1	Improvement in settleability and dewaterability of waste
2	activated sludge by solar photocatalytic treatment in
3	Ag/TiO <sub>2</sub> -coated glass tubular reactor
4	
5	Chunguang Liu <sup>a</sup> , Zhongfang Lei <sup>a</sup> , Yingnan Yang <sup>a</sup> , Haifeng Wang <sup>a</sup> , Zhenya Zhang <sup>a,*</sup>
6	
7	<sup>a</sup> Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1
8	Tennodai, Tsukuba, Ibaraki 305-8572, Japan
9	<sup>b</sup> Chinese Academy of Agricultural Mechanization Sciences, No.1 Beishatan
10	Deshengmen Wai, Beijing 100083, China
11	
12	
13	
14	
15	
16	
17	
18	
10	
19	
20	
21	
22	
23	
2J	

<sup>\*</sup>Corresponding author: Zhenya Zhang. Tel/fax.: +81 29 853 4712. E-mail address: zhang.zhenya.fu@u.tsukuba.ac.jp (Z. Zhang).

## 2 Abstract

3	In this study, photocatalysis was used to improve the dewaterability and
4	settleability of waste activated sludge (WAS) by a solar photocatalytic reactor with
5	transparent Ag/TiO <sub>2</sub> film as photocatalyst. Specific resistance of filtration (SRF) and
6	sludge volume index (SVI) were used to evaluate WAS dewaterability and settleability,
7	respectively, and the mechanism of photocatalysis was interpreted from the changes
8	of pellets, loosely/tightly bound extracellular polymeric substances
9	(LB-EPS/TB-EPS), proteins (PN) and polysaccharides (PS) in WAS. Results showed
10	that the SRF and SVI values decreased by $86.0\%$ and $80.0\%$ , respectively after
11	photocatalysis treatment for 18 h. The changes of LB-EPS/TB-EPS and morphology
12	of WAS indicated that WAS was degraded in a stepwise and mild manner, in which
13	the sludge pellets were possibly converted into TB-EPS and then LB-EPS.
14	Simultaneously, LB-EPS were degraded into carbon dioxide and water by Ag/TiO <sub>2</sub>
15	photocatalysis.
16	Key words: Ag/TiO <sub>2</sub> ; solar photocatalysis; waste activated sludge; dewaterability;
17	settleability
18	
19	1. Introduction
20	Large quantities of wastewater is treated successfully by activated sludge
21	technology. Meanwhile, a lot of waste activated sludge (WAS) is produced in this
22	process. Reducing the volume and water content of the WAS is still a major concern
23	(Yuan et al., 2011). The commonly used chemical treatment methods hardly decrease
24	water content below 80%, and the volume of dewatered sludge obviously increases

1	with the addition of inorganic conditioners (Chen et al., 2001). In order to dispose
2	WAS economically and efficiently, dewatering and settling processes are essential to
3	reduce the sludge volume, which is still a bottleneck for sludge treatment (Guan et al.,
4	2012).
5	The dewatering and settling characteristics of WAS are different based on
6	wastewater sources and treatment processes. Furthermore, detailed factors that
7	influence sludge dewaterability and settleability are not yet well understood (Yu et al.,
8	2008). Extracellular polymeric substances (EPS) concentration of WAS, proteins and
9	polysaccharides content of EPS are reported to play a predominant role in sludge
10	dewaterability and settleability (Chen et al., 2001; Li & Yang, 2007). Moreover, the
11	layered theory of EPS is proposed to explicate the mechanisms of EPS impact on
12	WAS dewaterability and settleability. EPS can be divided into loosely bound
13	extracellular polymeric substances (LB-EPS), tightly bound EPS (TB-EPS) and pellet
14	(Li & Yang, 2007; Yu et al. 2008).
15	Based on the theory above, many kinds of methods have been developed to
16	improve the sludge dewaterability and settleability, including acid or alkaline
17	treatment (Devlin et al., 2011; Thapa et al., 2009), metal ions (Fe <sup>3+</sup> , Ca <sup>2+</sup> ) addition
18	(Liu & Horn, 2012), electro-chemical treatment (Yuan et al., 2010), thermal treatment
19	(More et al., 2012), sonication (Feng et al., 2009; Saha et al., 2011), microwave (Tang
20	et al., 2010), explosive explosion shockwave (Chen & Yang, 2012), pressurised
21	electro-osmotic (Citeau et al., 2012) and biological treatment (More et al. 2010).

