

1 Sunlight Promotes Fast Release of Hazardous Cadmium  
2 from Widely-Used Commercial Cadmium Pigment

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14

## 15 **Abstract**

16 Cadmium pigments are widely used in the polymer and ceramic industry. Their potential  
17 environmental risk is under debate, being the major barrier for appropriate regulation. We show that  
18  $83.0 \pm 0.2$  % of hazardous cadmium ion ( $\text{Cd}^{2+}$ ) was released from the commercial cadmium  
19 sulfoselenide pigment (i.e., cadmium red) in aqueous suspension within 24 h under simulated sunlit  
20 conditions. This photo-dissolution process also generated sub-20 nm pigment nanoparticles.  $\text{Cd}^{2+}$  release  
21 is attributed to the reactions between photogenerated holes and the pigment lattices. The photo-  
22 dissolution process can be activated by both ultraviolet and visible light in the solar spectrum.  
23 Irradiation under alkaline conditions or in the presence of phosphate and carbonate species resulted in  
24 reduced charge carrier energy or the formation of insoluble and photo-stable cadmium precipitates on  
25 pigment surfaces, mitigating photo-dissolution. Tannic acid inhibited the photo-dissolution process by  
26 light screening and scavenging photogenerated holes. The fast release of  $\text{Cd}^{2+}$  from the pigment was  
27 further confirmed in river water under natural sunlight, with  $38.6 \pm 0.1$  % of the cadmium released  
28 within 4 h. Overall, this study underscores the importance to account for photochemical effects to  
29 inform risk assessments and regulations of cadmium pigments which are currently based on their low  
30 solubility.

31

## 32 **Introduction**

33 Cadmium pigments, including cadmium sulfide, cadmium selenide, and cadmium sulfoselenide, are  
34 widely used in the polymer and ceramic industries owing to their heat stability, chemical resistance,  
35 dispersibility, opacity, tinting strength, and brilliance.<sup>1, 2</sup> They are especially preferred in processes or  
36 applications involving elevated temperatures in which organic pigments are unstable. The annual global  
37 consumption of cadmium pigments exceeds 2,500 tons, with 90 % used in plastics and 9 % in ceramics.<sup>2</sup>  
38 There is a long debate on whether cadmium pigments pose a genuine risk to human health and the

39 environment.<sup>1,2</sup> Cadmium ion ( $\text{Cd}^{2+}$ ) is known to cause acute toxicity based on short-term animal tests,  
40 and is a probable human carcinogen.<sup>3</sup> Thus the dissolution of cadmium pigments and consequent release  
41 of hazardous  $\text{Cd}^{2+}$  are key processes that control their potential environmental impacts. Previous risk  
42 assessments suggested that the use of cadmium pigments poses little risk to humans and the  
43 environment (except in occupational settings) due to their extremely low solubility ( $K_{\text{sp,CdS}} = 7.94 \times 10^{-27}$   
44 and  $K_{\text{sp,CdSe}} = 6.31 \times 10^{-36}$ ),<sup>4</sup> and consequently low bioavailability.<sup>5-8</sup> Because of insufficient fate,  
45 transport, and toxicological studies, current cadmium pigment regulations are based on the  
46 precautionary principle.<sup>1</sup> For example, the European Union (EU) prohibits the use of cadmium pigments  
47 in 16 plastics with exemptions (see Regulation No. 494/2011). In China and EU, cadmium pigments are  
48 recommended to pass extraction tests for  $\text{Cd}^{2+}$ ,  $< 0.1$  wt % (Standards ISO 4620:1986, BS 6857-1987,  
49 and HG 2351-1992). However, these presumably conservative regulations may still underestimate  
50 associated risks by overlooking photochemical processes that enhance  $\text{Cd}^{2+}$  release.

51 The band gap of CdS and CdSe are 2.5 eV and 1.8 eV, respectively.<sup>9</sup> Cadmium sulfoselenide is the  
52 solid solution of CdS and CdSe, whose color can be fine-tuned from orange to red by increasing the  
53 amount of selenium.<sup>2,10</sup> Its band gap decreases from 2.5 eV to 1.8 eV with increasing Se content.<sup>9,11</sup>  
54 Thus cadmium pigments are photoactive under sunlight and are proposed to be used in photovoltaic  
55 devices to harvest solar energy.<sup>12,13</sup> However, for many metal-containing semiconductor photocatalysts,  
56 photo-corrosion process will lead to the dissolution and consequent release of metals.<sup>14-19</sup>

57 Photo-corrosion of CdS and CdSe nanoparticles/quantum dots and subsequent release of  $\text{Cd}^{2+}$  were  
58 investigated in previous studies.<sup>14,15,20-27</sup> The process can be induced by oxidative phototransients  
59 including photogenerated holes and reactive oxygen species (ROS). However, these studies were carried  
60 out using cadmium chalcogenide nanoparticles mostly in simple solution chemistry, and cannot be  
61 extrapolated to infer on the behavior of commercial cadmium pigments in natural settings. The photo-  
62 degradation of CdS pigment in air has also been studied by analyzing historical oil paintings in aim to  
63 minimize their deterioration process.<sup>28-30</sup> The discoloration of CdS pigment was attributed to photo-

64 induced oxidation over centuries, which yielded  $\text{CdSO}_4 \cdot x\text{H}_2\text{O}$  and other cadmium species (e.g.,  $\text{CdCO}_3$ )  
65 by secondary reactions. Nevertheless, our understanding of the photo-dissolution process of modern  
66 commercial cadmium pigments in natural aquatic systems is still limited, which hinders risk assessment  
67 and science-based regulation of these pigments and related colored consumer products.

68 Herein, we examine the photo-dissolution of a commercial cadmium sulfoselenide pigment (i.e.,  
69 cadmium red) under simulated sunlight at neutral pH, mimicking natural conditions. The band gap of  
70 the pigment and the phototransients generated during irradiation were determined to understand its  
71 photochemistry within the solar spectrum. The influence of solution chemistry including pH, phosphate,  
72 carbonate, and tannic acid on the photo-dissolution kinetics was further examined to inform the  
73 environmental release process. The photo-dissolution of cadmium pigments was also examined in river  
74 water under natural sunlit conditions to corroborate our findings. In addition to discerning the photo-  
75 induced dissolution mechanism, we underscore the importance to consider photochemical processes to  
76 accurately assess the associated risks and inform the regulatory process.

