 5 (2012) 5133-5146.

[46] X. Shen, C. Shen, J. Wang, D. Shi, Z. Wang, N. Liu, B. Ding, Rolling up gold nanoparticle-dressed DNA origami into three-dimensional plasmonic chiral nanostructures. *J. Am. Chem. Soc.* 134 (2012) 146-149.

[47] J. Lee, T. Javed, T. Skeini, A.O. Govorov, G.W. Bryant, N.A. Kotov, Bioconjugated Ag nanoparticles and CdTe nanowires: Metamaterials with field-enhanced light absorption. *Angewandte Chemie Int. Ed.* 45 (2006) 4819-4823.

[48] J. Liao, B. Lei, D. Kuang, C. Su, Tri-functional hierarchical TiO₂ spheres consisting of anatase nanorods and nanoparticles for high efficiency dye-sensitized solar cells. *Energy Environ. Sci.* 4 (2011) 4079-4085.

[49] Y. Ohsaki, N. Masaki, T. Kitamura, Y. Wada, T. Okamoto, T. Sekino, K. Niihara, S. Yanagida, Dye-sensitized TiO₂ nanotube solar cells: fabrication and electronic characterization. *Phys. Chem. Chem. Phys.* 7 (2005) 4157-4163.

- [50] M.D. Brown, T. Suteewong, R.S.S. Kumar, V. d’Innocenzo, A. Petrozza, M.M. Lee, U. Wiesner, H.J. Snaith, Plasmonic dye-sensitized solar cells using core-shell metal-insulator nanoparticles. *Nano Lett.* 11 (2011) 438-445.
- [51] H.J. Son, C. Prasittichai, J.E. Mondloch, L. Luo, J.K.D.W. Wu, O.K., Farha, J.T. Hupp, Dye stabilization and enhanced photoelectrode wettability in water-based dye-sensitized solar cells through post-assembly atomic layer deposition of TiO₂. *J. Am. Chem. Soc.* 135 (2013) 11529-11532.
- [52] C. Law, S.C. Pathirana, X. Li, A.Y. Anderson, P.R.F. Barnes, A. Listorti, T.H. Ghaddar, B.C. O’Regan, Water-based electrolytes for dye-sensitized solar cell. *Adv. Mater.* 22 (2010) 4505-4509.
- [53] Y. Liu, Y., A. Hagfeldt, X.R. Xiao, S.E. Lindquist, Investigation of influence of redox species on the interfacial energetics of a dye-sensitized nanoporous TiO₂ solar cell. *Solar Energy Materials Solar Cells* 55 (1998) 267-281.
- [54] H. Zhang, L. Qiu, X. Dan, W. Zhang, F. Yan, Performance enhancement of water based dye-sensitized solar cells via addition of ionic surfactants. *J. Mater. Chem.* 2 (2014) 2221-2226.
- [55] T. Daeneke, Y. Uemura, N.W. Duffy, A.J. Mozer, N. Koumura, U. Bach L. Spiccia, Aqueous dye-sensitized solar cell electrolytes based on the ferricyanide-ferrocyanide redox couple. *Advan. Mater.* 14 (2012) 1222-1225.
- [56] Y. Jung, B. Yoo, M.K. Lim, S.Y. Lee, K.J. Kim, Effect of triton-X in water-added electrolytes on the performance of dye-sensitized solar cells. *Electrochimica Acta* 54 (2009) 6286-6291.

Figure Captions

Fig. 1. Schematic diagram of the cell.

Fig. 2. Microscopy and schematic drawing of Ag/AgCl @ chiral TiO₂ nanofibers. (A) SEM image of Ag/AgCl @ chiral TiO₂ nanofibers. (B, C) TEM images of Ag/AgCl @ chiral TiO₂ nanofibers, which shows there are some nanoparticles deposited on the surfaces of Ag/AgCl @ chiral TiO₂ nanofibers. (D) Structural model showing Ag/AgCl nanoparticles deposited on the double helices. 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, Cu²⁺ 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 H₂ in the cell (■) and rate of H₂ production (●). The pH of wastewater was adjusted to 6.0.

Fig. 6. (A) UV-vis absorption spectrums of (a) Pure chiral TiO₂ nanofibers. (b) Ag/AgCl @ broken chiral TiO₂ nanofibers. (c) Ag/AgCl @ chiral TiO₂ 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.

Figures

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 TiO₂ nanofibers

Supplementary Material

[Click here to download Supplementary Material: Revised Supplementary Material \(10.25\).doc](#)