22 Although these technologies exhibit some enhancement effect on sludge

1	dewaterability and settleability, some problems limit their application. On the other
2	hand, photocatalytic technology may be proposed to improve sludge dewaterability
3	and settleability by degrading EPS in WAS. Moreover, it is eco-friendly compared to
4	acid or alkaline treatment, metal ions addition and electro-chemical treatment, and
5	low-energy consumption compared to thermal treatment, sonication, microwave,
6	explosive explosion shockwave, and pressurised electro-osmotic treatment. It is also a
7	low-cost method compared to other treatment methods because it uses sunlight.
8	TiO <sub>2</sub> photocatalytic technology, an advanced oxidation process (AOP) utilizing free
9	radicals as a primary oxidant, has been successfully applied in wastewater treatment
10	(Gaya & Abdullah, 2008). Many organics can be degraded due to its non-selective
11	oxidation capability. It is supposed that the pore water and interstitial water in WAS
12	could be released with the degradation of WAS. In addition, the odour, turbidity and
13	organics content in WAS can be decreased during the process. Two kinds of
14	photoctalytic reactors (suspended- and supported-type) can be used in the treatment of
15	WAS. Although having higher photocatalytic activity, the suspended-type $TiO_2$
16	photocatalysis has higher cost of post-treatment (Mozia, 2010). Due to lower
17	interaction efficiency with contaminants and higher recombination rate of
18	electron-hole, the supported-type $TiO_2$ photocatalysis has lower photocatalytic
19	activity (van Grieken et al., 2009). Therefore, it is promising to synthesize some novel
20	and effective immobilized photocatalysts. Ag exhibits an efficient plasmon resonance
21	effect under sunlight and plays an important role of electron-hole separation produced
22	by TiO <sub>2</sub> (Ma et al., 2012). Thus, several modified TiO <sub>2</sub> photocatalysts with Ag-doped

1	have been developed (Ji et al., 2011). However, the effect of photocatalysis on WAS
2	dewaterability and settleability has not been reported up to now.
3	The objective of this research is to synthesize a novel $Ag/TiO_2$ immobilized as
4	photocatalyst which can be used under sunlight irradiation to improve WAS
5	dewaterability and settleability. The changes of LB-EPS, TB-EPS, proteins (PN) and
6	polysaccharides (PS) in WAS have been investigated during the photocatalytic
7	process in addition to their effects on specific resistance of filtration (SRF) and sludge
8	volume index (SVI) values. In addition, the variation of morphology was compared
9	between the WAS samples before and after photocatalysis by scanning Electron
10	Microscopy (SEM). The related mechanisms, especially the role of EPS in WAS
11	dewaterability and settleability are also discussed.
12	2. Methods
12 13	2. Methods 2.1. WAS and catalyst
13	2.1. WAS and catalyst
13 14	2.1. WAS and catalyst The WAS was collected from a domestic wastewater treatment plant in Shimodate,
13 14 15	<ul><li>2.1. WAS and catalyst</li><li>The WAS was collected from a domestic wastewater treatment plant in Shimodate,</li><li>Ibaraki, Japan. The sludge sample was immediately transferred to the lab and stored</li></ul>
13 14 15 16	<ul> <li>2.1. WAS and catalyst</li> <li>The WAS was collected from a domestic wastewater treatment plant in Shimodate,</li> <li>Ibaraki, Japan. The sludge sample was immediately transferred to the lab and stored</li> <li>in a plastic container at 4° for use. The initial characteristics of WAS were as follows</li> </ul>
<ol> <li>13</li> <li>14</li> <li>15</li> <li>16</li> <li>17</li> </ol>	<ul> <li>2.1. WAS and catalyst</li> <li>The WAS was collected from a domestic wastewater treatment plant in Shimodate,</li> <li>Ibaraki, Japan. The sludge sample was immediately transferred to the lab and stored</li> <li>in a plastic container at 4° for use. The initial characteristics of WAS were as follows</li> <li>(g/l except pH): pH 6.7, total solid (TS) 4.0, volatile suspended solid (VSS) 3.6, total</li> </ul>
<ol> <li>13</li> <li>14</li> <li>15</li> <li>16</li> <li>17</li> <li>18</li> </ol>	2.1. WAS and catalyst The WAS was collected from a domestic wastewater treatment plant in Shimodate, Ibaraki, Japan. The sludge sample was immediately transferred to the lab and stored in a plastic container at 4° for use. The initial characteristics of WAS were as follows (g/l except pH): pH 6.7, total solid (TS) 4.0, volatile suspended solid (VSS) 3.6, total and soluble chemical oxygen demand (TCOD and SCOD) 8.7 and 0.31, respectively.
<ol> <li>13</li> <li>14</li> <li>15</li> <li>16</li> <li>17</li> <li>18</li> <li>19</li> </ol>	2.1. WAS and catalyst The WAS was collected from a domestic wastewater treatment plant in Shimodate, Ibaraki, Japan. The sludge sample was immediately transferred to the lab and stored in a plastic container at 4° for use. The initial characteristics of WAS were as follows (g/l except pH): pH 6.7, total solid (TS) 4.0, volatile suspended solid (VSS) 3.6, total and soluble chemical oxygen demand (TCOD and SCOD) 8.7 and 0.31, respectively. The catalysts used in this study were TiO <sub>2</sub> (control, main characteristics, bought