77

## 78 **Materials and Methods**

79 Commercial cadmium sulfoselenide pigment powder (cadmium red) was purchased from Kela Co.,  
80 Ltd., China. Dimethyl sulfoxide (DMSO,  $\geq 99.0\%$ ), sodium chloride ( $\text{NaCl}$ ,  $\geq 99.5\%$ ), sodium  
81 carbonate ( $\text{Na}_2\text{CO}_3$ ,  $\geq 99.8\%$ ), sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $\geq 99\%$ ) and sodium  
82 sulfate ( $\text{Na}_2\text{SO}_4$ ,  $\geq 99\%$ ) were purchased from Nanjing Chemical Reagent Co., Ltd., China. 5,5-  
83 Dimethyl-1-pyrroline-N-oxide (DMPO,  $\geq 97\%$ ) was obtained from J&K Scientific Ltd., USA. Sodium  
84 selenite ( $\text{Na}_2\text{SeO}_4$ ,  $\geq 98\%$ ) was purchased from Chengdu Micxy Chemical Co., Ltd., China. Methyl  
85 viologen dichloride hydrate ( $\text{MV}^{2+}$ ,  $\geq 98\%$ ), sodium phosphate ( $\text{Na}_3\text{PO}_4$ ,  $96\%$ ), sodium selenite  
86 pentahydrate ( $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\geq 90\%$ ), 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2*H*-tetrazolium-5-  
87 carboxanilide (XTT,  $> 90\%$ ), terephthalic acid (TPA,  $98\%$ ), *N,N*-diethyl-*p*-phenylenediamine sulfate  
88 salt (DPD,  $\geq 99\%$ ), and horseradish peroxidase (HRP,  $\geq 250$  units/mg) were purchased from Sigma-

89 Aldrich, USA. Tannic acid (95 %) was purchased from Acros Organics, USA. All solutions were  
90 prepared using deionized water (18.2 MΩ•cm at 25 °C) obtained from an ELGA Labwater system  
91 (PURELAB Ultra, ELGA LabWater Global Operations, UK).

92 **Irradiation experiments.** The stock suspension of commercial cadmium sulfoselenide pigment was  
93 prepared by mixing 10 mg pigment with 100 mL deionized water and sonicated using a flat-tip probe  
94 sonicator (JY92-IIN, Ningbo Scientz Biotechnology Co., Ltd., China) for 10 min. The sonication probe  
95 was operated at a power of 65 W with a mode of five-second sonication and five-second pause.

96 The sunlight irradiation was simulated by a 50 W Xe lamp (CEL-HXF300, AULTT, China) shining  
97 from the top of a cylindrical cell which was equipped with a water-circulating jacket at  $20 \pm 0.1$  °C  
98 (DC0506, Shanghai FangRui Instrument Co., Ltd., China). The irradiation energy at the water surface  
99 was 202 mW/cm<sup>2</sup> as measured by a radiometer (CEL-NP2000-2, AULTT). The detailed information  
100 regarding the irradiation system can be found in Figure S1. The lamp spectrum was similar to that of  
101 natural sunlight with the wavelength > 300 nm as measured by a spectrometer (USB2000+, Ocean  
102 Optics, FL, USA) (Figure S2). In the irradiation experiments, twenty milliliter cadmium sulfoselenide  
103 pigment stock suspension (100 mg/L) and 10 mL NaCl stock solution (20 mM) were mixed and diluted  
104 to 200 mL with deionized water in a 250 mL beaker, yielding a suspension containing 10 mg/L  
105 cadmium sulfoselenide pigment and 1 mM NaCl. The beaker was then placed in the cylindrical cell for  
106 temperature control. The suspension was stirred at 100 rpm during the irradiation experiments. NaCl  
107 added in the suspension was used to simulate the ionic strength in freshwater systems. The un-adjusted  
108 pH of the mixture was  $6.77 \pm 0.33$ . During the irradiation, 4 mL suspension was withdrawn periodically  
109 from the beaker and filtered using ultrafiltration membranes (Amicon Ultra-15 3 kD, Millipore, MA,  
110 USA) to separate the dissolved ions from the particles. The Cd<sup>2+</sup> concentration was determined by  
111 atomic absorption spectrophotometry (AAS, M6, Thermo, USA). The concentrations of other ions  
112 presented in irradiated pigment suspensions were determined by ion chromatography (ICS-1000,  
113 Dionex, USA) with a Dionex IonPac AS11-HC analytical column (250 mm × 4 mm). Dark controls

114 were carried out in the same experimental setting with the Xe lamp off and the beaker wrapped with  
115 aluminum foil. In some irradiation experiments, different reagents ( $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ , and tannic acid) and  
116 scavengers ( $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{MV}^{2+}$ ) were added in the reaction suspension.

117 The photo-dissolution kinetics was also measured in a natural water sample under solar irradiation.  
118 The freshwater sample was collected from a river in Yixing, China ( $\text{N}31^\circ15'37.56''$ ,  $\text{E}119^\circ53'28.61''$ ).  
119 The sample was filtered through 0.45- $\mu\text{m}$  membranes (Pall, USA) and stored at 4 °C before use. Solar  
120 irradiation was carried out in the same experimental installation without temperature control on the  
121 campus of Nanjing University in Nanjing, Jiangsu, China ( $\text{N}32^\circ07'15.27''$ ,  $\text{E}118^\circ56'49.63''$ ) from 11  
122 a.m. to 3 p.m. on 11/04/2016.

123 **Characterization of cadmium sulfoselenide pigment.** The size and morphology of pigment particles  
124 were analyzed using a scanning electron microscope (SEM, S-3400N II, Hitachi, Japan) and a  
125 transmission electron microscope (TEM, JEM-200CX, JEOL, Japan). The elemental composition of the  
126 pigment was determined by an inductively coupled plasma mass spectrometry (ICP-MS, NexIon300X,  
127 PerkinElmer, USA) after microwave digestion (ETHOS UP, Milestone, Italy). The structure of pigment  
128 was examined using an X-ray powder diffractometer (XRD, D8 Advance, AXS, German) and an X-ray  
129 photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, UIVAC-PHI, Japan). The XRD pattern was  
130 acquired between  $20^\circ$  to  $60^\circ$  in  $2\theta$  mode using with  $\text{Cu K}\alpha$  radiation at room temperature. The XPS  
131 analyses were performed using the monochromatic  $\text{Al K}\alpha$  X-ray source and the spectrometer was  
132 calibrated to the position of the  $3d_{5/2}$  line of sputtered-clean Ag. The diffuse reflectance ultraviolet-  
133 visible spectroscopy (DRS) spectrum of the pigment powder was collected by a SHIMAD UV-3600  
134 UV-vis spectrometer referenced by  $\text{BaSO}_4$ . The Mott–Schottky plot of the pigment was measured using  
135 an electrochemical analyzer (CHI 760E, CH instrument, China). The impedance - potential tests were  
136 taken in a three-electrode setup with a platinum wire as the counter electrode and the saturated calomel  
137 electrode (SCE) as the reference electrode. The working electrode was prepared by casting the  
138 commercial cadmium sulfoselenide suspension (0.2 g/L in ethanol) over a clean indium tin oxide (ITO)

139 glass plate (Huanan Xiangcheng Co. Ltd., China, 2.5 cm × 2.5 cm, 1.1 mm thick, sheet resistance of 6-8  
140  $\Omega/\text{in}^2$ ). The electrode was then dried at 60 °C for 2 h. The electrolyte was 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous  
141 solution with pH of 5.5. The ac amplitude and frequency were set to be 5 mV and 1.5 KHz, respectively.  
142 The  $\zeta$ -potential of the pigment particles was measured by phase analysis light scattering (PALS) using a  
143 ZEN 3500 Zetasizer Nano ZS (Malvern, Worcestershire, UK). Each sample was measured five times at  
144 25 °C in a folded capillary cell (Malvern, Worcestershire, UK).