1	$TiO_2$ -film coated glass tubes were impregnated by immersing into $AgNO_3$ (which
2	company, country?) solution (0.5 mol/l) for 20 min with UV light irradiation; then the
3	glass tubes were calcined (300°C, 1 h) in a vacuum oven (Hasuc, Shanghai, China);
4	and finally, cooled to room temperature under UV-light. The phase composition and
5	the degree of crystallinity in $TiO_2$ and $Ag/TiO_2$ were determined by X-ray diffraction
6	(XRD). The XRD patterns of the as-prepared samples ( $2\theta$ ranges from $10^{\circ}$ to $90^{\circ}$ )
7	were recorded at room temperature with scanning speed of $10^{\circ} \text{ min}^{-1}$ using Cu Ka
8	radiation ( $\lambda$ = 0.154 Å) from a 40 kV X-ray source (Bruker D8 Advance).
9	2.2. Experimental set-up
10	All the experiments were carried out in a solar photocatalytic reactor with support
11	catalyst (shown in Fig.1), which contained 10 glass tubes (18cm in length, 1 cm in
12	diameter ) with TiO <sub>2</sub> or Ag/TiO <sub>2</sub> film coated on inside wall. The working volume of
13	the reactor was 700 ml, and the WAS flowed in the reactor at 100 ml/min by a
14	peristaltic pump (??Which company, country). In this study, sunlight was used as light
15	source, and the mean UV-light intensity (290 nm – 390 nm) in sunlight was recorded
16	from 9:00 to 15:00 (shown in Fig.2(a)). The control experiments were conducted by
17	using the same reactor under the same light conditions but without catalyst on the
18	inner wall of the glass tubes.
19	2.3. Experimental procedure
20	The WAS was treated in the solar photocatalytic reactor for 48 h (6 h photocatalysis
21	for one day under the sunlight, then the reactor was covered with a black cloth

22 avoiding sunshine) during September 2012. Sampling was done right after

photocatalysis every day for subsequent analysis. Specific resistance of filtration
 (SRF) and sludge volume index (SVI) were checked to assess the dewaterability and
 settleability of the WAS before and after photocatalysis. LB-EPS, TB-EPS, PN and PS
 concentrations of the sludge samples were also measured to disclose the mechanisms
 related with the changes of sludge dewaterability and settleability.

6 2.4. EPS extraction

7 LB-EPS and TB-EPS were extracted from WAS by a modified heat extraction method (Li & Yang, 2007). The WAS was first centrifuged (MX-301, TMY) at 4000 g 8 9 for 5 min in a 15-ml centrifuge tube to dewater, then the sludge sediment in the centrifuge tube was re-suspended with NaCl solution (0.05%, 70°C) to the original 10 11 volume. Without any delay, the sludge suspension was sheared by a vortex mixer 12 (VORTEX-GENIE G-560, scientific industries, INC.) for 2 min, followed by centrifugation at 4000 g for 10 min. The organic matter in the supernatant was the 13 14 LB-EPS of WAS. For the TB-EPS, the WAS was firstly centrifuged at 4000 g for 5 15 min in a 15-ml centrifuge tube, then the liquid phase was discarded and the solid 16 phase was re-suspended with 0.05% NaCl solution to its original volume of 15 ml. 17 Secondly, the WAS suspension was heated to  $60^{\circ}$ C (confirm this temperature, 70?) for 30 min in an incubator (WFO-700, EYL4). Finally, the re-suspension was centrifuged 18 19 (MX-301, TMY) at 4000 g for 15 min and the supernatant was collected for TB-EPS analysis. The residue in the centrifuge cube was again re-suspended by adding NaCl 20 21 solution (0.05%, 70°C) to the original volume of 15 ml. This fraction was the pellet. 22 2.5. Indices and analytical methods

1	The photocatalytic activity of the $TiO_2$ and $Ag/TiO_2$ was assessed by the
2	degradation rate of methyl orange (company name, country). The changes of WAS
3	dewaterability and settleablity were assessed based on the specific resistance of
4	filtration (SRF) and sludge volume index (SVI), respectively before and after
5	treatment. The SRF was measured using a slightly modified method of Li & Yang
6	(2007). The SRF(cm/g) of the sludge was calculated by
7	$SRF = 2 \cdot b \cdot p \cdot A^2 / (\mu C)$
8	where p (60 kPa) is the pressure applied, A (3.0×10 <sup>-4</sup> m <sup>2</sup> ) is the filter area, $\mu$ (1.0mPa s)
9	is the viscosity of the permeate, C is the sludge concentration in mixed liquor
10	suspended solids (MLSS,kg/m <sup><math>3</math></sup> ) and b (s/m <sup><math>6</math></sup> ) is the time-to-filtration ratio, which is
11	the slope of the curve obtained by plotting the ratio of the time of filtration to the
12	volume of filtrate $(t/V)$ versus the filtrate volume $(V)$ .
13	The SVI value of WAS was obtained by measuring the sludge volume change in a
14	100-ml cylinder (100ml, ARROW) after 30 min settlement together with MLSS
15	concentration.
16	The morphology of untreated or photocatalysis treated WAS was obtained by
17	scanning electronic microscope (SEM, XL30, Philips, Holland). EPS (LB-EPS and
18	TB-EPS) concentrations were analyzed for COD, proteins (PN) and polysaccharides
19	(PS). COD and MLSS were detected in accordance with the standard methods
20	(Pawlowski, 1994). Phenol sulfuric method (Mecozzi, 2005) with glucose as standard
21	and Lowry method (Dawson & Heatlie, 1984) with bovine serum albumin as standard
22	

## **3. Results and discussion**

## 2 3.1. Characterization and photocatalytic capacity of $TiO_2$ and $Ag/TiO_2$

3	The XRD patterns of pure $TiO_2$ (1) and Ag/TiO <sub>2</sub> (2) samples are shown in
4	supplementary Fig.S1(a). The XRD patterns indicate that anatase is the only
5	crystalline phase of $TiO_2$ in the pure $TiO_2$ sample. The presence of Ag diffraction lines
6	(peaks marked by arrowhead in supplementary Fig.S1(a)) was clearly detected at
7	approximately 22.55° (2 $\theta$ ) for the Ag/TiO <sub>2</sub> sample.
8	The photocatalytic activity of $TiO_2$ and $Ag/TiO_2$ was assessed by the degradation of
9	methyl orange (MO, 20 mg/l) under the sunlight for 2 h from 11:00 to 13:00. The
10	UV-intensity (290 nm $-$ 390 nm) is shown in Fig.2(b) and the degradation rate of MO
11	is shown in supplementary Fig.S1(b). It was found that $Ag/TiO_2$ exhibited much
12	higher MO degradation rate (99.0%) than pure TiO <sub>2</sub> (35.2%), and the MO degradation
13	could be negligible under single sunlight condition. This observation indicates that
14	Ag/TiO <sub>2</sub> possesses better photocatalytic activity than pure TiO <sub>2</sub> . The improvement is
15	probably owing to the Ag particles deposited on the TiO <sub>2</sub> acting as electron-hole
16	separation and interfacial charge transfer (van Grieken et al., 2009). The charge
17	separation resulted from the formation of Schottky barriers at the $Ag/TiO_2$ interaction
18	region is attributable to the electron transfer from the $TiO_2$ conduction band to silver
19	particles (van Grieken et al., 2009). Due to the fact that the trapping of electrons by
20	Ag deposits is faster than its recombination with holes (Krejčíková et al., 2012), the
21	silver deposits on the surface can accelerate the transfer of trapped electrons in the Ag
22	deposits to the oxygen molecules to form superoxide radicals in solution and then

1	improve the photocatalytic activity (Pulido Melián et al., 2012). Because of having
2	higher photocatalytic activity than $TiO_2$ , Ag/ $TiO_2$ was chosen as photocatalyst in the
3	following experiments.
4	3.2. Effect of Ag/TiO <sub>2</sub> photocatalytic treatment on sludge dewaterability
5	The effect of Ag/TiO <sub>2</sub> photocatalytic treatment on sludge dewaterability was
6	evaluated by measuring SRF value (Fig.3a). It can be seen that the sludge
7	dewaterability could be greatly enhanced after Ag/TiO <sub>2</sub> photocatalytic treatment for18
8	h. Further prolonging the photocatalysis duration has little enhancement effect. The
9	SRF value decreased from $2.42 \times 10^9$ cm/g (untreated WAS) to $3.4 \times 10^8$ , $3.83 \times 10^8$ and
10	$4.7 \times 10^8$ cm/g after photocatalytic treatment for 18 h, 24 h and 36 h, respectively.
11	Therefore, in this study, 18 h was chosen as the optimal photocatalysis time, under
12	which the SRF value could be reduced by 86.0%.
13	The above effect of photocatalysis on sludge dewaterability can be explained as
14	follows. The flocs of WAS are in layered structure (Nguyen et al., 2008), in which the
15	loose surface layer can be first damaged and dispersed into the aqueous solution and
16	
10	then quickly oxidized into carbon dioxide by photocatalysis within a few hours. Later
17	then quickly oxidized into carbon dioxide by photocatalysis within a few hours. Later the free water, pore water and some bound water are released resulting in rapid
17	the free water, pore water and some bound water are released resulting in rapid
17 18	the free water, pore water and some bound water are released resulting in rapid decrease in SRF value. With the degradation of the loose surface layer, the highly
17 18 19	the free water, pore water and some bound water are released resulting in rapid decrease in SRF value. With the degradation of the loose surface layer, the highly porous sludge flocs can become compacted spheroidal structure thus the flocs density