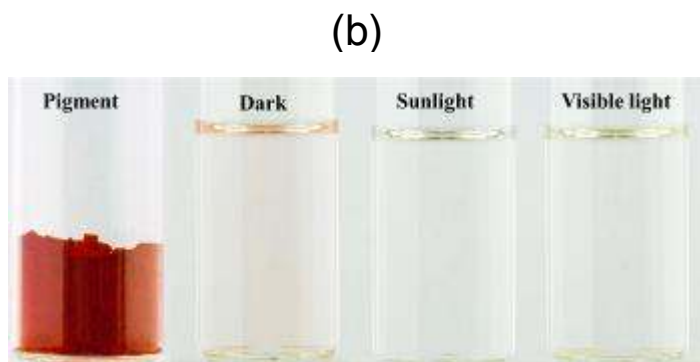
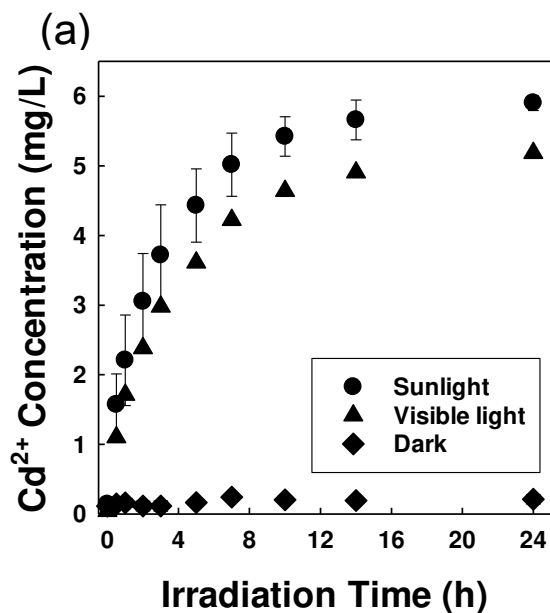
145 **ROS determination.** The production of superoxide ( $\text{O}_2^{\cdot-}$ ), hydroxyl radical ( $\cdot\text{OH}$ ), and hydrogen  
146 peroxide ( $\text{H}_2\text{O}_2$ ) by pigment suspensions was measured using probe molecules as described  
147 previously.<sup>31-35</sup> Superoxide generation was quantified by the formation of XTT formazan from XTT at  
148 an initial concentration of 0.05 mM. XTT formazan was quantified by its absorption at 475 nm using a  
149 UV-vis spectra. The extinction coefficient of XTT formazan is  $21600 \text{ M}^{-1}\text{cm}^{-1}$ .<sup>31, 34</sup> Hydroxyl radical  
150 production was quantified by monitoring the degradation of *p*CBA.<sup>32-34</sup> The *p*CBA concentration was  
151 measured at a detection wavelength of 254 nm using a high performance liquid chromatography (HPLC,  
152 Agilent 1100, Agilent Technologies, USA) with a Zorbax Eclipse XDB-C18 column (Agilent). The  
153 mobile phase was 30 % acetonitrile and 70 % 0.1 wt% phosphoric acid at a flow rate of 1 mL/min.  $\text{H}_2\text{O}_2$   
154 generation was measured by the HRP (5 mg/L) catalyzed oxidation of DPD (1mM).<sup>35</sup> The stable  
155 oxidation product,  $\text{DPD}^{*+}$ , was measured by the UV-vis absorbance at 551 nm. The spin-trapping  
156 electron spin resonance (ESR) spectra were recorded on a Bruker EMX-10/12 spectrometer (Germany)  
157 at room temperature with X-band, microwave power of 20 mW, sweep width of 200 G, modulation  
158 width of 1 G, modulation frequency of 100 kHz.

## 159 **Results and Discussion**

### 160 **Simulated sunlight exposure results in rapid release of $\text{Cd}^{2+}$ from commercial cadmium** 161 **sulfoselenide pigment**

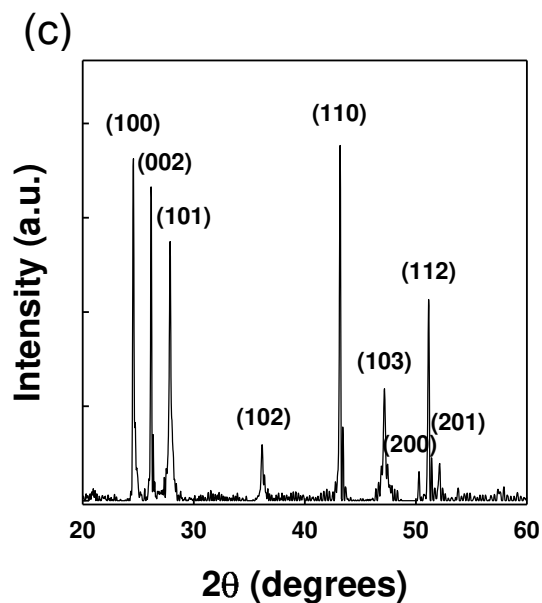
162 The dissolution kinetics of a representative cadmium pigment, cadmium sulfoselenide ( $\text{CdS}_x\text{Se}_{1-x}$ )  
163 was examined to assess its ability to release hazardous  $\text{Cd}^{2+}$ . The commercial cadmium sulfoselenide

164 pigment used here was a fine powder with brilliant red color (Figure 1). The SEM and TEM  
165 micrographs showed that pigment particles were quasi-spherical with a number average diameter of  
166  $186.1 \pm 95.8$  nm based on TEM micrographs (Figure 2). The commercial pigment can be readily  
167 dispersed in water (Figure 1b). The observed colloidal stability can be attributed to the small size and  
168 negative surface charge of the pigment particles with a  $\zeta$ -potential of  $-24.37 \pm 1.48$  mV (electrophoretic  
169 mobility of  $-1.91 \pm 0.12$   $\mu\text{m}\cdot\text{cm}/\text{Vs}$ ), which facilitates their colloidal stability through electrostatic  
170 repulsion as suggested by the Derjaguin-Landau-Verwey-Overbeek theory.<sup>36, 37</sup> The XRD pattern of the  
171 commercial pigment is shown in Figure 1c. The XRD spectrum has sharp peaks corresponding to the  
172 crystal structure of cadmium sulfoselenide, including  $2\theta$  at  $24.66^\circ$  (100),  $26.28^\circ$  (002),  $27.99^\circ$  (101),  
173  $36.34^\circ$  (102),  $43.30^\circ$  (110),  $47.28^\circ$  (103),  $50.38^\circ$  (200),  $51.28^\circ$  (112), and  $52.19^\circ$  (201).<sup>12, 38</sup> ICP-MS  
174 measurements suggested the atomic ratio of S:Se of the pigment was  $1.9 \pm 0.1$ .