1	photocatalysis, which may contribute to the fluctuation of SRF values during the 24
2	and 48 h treatment. This observation is in some agreement with the finding of Feng et
3	al. (2009) who treated WAS by ultrasound conditioning and pointed out that sludge
4	dewaterability could be slightly enhanced at low specific energy dosages while
5	significantly deteriorated at larger specific energy dosages (>4400 kJ/kg TS).
6	3.3. Effect of $Ag/TiO_2$ photocatalytic treatment on sludge settleability
7	The settleability, indicated by SVI, is an important factor influencing the operation
8	of sewage treatment plant. The change of SVI values is shown in Fig.3(b). Clearly, the
9	SVI decreased quickly from 161.4 ml/g to 86.7 ml/g and 58.7 ml/g after
10	photocatalysis for 12 h and 18 h, and increased slightly to 69.4 ml/g at 36 h,
11	respectively. On the other hand, the SVI value of the untreated WAS (control)
12	fluctuated between 159.1 ml/g and 172.1 ml/g during the 48 h photocatalysis
13	treatment. After 18 h photocatalysis treatment, the sludge settlability was comparable
14	to that of thermophilic aerobic granular biomass (SVI = $60 \text{ ml/g}$ ) (Zitomer et al.,
15	2007).
16	As it is known, the WAS has high SVI value due to some unfavorable operation
17	conditions resulting in slowly settleable large flocs (supplementary Fig.S2(a)).
18	However, the loose surface of flocs can be changed by $Ag/TiO_2$ photocatalysis as the
19	reaction progresses. The flocs become compact granule-like structure and the surface
20	roughness reduces, and then the frictional resistance between flocs begins to decline
21	during the settlement process. When the flocs are severely destructed and the EPS are
22	released gradually, the sludge density become smaller and the particles surface area

1	become larger resulting in increased buoyancy force, ultimately leading to a slight
2	increase in SVI value (Jin et al., 2003). Meanwhile, the released EPS may be
3	degraded by Ag/TiO <sub>2</sub> photocatalysis subsequently. That is, the concentration of EPS
4	could have some contribution to the fluctuation of SVI values between the 24 h and
5	48 h photocatalysis.
6	3.4. Changes of EPS, PN and PS concentrations in WAS during $Ag/TiO_2$
7	photocatalysis process
8	3.4.1 Changes of LB-EPS, PN and PS concentrations in WAS
9	The changes in LB-EPS (expressed in COD), PN and PS concentrations of the
10	WAS are shown in Fig.4. The concentrations of LB-EPS and PN in LB-EPS
11	(LB-EPS/PN) declined from the initial 364.0 mg/l and 248.2 mg/l to 210.8 mg/l and
12	164.3 mg/l at 18 h, and increased to 269.1 mg/l and 221.0 mg/l at 24 h, and then
13	decreased to 220.6 mg/l and 182.7 mg/l at 36 h, respectively. However, the
14	concentrations of LB-EPS and LB-EPS/PN increased to 439.5 mg/l and 306.5 mg/l at
15	48 h, respectively. On the other hand, the concentration of PS in LB-EPS (LB-EPS/PS)
16	decreased from the start to the end of the $Ag/TiO_2$ photocatalytic treatment. When the
17	SRF and SVI reached the minimal values after 18 h photocatalysis yielding its
18	maximum dewaterability and settability, the LB-EPS concentration in the treated
19	sludge was 210.8 mg/l (Figs.3 and 4), less than the result (400-500mg/l) obtained by
20	Feng et al. (2009). Moreover, during the first 36 h duration of Ag/TiO <sub>2</sub> photocatalysis,
21	LB-EPS concentration was found to have a similar change tendency with the SRF and
22	SVI values of the sludge (Figs.3 and 4).

1	The above phenomena can be interpreted as that the widely dispersed LB-EPS in
2	the aqueous phase has more chance to interact with the photocatalyst, possibly leading
3	to its rapid degradation into carbon dioxide. With the degradation of LB-EPS, an
4	abundant amount of bound water is released, resulting in the decrease of SRF and SVI
5	values. The main components of LB-EPS are PN and PS, and the concentration of PN
6	is much higher than that of PS (Yu et al., 2008), which may be the reason why PN
7	concentration changed in a similar tendency as LB-EPS did. When the sludge flocs
8	are destroyed further by $Ag/TiO_2$ photocatalysis, more EPS and cellular substances
9	can be released into the aqueous phase, bringing about the increase in protein and
10	polysaccharide levels. On the other hand, EPS may be released from the pellets of
11	WAS along with its degradation. That is, the degradation and release rate of LB-EPS
12	in WAS dominates the SVI and SRF values.
13	3.4.2 Changes of TB-EPS, PN and PS concentrations in WAS
14	During the first 12 h photocatalysis, the concentrations of TB-EPS and PN in
15	TB-EPS (TB-EPS/PN) decreased slightly from 470.8 mg/l and 430.0 mg/l , and their
16	concentrations varied with the same tendency as the SVI and SRF values of WAS (Fig.
17	4). After that the concentrations of TB-EPS and TB-EPS/PN increased significantly
18	till the 24 h, and then decreased. This observation is inconsistent with the variation of
19	SVI and SRF values (Figs. 3 and 4). Still the concentration of PS in TB-EPS
20	(TB-EPS/PS) decreased gradually during the whole photocatalysis process.
21	The reduction of TB-EPS in the initial phase is probably due to the conversion of
22	TB-EPS to LB-EPS by Ag/TiO <sub>2</sub> photocatalysis, and during this period the WAS

1	pellets haven't been disrupted into TB-EPS or LB-EPS. With the photocatalysis going
2	on, the pellets are disrupted, and then more and more LB-EPS and TB-EPS are
3	released, leading to the increase of TB-EPS in WAS. Simultaneously, the increase of
4	TB-EPS can supply more LB-EPS. When the increasing portion of TB-EPS is more
5	than its decreasing counterpart, the concentration of TB-EPS will increase and vice
6	versa. However, no direct correlation has been found between TB-EPS and the SVI or
7	SRF value in this study. LB-EPS content appears to have a closer correlation with the
8	sludge characteristics in settleability and dewaterability than the TB-EPS, which
9	agrees with the finding of Yuan et al. (2011). Detailed and followed-up research is
10	necessary.
11	3.5. Effect of $Ag/TiO_2$ photocatalytic treatment on the morphological change of WAS
12	The morphological change between untreated and photocatalysis treated WAS
13	samples is obvious (supplementary Fig.S2). From the direct observation as shown in
14	supplementary Fig.S2(a), the color of sludge was changed from the original dark-gray
15	to the earth-yellow, and the concentration of flocs in WAS decreased after treatment
16	by Ag/TiO <sub>2</sub> photocatalysis. In addition, the obvious difference in the microstructures
17	of WAS could be observed by SEM. The surface of untreated WAS sample
18	(supplementary Fig.S2(b)) had a relatively rough surface and layered structure, while
19	the surface of photocatalysis treated WAS (after 18 h treatment) became level and
20	smooth (supplementary Fig.S2 (c)). This morphological change indicates that the
21	WAS could be degraded gradually by Ag/TiO <sub>2</sub> photocatalysis. When the flocs in WAS
22	are gradually degraded from surface to inside, free water and pore water can be

1	released and the frictional resistance between flocs decreases, which may contribute
2	to the decrease of SRF and SVI values. This mechanism is different from other sludge
3	treatment methods such as explosive explosion shockwave, microwave and ultrasonic
4	processes characterized as rapid and violent (Chen & Yang, 2012; Feng et al., 2009;
5	Tang et al., 2010). The appearance of photocatalysis treated WAS (for 36 h) became
6	rough, fluffy and irregularly shaped again, but not the layered structure as before
7	(supplementary Fig.S2 (d)). This observation indicates that the sludge flocs might be
8	broken, and the intracellular substances could be solubilized into the aqueous phase,
9	leading to the increase of EPS. Meanwhile, some of the EPS, especially LB-EPS, can
10	be degraded by Ag/TiO <sub>2</sub> photocatalysis (shown in Fig.4 (a)). So the physically bound
11	water and interstitial cell water can be released into the solution during the
12	degradation progress of EPS, enhancing sludge dewaterability and settleability.
12 13	degradation progress of EPS, enhancing sludge dewaterability and settleability.
13	4. Conclusions
13 14	<b>4. Conclusions</b> A photocatalyst of Ag/TiO <sub>2</sub> film was synthesized and immobilized successfully, and
13 14 15	<b>4. Conclusions</b> A photocatalyst of Ag/TiO <sub>2</sub> film was synthesized and immobilized successfully, and its photocatalytic activity was significantly higher than $TiO_2$ film. The effect of
13 14 15 16	4. Conclusions A photocatalyst of Ag/TiO <sub>2</sub> film was synthesized and immobilized successfully, and its photocatalytic activity was significantly higher than $TiO_2$ film. The effect of Ag/TiO <sub>2</sub> photocatalysis on WAS dewaterability and settleability was dependent on
13 14 15 16 17	4. Conclusions A photocatalyst of Ag/TiO <sub>2</sub> film was synthesized and immobilized successfully, and its photocatalytic activity was significantly higher than TiO <sub>2</sub> film. The effect of Ag/TiO <sub>2</sub> photocatalysis on WAS dewaterability and settleability was dependent on photocatalytic time. The optimal photocatalytic time was 18 h with Ag/TiO <sub>2</sub> as
<ol> <li>13</li> <li>14</li> <li>15</li> <li>16</li> <li>17</li> <li>18</li> </ol>	<b>4. Conclusions</b> A photocatalyst of Ag/TiO <sub>2</sub> film was synthesized and immobilized successfully, and its photocatalytic activity was significantly higher than TiO <sub>2</sub> film. The effect of Ag/TiO <sub>2</sub> photocatalysis on WAS dewaterability and settleability was dependent on photocatalytic time. The optimal photocatalytic time was 18 h with Ag/TiO <sub>2</sub> as photocatalyst, and the SRF and SVI values were reduced by 86.0% and 80.0%,
<ol> <li>13</li> <li>14</li> <li>15</li> <li>16</li> <li>17</li> <li>18</li> <li>19</li> </ol>	<b>4. Conclusions</b> A photocatalyst of Ag/TiO <sub>2</sub> film was synthesized and immobilized successfully, and its photocatalytic activity was significantly higher than TiO <sub>2</sub> film. The effect of Ag/TiO <sub>2</sub> photocatalysis on WAS dewaterability and settleability was dependent on photocatalytic time. The optimal photocatalytic time was 18 h with Ag/TiO <sub>2</sub> as photocatalyst, and the SRF and SVI values were reduced by 86.0% and 80.0%, respectively. The LB-EPS and PN had more positive relation with SRF and SVI