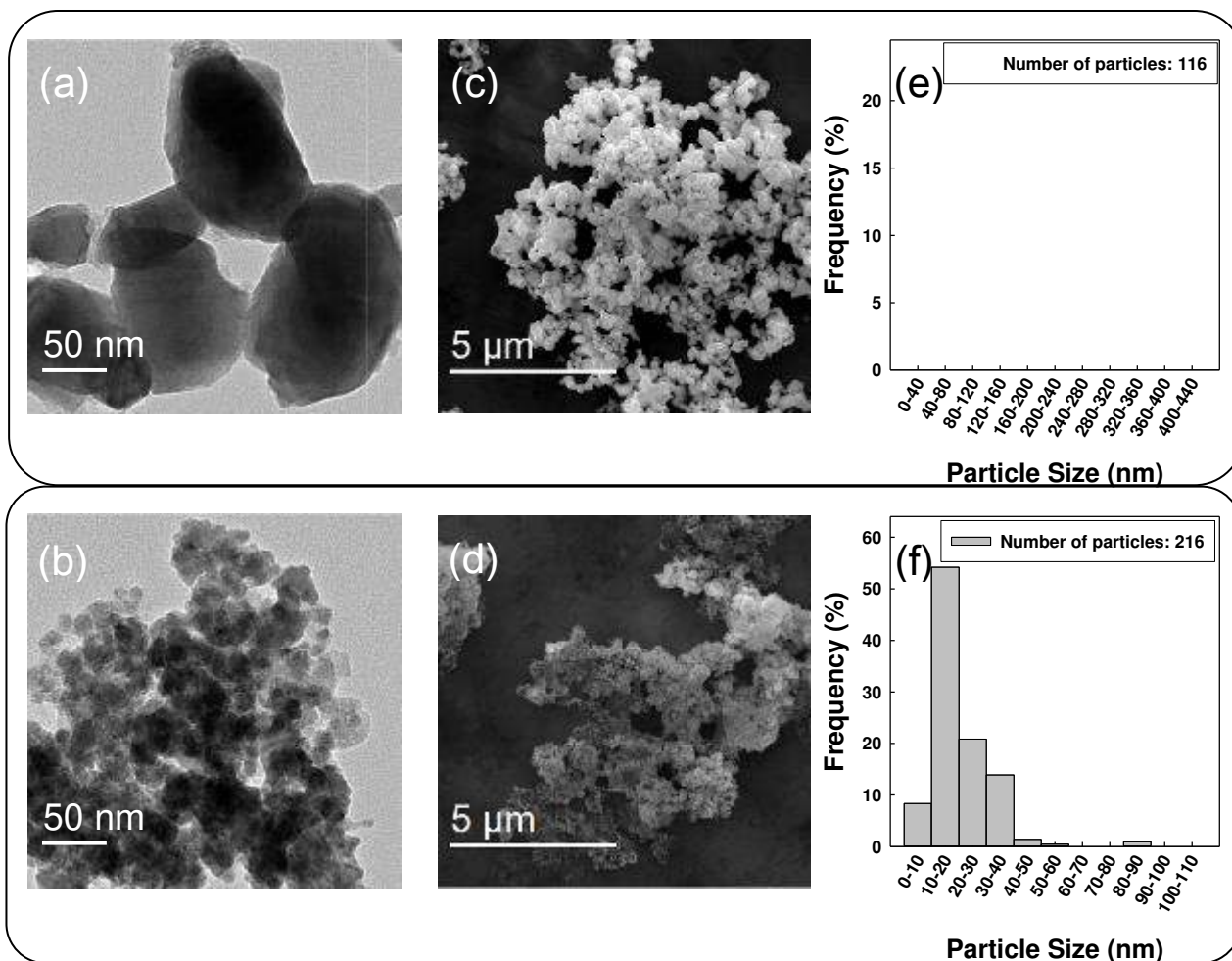
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177 Figure 1. (a) Cadmium release kinetics of 10 mg/L commercial cadmium sulfoselenide pigment in 1  
178 mM NaCl solution at initial pH of  $6.77 \pm 0.33$  under dark, simulated sunlight ( $202 \text{ mW/cm}^2$ ), and  
179 visible light irradiation ( $152 \text{ mW/cm}^2$ ). Error bars represent  $\pm$  one standard deviation from the average  
180 of triplicate tests; (b) photos of the commercial cadmium sulfoselenide pigment sample used in this  
181 work and its suspension (10 mg/L) in 1 mM NaCl solution after 24 h under dark, simulated sunlight,  
182 and visible light conditions; (c) XRD spectrum of commercial cadmium sulfoselenide pigment.



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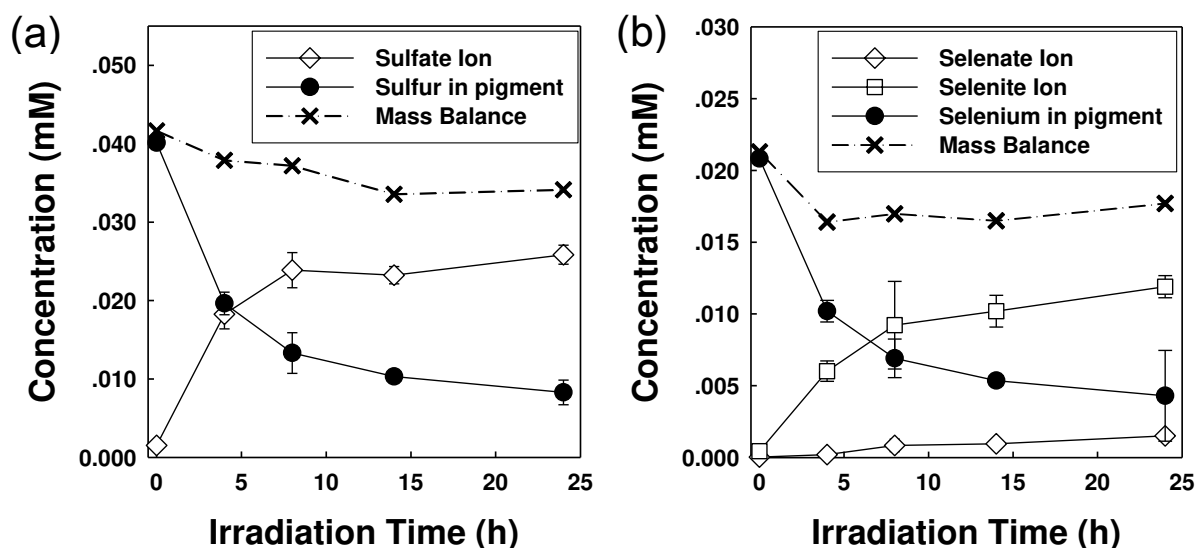
184 Figure 2. Morphology and size distribution of commercial cadmium sulfoselenide pigment particles  
 185 before and after 7-h simulated sunlight exposure. TEM micrographs of commercial cadmium  
 186 sulfoselenide pigment particles (a) before and (b) after sunlight exposure; SEM micrographs of  
 187 commercial cadmium sulfoselenide pigment particles (c) before and (d) after sunlight exposure; size  
 188 distribution of commercial cadmium sulfoselenide pigment particles (e) before and (f) after sunlight  
 189 exposure based on TEM micrographs.