## 1 Acknowledgements

2	r	The authors are grateful to Ms. Yingxin Zhao (Graduate School of Life and
3	En	vironmental Sciences, the University of Tsukuba) for her help with a part of the
4	exp	periments. The authors also appreciate Ms. Huiling Zhang (Chinese Language &
5	Cu	lture College, the Beijing Normal University) for providing language help and
6	wr	iting assistance.
7	Su	pplementary data
8	r	The supplementary data associated with this article included Fig.S1 (XRD patterns
9	and	d photocatalytic activity of pure $TiO_2$ and $Ag/TiO_2$ ) and Fig.S2 (morphological
10	cha	anges of WAS).
11	Re	ferences
12	1.	Chen, D., Yang, J. 2012. Effects of explosive explosion shockwave pretreatment
13		on sludge dewaterability. Bioresour. Technol. 119, 35-40.
14	2.	Chen, Y., Yang, H., Gu, G. 2001. Effect of acid and surfactant treatment on
15		activated sludge dewatering and settling. Water Res. 35, 2615-2620.
16	3.	Citeau, M., Olivier, J., Mahmoud, A., Vaxelaire, J., Larue, O., Vorobiev, E. 2012.
17		Pressurised electro-osmotic dewatering of activated and anaerobically digested
18		sludges: Electrical variables analysis. Water Res. 46, 4405-4416.
19	4.	Dawson, J.M., Heatlie, P.L. 1984. Lowry method of protein quantification:
20		Evidence for photosensitivity. Anal. Biochem. 140, 391-393.
21	5.	Devlin, D.C., Esteves, S.R.R., Dinsdale, R.M., Guwy, A.J. 2011. The effect of
22		acid pretreatment on the anaerobic digestion and dewatering of waste activated

sludge. Bioresour. Technol. 102, 4076-4082.

2	6.	Feng, X., Deng, J., Lei, H., Bai, T., Fan, Q., Li, Z. 2009. Dewaterability of waste
3		activated sludge with ultrasound conditioning. Bioresour. Technol. 100,
4		1074-1081.
5	7.	Gaya, U.I., Abdullah, A.H. 2008. Heterogeneous photocatalytic degradation of
6		organic contaminants over titanium dioxide: A review of fundamentals, progress
7		and problems. J. Photoch. Photobio C- Photoch. rev. 9, 1-12.
8	8.	Guan, B., Yu, J., Fu, H., Guo, M., Xu, X. 2012. Improvement of activated sludge
9		dewaterability by mild thermal treatment in CaCl2 solution. Water Res. 46,
10		425-432.
11	9.	Ji, Z., Ismail, M.N., Callahan Jr, D.M., Pandowo, E., Cai, Z., Goodrich, T.L.,
12		Ziemer, K.S., Warzywoda, J., Sacco Jr, A. 2011. The role of silver nanoparticles
13		on silver modified titanosilicate ETS-10 in visible light photocatalysis. Appl.
14		Catal. B- Environ. 102, 323-333.
15	10.	Jin, B., Wilén, BM., Lant, P. 2003. A comprehensive insight into floc
16		characteristics and their impact on compressibility and settleability of activated
17		sludge. Chem. Eng. J., 95, 221-234.
18	11.	Krejčíková, S., Matějová, L., Kočí, K., Obalová, L., Matěj, Z., Čapek, L.,
19		Šolcová, O. 2012. Preparation and characterization of Ag-doped crystalline titania
20		for photocatalysis applications. Appl. Catal. B- Environ. 111-112, 119-125.
21	12.	Li, X.Y., Yang, S.F. 2007. Influence of loosely bound extracellular polymeric
22		substances (EPS) on the flocculation, sedimentation and dewaterability of

activated sludge. Water Res. 41, 1022-1030.

2	13.	Liu, C., Yang, Y., Wang, Q., Kim, M., Zhu, Q., Li, D., Zhang, Z. 2012a.
3		Photocatalytic degradation of waste activated sludge using a circulating bed
4		photocatalytic reactor for improving biohydrogen production. Bioresour. Technol.
5		125, 30-36.
6	14.	Liu, F., Zhou, L., Zhou, J., Song, X., Wang, D. 2012b. Improvement of sludge
7		dewaterability and removal of sludge-borne metals by bioleaching at optimum pH.
8		J. Hazard. Mater. 221–222, 170-177.
9	15.	Liu, S., Horn, H. 2012. Effects of Fe(II) and Fe(III) on the single-stage
10		deammonification process treating high-strength reject water from sludge
11		dewatering. Bioresour. Technol. 114, 12-19.
12	16.	Ma, B., Guo, J., Dai, WL., Fan, K. 2012. Ag-AgCl/WO <sub>3</sub> hollow sphere with
13		flower-like structure and superior visible photocatalytic activity. Appl. Catal. B-
14		Environ. 123–124, 193-199.
15	17.	Mecozzi, M. 2005. Estimation of total carbohydrate amount in environmental
16		samples by the phenol-sulphuric acid method assisted by multivariate calibration.
17		Chemometr. Intell. Lab. 79, 84-90.
18	18.	More, T.T., Yan, S., Hoang, N.V., Tyagi, R.D., Surampalli, R.Y. 2012. Bacterial
19		polymer production using pre-treated sludge as raw material and its flocculation
20		and dewatering potential. Bioresour. Technol. 121, 425-431.
21	19.	More, T.T., Yan, S., Tyagi, R.D., Surampalli, R.Y. 2010. Potential use of
22		filamentous fungi for wastewater sludge treatment. Bioresour. Technol. 101,

1	7691-7700.