190

191 The release kinetics of  $\text{Cd}^{2+}$  from cadmium sulfoselenide pigment was determined under both dark  
 192 and simulated sunlight irradiation (Figure 1a, see the release kinetics for other cadmium sulfoselenide  
 193 pigments from different vendors in Figure S3). A small amount of  $\text{Cd}^{2+}$ ,  $0.21 \pm 0.07$  mg/L ( $< 3.0$  % of  
 194 the total Cd), was released in the dark condition within 24 h. It can be attributed to the dissolution of

195 cadmium sulfoselenide or the  $\text{Cd}^{2+}$  release during the dispersion process by sonication. Considering the  
196 extremely low solubility of CdS (solubility product constant,  $K_{\text{sp}} = 7.94 \times 10^{-27}$ ) and CdSe ( $K_{\text{sp}} =$   
197  $6.31 \times 10^{-36}$ ),<sup>4</sup> the majority of  $\text{Cd}^{2+}$  released in dark condition is expected to be the latter. However, fast  
198 and significant release of  $\text{Cd}^{2+}$  was observed in the presence of simulated sunlight. The concentration of  
199  $\text{Cd}^{2+}$  in the suspension increased to  $5.01 \pm 0.45$  mg/L within a 7-h irradiation, and to  $5.90 \pm 0.10$  mg/L  
200 at the end of the 24-h irradiation test. This means that  $83.0 \pm 0.2$  % of the total cadmium was released,  
201 far exceeding the 0.1 % limit stipulated by ISO Standard 4620:1986. The pseudo-second-order reaction  
202 rate constant was  $3.0$  L/(mmol·h) ( $R^2 = 0.93$ ), 334 times higher than that under dark conditions. The rate  
203 constant decreased from  $3.0$  to  $1.5$  L/(mmol·h) ( $R^2 = 0.95$ ) after a cut-off filter was applied to remove  
204 the UV component of the simulated sunlight (Figure 1a). This indicates that the photo-dissolution can be  
205 induced by visible light in the solar spectrum which comprises the majority of the photon flux in solar  
206 irradiation.<sup>39</sup>

207 During irradiation, the color of the cadmium sulfoselenide pigment suspension changed from red to  
208 transparent, supporting the fast photo-dissolution of the pigment (Figure 1b). The  $\zeta$ -potential of the  
209 pigment particles was stable at  $-26.15 \pm 1.24$  mV (Figure S4). TEM and SEM micrographs of pigment  
210 particles suggest that particle size was significantly decreased owing to the photo-dissolution process  
211 (Figure 2a-d). Based on the size distribution diagrams (Figure 2e and 2f), the number average size of the  
212 pigment particles sharply decreased from  $186.1 \pm 95.8$  nm to  $19.7 \pm 8.7$  nm after 7-h irradiation. The  
213 size distribution also became narrower (i.e., less heterogeneous) after irradiation. The majority of the 7-  
214 h-irradiated pigment particles had sizes within the range of 10 ~ 20 nm.



215

216 Figure 3. (a) The concentrations and mass balance of sulfur species, including sulfur in the pigment and

217 sulfate ion ( $\text{SO}_4^{2-}$ ), as a function of simulated sunlight irradiation time at initial pH of  $6.77 \pm 0.33$ . (b)

218 The concentrations and mass balance of selenium species, including selenium in the pigment, selenite

219 ion ( $\text{SeO}_3^{2-}$ ), and selenate ion ( $\text{SeO}_4^{2-}$ ), as a function of simulated sunlight irradiation time.

220

221 The release of sulfur and selenium species and their mass balance were examined during the photo-

222 dissolution of commercial cadmium sulfoselenide pigment (Figure 3). The solution concentration of

223  $\text{SO}_4^{2-}$  increased with decreasing sulfur remaining in the pigment (Figure 3a). No  $\text{SO}_3^{2-}$  or S was detected

224 using ion chromatography and HPLC, respectively. The mass balance of sulfur species was 81.8 % at 24

225 h. Similar analysis was applied to selenium species (Figure 3b). Both  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  were detected

226 as reaction products, with  $\text{SeO}_4^{2-}$  being the major product and  $\text{SeO}_3^{2-}$  being the intermediate product.

227 The mass balance of selenium species was 83.1 % at 24 h.

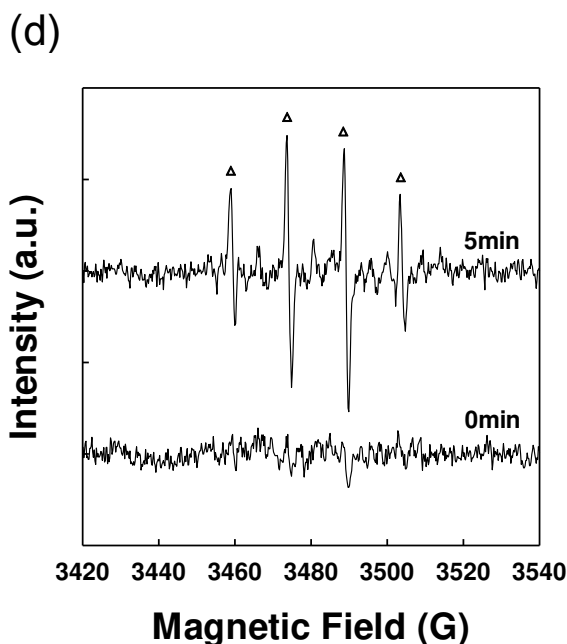
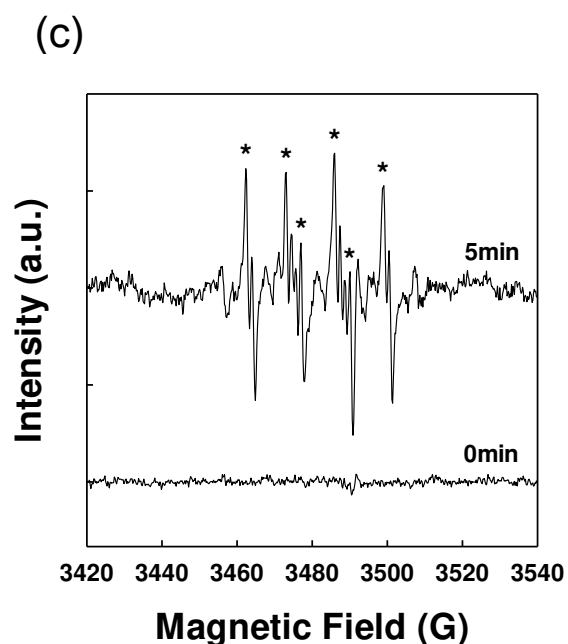
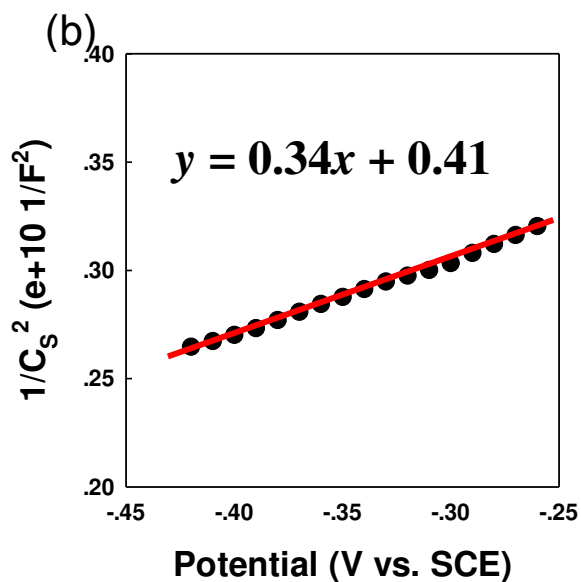
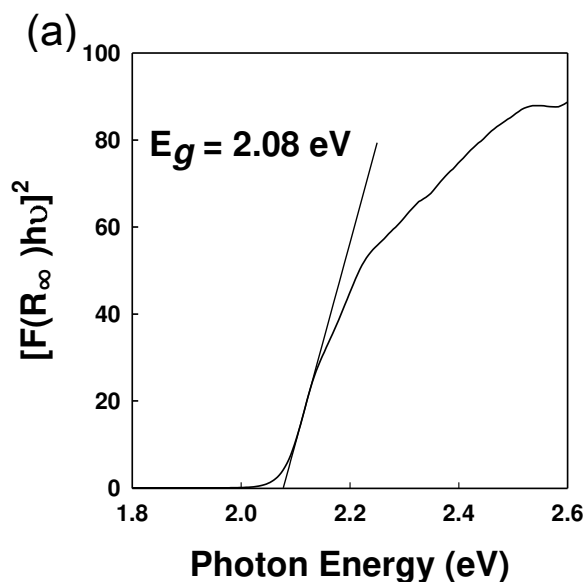
## 228 Mechanisms of the photo-dissolution of commercial cadmium sulfoselenide pigments