2	20.	Mozia, S. 2010. Photocatalytic membrane reactors (PMRs) in water and
3		wastewater treatment. A review. Sep. Purif. Technol. 73, 71-91.
4	21.	Nguyen, T.P., Hilal, N., Hankins, N.P., Novak, J.T. 2008. The relationship
5		between cation ions and polysaccharide on the floc formation of synthetic and
6		activated sludge. Desalination 227, 94-102.
7	22.	Pawlowski, L. 1994. Standard methods for the examination of water and
8		wastewater, 18th edition: Arnold E. Greenberd, Lenore S. Clesceri, Andrew D.
9		Eaton (Editors) Water Environment Federation, Alexandria, USA, 1992; 1025 pp;
10		ISBN 0-87553-207-1. Science of The Total Environment, 14, 227-228.(confirm?)
11	23.	Pulido Melián, E., González Díaz, O., Doña Rodríguez, J.M., Colón, G., Navío,
12		J.A., Macías, M., Pérez Peña, J. 2012. Effect of deposition of silver on structural
13		characteristics and photoactivity of TiO2-based photocatalysts. Appl. Catal. B-
14		Environ. 127, 112-120.
15	24.	Saha, M., Eskicioglu, C., Marin, J. 2011. Microwave, ultrasonic and
16		chemo-mechanical pretreatments for enhancing methane potential of pulp mill
17		wastewater treatment sludge. Bioresour. Technol. 102, 7815-7826.
18	25.	Schuler, A.J., Jang, H. 2007. Microsphere addition for the study of biomass
19		properties and density effects on settleability in biological wastewater treatment
20		systems. Water Res. 41, 2163-2170.
21	26.	Tang, B., Yu, L., Huang, S., Luo, J., Zhuo, Y. 2010. Energy efficiency of
22		pre-treating excess sewage sludge with microwave irradiation. <i>Bioresour. Technol.</i>

1 101, 5092-5097.

2	27.	Thapa, K.B., Qi, Y., Clayton, S.A., Hoadley, A.F.A. 2009. Lignite aided
3		dewatering of digested sewage sludge. Water Res. 43, 623-634.
4	28.	van Grieken, R., Marugán, J., Sordo, C., Martínez, P., Pablos, C. 2009.
5		Photocatalytic inactivation of bacteria in water using suspended and immobilized
6		silver-TiO <sub>2</sub> . Appl. Catal. B- Environ. 93, 112-118.
7	29.	Yu, GH., He, PJ., Shao, LM., He, PP. 2008a. Stratification Structure of
8		Sludge Flocs with Implications to Dewaterability. Environ. Sci. Technol. 42,
9		7944-7949.
10	30.	Yu, GH., He, PJ., Shao, LM., Zhu, YS. 2008b. Extracellular proteins,
11		polysaccharides and enzymes impact on sludge aerobic digestion after ultrasonic
12		pretreatment. Water Res. 42, 1925-1934.
13	31.	Yuan, Hp., Cheng, Xb., Chen, Sp., Zhu, Nw., Zhou, Zy. 2011. New sludge
14		pretreatment method to improve dewaterability of waste activated sludge.
15		Bioresour. Technol. 102, 5659-5664.
16	32.	Yuan, H., Zhu, N., Song, L. 2010. Conditioning of sewage sludge with
17		electrolysis: Effectiveness and optimizing study to improve dewaterability.
18		Bioresour. Technol. 101, 4285-4290
19	33.	Zitomer, D.H., Duran, M., Albert, R., Guven, E. 2007. Thermophilic aerobic
20		granular biomass for enhanced settleability. Water Res.41, 819-825.
21		

1	Figure captions
2	Fig.1. Schematic of Ag/TiO <sub>2</sub> -coated glass tubular photocatalytic reactor.
3	Fig.2. UV-light mean intensity used in WAS treatment (a) and used in methyl orange
4	treatment (b).
5	Fig.3. Effect of Ag/TiO <sub>2</sub> photocatalytic treatment on sludge dewaterability (a) and
6	settleability (b).
7	Fig.4. Changes of LB-EPS and TB-EPS concentrations in WAS during the Ag/TiO $_2$
8	photocatalysis process (a); Changes of PN and PS in LB-EPS and TB-EPS during the
9	Ag/TiO <sub>2</sub> photocatalysis process (b).
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	
20	
21	
22	
23	
24	
25 26	
26 27	
27	
28 29	
30	
31	
32	
33	
34	