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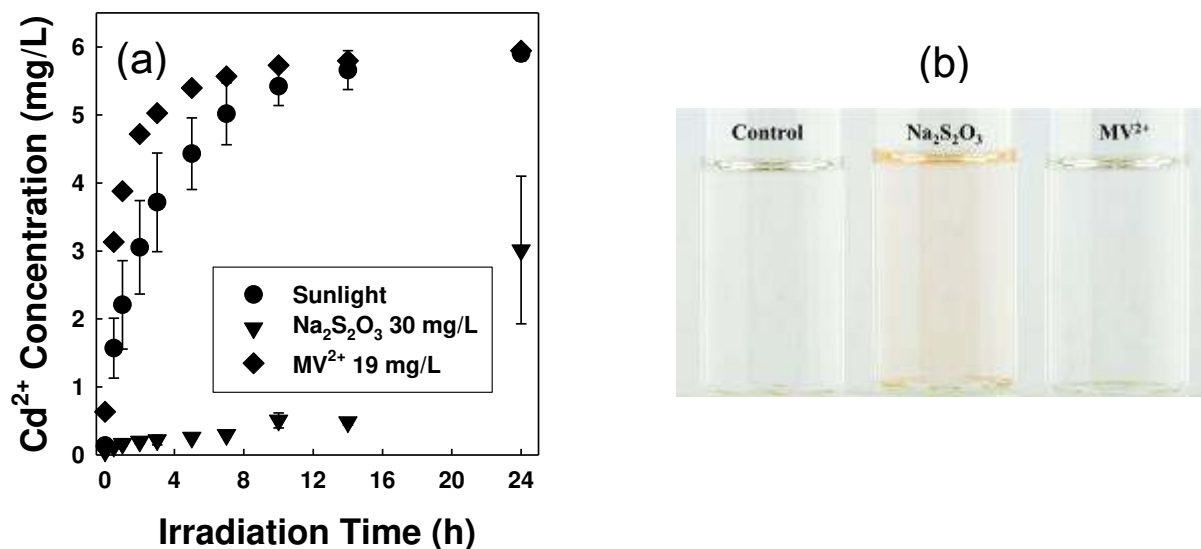


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235 Figure 4. (a) Kubelka-Munk function,  $(F(R_\infty)/\hbar\nu)^2$ , as a function of photon energy. (b) Mott-Schottky  
 236 plot of the commercial cadmium sulfoselenide pigment. (c) ESR spectra recorded under simulated  
 237 sunlight irradiation with 10 mg/L commercial cadmium sulfoselenide pigment and 100 mM spin trap  
 238 DMPO in 80 % DMSO, indicating the generation of superoxide ( $\text{O}_2^{\cdot-}$ ). (d) ESR spectra recorded during  
 239 simulated sunlight irradiation with 10 mg/L commercial cadmium sulfoselenide pigment and 100 mM  
 240 spin trap DMPO in water, indicating the generation of hydroxyl radicals ( $\cdot\text{OH}$ ).

241



242

243 Figure 5. (a) Cadmium release kinetics of 10 mg/L commercial cadmium sulfoselenide pigment in 1  
 244 mM NaCl solution at initial pH of  $6.86 \pm 0.43$  in the presence of 30 mg/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or 19 mg/L methyl  
 245 viologen (MV<sup>2+</sup>) under simulated sunlight (202 mW/cm<sup>2</sup>). Error bars represent  $\pm$  one standard deviation  
 246 from the average of triplicate tests. (b) Photos of 10 mg/L commercial cadmium sulfoselenide pigment  
 247 in 1 mM NaCl solution in the presence of 30 mg/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or 19 mg/L MV<sup>2+</sup> after 24 h simulated  
 248 sunlight irradiation.

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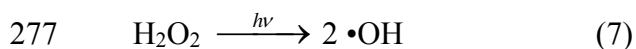
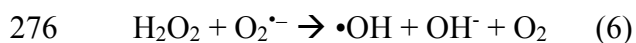
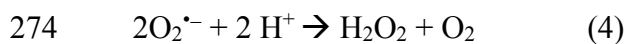
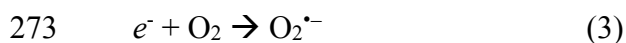
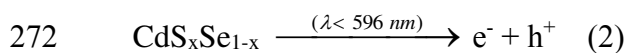
250 To better understand the photochemistry of commercial cadmium sulfoselenide pigment in the solar  
 251 spectrum, its band gap energy ( $E_g$ ) was determined by DRS (Figure 4a). The commercial pigment  
 252 showed strong light absorbance up to  $\sim 600$  nm. Its DRS spectrum was transformed to the Kubelka-  
 253 Munk function,  $(F(R_\infty)h\nu)^2$ , versus the photon energy plot as shown in Figure 4a.<sup>40, 41</sup>

254 
$$F(R_\infty) = (1-R)^2 / (2R) \quad (1)$$

255 In which, R is the reflectance, h is Planck's constant, and  $\nu$  is the light frequency. The  $E_g$  was  
 256 determined to be 2.08 eV by extrapolating the steepest slope to the x axis (Figure 4b).<sup>41</sup> This value is  
 257 generally consistent with the typical range of the  $E_g$  of cadmium sulfoselenide nanocrystals.<sup>9</sup> Thus,  
 258 commercial cadmium sulfoselenide pigment used in this study can be activated by irradiation

259 wavelength < 596 nm (i.e., 2.08 eV), which covers the major part of the solar spectrum. This agrees  
260 well with the fact that the photo-dissolution kinetics was still fast after filtering the UV light in the  
261 simulated sunlight (Figure 1a).

262 The flat-band potential of the pigment was determined using the Mott-Schottky method (Figure 4b).  
263 The slope of the linear regression is positive, indicating that the cadmium sulfoselenide pigment is a n-  
264 type semiconductor, for which the flat-band potential is close to the conduction band potential.<sup>42</sup> The  
265 conduction band potential of the cadmium pigment used in this study is -0.97 V vs. NHE (i.e., -1.21 V  
266 vs. SCE) at pH 5.5 as determined by the linear extrapolation method. The position of conduction band  
267 edge is a function of the solution pH, ~ 0.059 V/pH.<sup>43</sup> Thus, the conduction band potential is estimated  
268 to be -1.06 V at pH 7.0. The valence band is calculated to be 1.02 V based on the conduction band  
269 potential and E<sub>g</sub>. When excited by incident photons with energy higher than the band gap energy,  
270 cadmium sulfoselenide pigment generates electron-hole pairs which migrate to the surface of particles  
271 (Equation 2).



278 Colloidal semiconductors usually contain a large number of surface defect sites, which can trap  
279 charge carriers upon excitation.<sup>44</sup> Some of these charge carriers will react with surrounding molecules to  
280 form phototransients. The conduction band potential of the pigment is more negative than the redox  
281 potential of O<sub>2</sub>/ O<sub>2</sub><sup>•-</sup> (-0.28 V vs. NHE), thus the photogenerated electrons can transfer to O<sub>2</sub> and form  
282 O<sub>2</sub><sup>•-</sup>. We carried out ESR experiments under simulated sunlight irradiation using DMPO as a spin trap  
283 to detect these phototransients. In the presence of 10 mg/L pigment and 80 % DMSO as the •OH

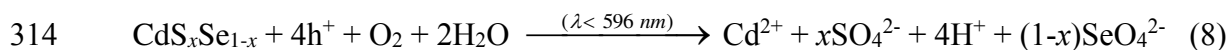
284 quencher, a characteristic fingerprint of the DMPO•OO(H) adduct ( $a_N = 12.7$  G,  $a_H = 10.3$  G) was  
285 observed, indicating the generation of  $O_2^{\bullet-}$  (Figure 4c).<sup>45</sup> Control test suggested that there was no ESR  
286 peaks in the same sample without simulated sunlight irradiation. Thus the electrons generated by the  
287 pigment can combine with oxygen molecules to yield  $O_2^{\bullet-}$  (Equation 3). The production of  $O_2^{\bullet-}$  was also  
288 examined by molecular probe, XTT, which can readily react with  $O_2^{\bullet-}$ , producing XTT formazan.<sup>31</sup> The  
289 formation of XTT formazan in the pigment suspension was a function of irradiation time (Figure S5a).  
290 It is worth noting that the XTT assay might not be specific to  $O_2^{\bullet-}$  in some cases under UV irradiation.<sup>46</sup>  
291 Nevertheless, the generation of XTT formazan was almost completely inhibited in the presence of  
292 superoxide dismutase (Figure S5b), confirming the generation of  $O_2^{\bullet-}$ .<sup>46</sup>

293 In 10 mg/L pigment water suspension, we observed an ESR pattern consisting of a 1:2:2:1 quartet  
294 with  $a_N = a_H = 14.9$  G under simulated sunlight, which is the hallmark for the DMPO•OH adduct (Figure  
295 4d), indicating the generation of •OH.<sup>45</sup> By using molecular probe, *p*CBA, the generation of •OH was  
296 confirmed in the illuminated pigment suspension (Figure S5c).<sup>32, 33</sup> The valence band potential of the  
297 pigment (+1.02 V vs. NHE) is lower than the redox potential of •OH/H<sub>2</sub>O (+2.27 V vs. NHE) and  
298 •OH/OH<sup>-</sup> (+1.99 V vs. NHE). Thus, the generation of •OH was not caused by the reactions between  
299 holes and H<sub>2</sub>O or surface-bound OH<sup>-</sup>. H<sub>2</sub>O<sub>2</sub> was detected in the irradiated pigment suspension as shown  
300 in Figure S5d, which was the product of the disproportionation of  $O_2^{\bullet-}$  (Equation 4). Therefore, the  
301 detected •OH was most likely formed through the H<sub>2</sub>O<sub>2</sub> reduction pathway (Equation 5-6).<sup>47</sup>

302 The valence band edge (+1.02 V vs. NHE) is higher than the standard potential for anodic dissolution  
303 of cadmium chalcogenide, around +0.32 V vs. NHE,<sup>48</sup> leading to the corrosion of pigment surface sites  
304 by photogenerated holes.<sup>15, 19, 49, 50</sup> To test this hypothesis, we added electron/hole scavengers into the  
305 reaction system. The photo-dissolution of the pigment was completely inhibited initially by the addition  
306 of 30 mg/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, a hole scavenger,<sup>51</sup> highlighting the predominant role of photogenerated holes  
307 (Figure 5). The release of Cd<sup>2+</sup> was observed after 7-h irradiation likely due to the consumption of  
308 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. On the other hand, the photo-dissolution of Cd<sup>2+</sup> was enhanced in the presence of an electron



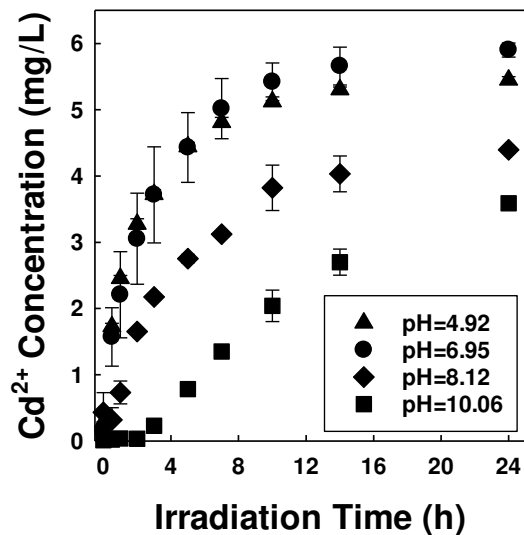
309 scavenger,  $MV^{2+15}$  (Figure 5). The  $MV^{2+}$  quickly reacted with photogenerated electrons, decreasing the  
310 recombination of photogenerated electron-hole pairs and consequently leaving more holes involved in  
311 the reactions with pigment lattices.<sup>15, 22</sup> Based on the evidence presented above as well as earlier reports  
312 on the photo-corrosion of CdS and CdSe nanocrystals, we proposed a mechanism for the sunlight-  
313 induced dissolution of commercial cadmium sulfoselenide pigments:



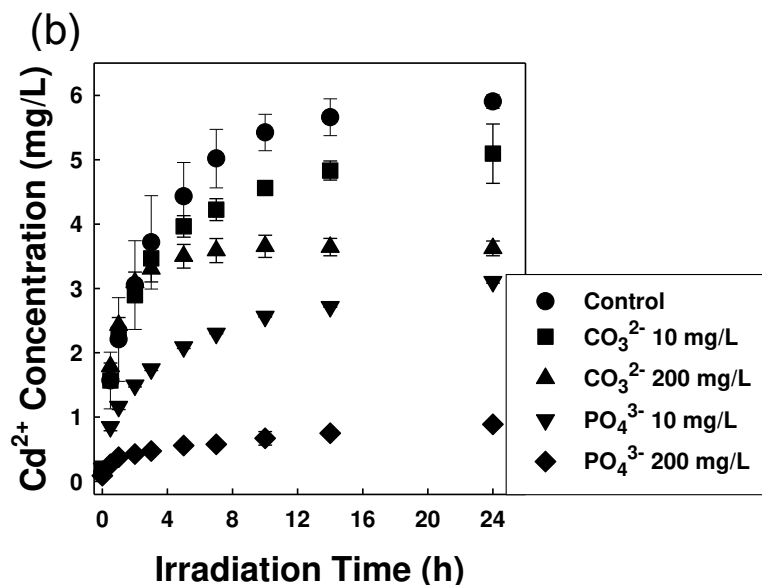
315 **Impact of water chemistry on the photo-dissolution kinetics of commercial cadmium**  
316 **sulfoselenide pigments**

317

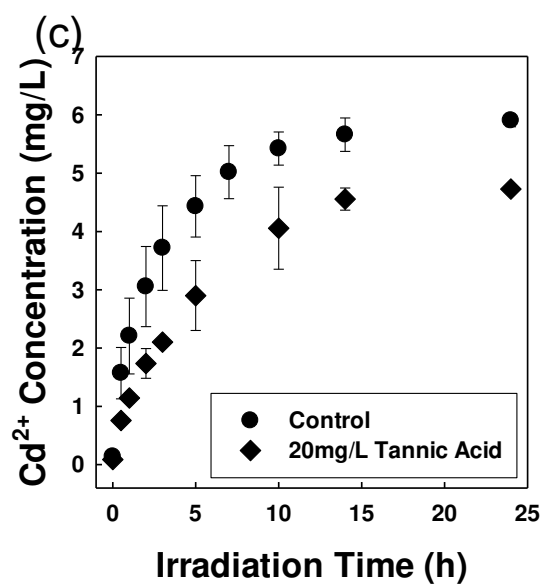
(a)



318



319



320

321 Figure 6. Dissolution kinetics of 10 mg/L commercial cadmium sulfoselenide pigment in 1 mM NaCl  
 322 solution under simulated sunlight irradiation (a) at various initial pH, (b) in the presence of PO<sub>4</sub><sup>3-</sup> or  
 323 CO<sub>3</sub><sup>2-</sup> species at initial pH of 6.90 ± 0.30, and (c) in the presence of tannic acid at initial pH of 6.51 ±  
 324 0.10. Error bars represent ± one standard deviation from the average of triplicate tests.

325

326 To better discern the environmentally-relevant release process, the impact of solution chemistry  
 327 including pH, phosphate, carbonate, and tannic acid on the photo-dissolution kinetics was further  
 328 examined. The photo-dissolution process was highly pH-dependent (Figure 6a). There was no

329 significant change of the photo-dissolution rate in acidic conditions as the initial pH increased from 4.92  
330  $\pm 0.03$  to  $6.95 \pm 0.02$ . However, photo-dissolution drastically decreased as the initial pH increased from  
331  $6.95 \pm 0.02$  to  $10.06 \pm 0.02$ . This could be attributed to the reduced valence band edge of the pigment,  
332 which decreases from +1.02 V (NHE) to +0.84 V (NHE) as pH increases from 7 to 10. Nevertheless, the  
333 photogenerated holes are still able to oxidize the cadmium pigment at pH 10 since the standard potential  
334 for anodic dissolution of cadmium chalcogenide is around +0.32 V vs. NHE.<sup>43, 48</sup> Another potential  
335 offsetting mechanism is the formation of Cd(OH)<sub>2</sub> precipitates ( $K_{sp}$ , Cd(OH)<sub>2</sub> =  $7.2 \times 10^{-15}$ )<sup>52</sup> or sorption  
336 of OH<sup>-</sup> on the particle surfaces under alkaline conditions.<sup>50</sup> These processes effectively blocked the  
337 surface sites suitable for trapping holes, leading to higher recombination of excitons and consequently  
338 less reaction with surface trapped holes.<sup>22</sup> Consistently, the XPS measurements suggest the atomic ratio  
339 of oxygen in hydroxide to cadmium on the pigment surface increased from 34.2% to 55.0% after 1 h  
340 irradiation at pH 10 (Figure S6). For experiments done at initial pH of  $10.06 \pm 0.02$ , the photo-  
341 dissolution process was slow during the initial 2 h, and then drastically increased afterwards. This is  
342 because the overall reaction releases protons (Equation 8) and lowers the pH of the system, facilitating  
343 the photo-dissolution process. The final pH of the samples with initial pH of  $10.06 \pm 0.02$  was  $6.81 \pm$   
344  $0.09$ , consistent with this argument.

345 Naturally occurring anions including phosphate and carbonate significantly affected the photo-  
346 dissolution process. The release of Cd<sup>2+</sup> from cadmium sulfoselenide pigment during simulated sunlight  
347 irradiation was inhibited in the presence of 10 mg/L phosphate or carbonate species (Figure 6b). The  
348 inhibitory effect of phosphate and carbonate was exacerbated as their concentration was further  
349 increased to 200 mg/L. The inhibition mechanism is the formation of photo-stable cadmium salts, which  
350 are highly insoluble in water ( $K_{sp}$ , Cd<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> =  $2.5 \times 10^{-33}$ , and  $K_{sp}$ , CdCO<sub>3</sub> =  $5.7 \times 10^{-13}$ ).<sup>53, 54</sup> Meanwhile,  
351 the anions in these cadmium salts, PO<sub>4</sub><sup>3-</sup> and CO<sub>3</sub><sup>2-</sup>, cannot be oxidized by photogenerated holes. As a  
352 result, these insoluble and photo-stable cadmium salts can passivate the pigment surface, inhibiting the  
353 oxidation of cadmium sulfoselenide and the consequent release of Cd<sup>2+</sup>.

354 The presence of 20 mg/L tannic acid, a surrogate for dissolved organic matter (DOM),<sup>55</sup> inhibited the  
355 photo-dissolution of cadmium sulfoselenide pigment. The inhibitory effect can be attributed to two  
356 mechanisms. Tannic acid molecules can absorb light, exerting a screening effect. This decreases the  
357 amount of photons received by pigment particles and consequently hinders the photo-dissolution  
358 process. Furthermore, tannic acid is a plant polyphenol with antioxidant properties.<sup>56</sup> It can scavenge  
359 photogenerated holes, mitigating oxidation of the pigment.<sup>57</sup> On the other hand, photoactive DOM can  
360 produce phototransients such as singlet oxygen, hydrogen peroxide, hydroxyl radical, and superoxide,<sup>58</sup>  
361 which could enhance the oxidative dissolution of pigment particles. The overall effect of photoactive  
362 DOM will depend on the interplay of its screening, hole scavenging, and photoactivity.

### 363 **Photo-dissolution of commercial cadmium sulfoselenide pigment in a natural setting**

364 In order to gain further insight into the natural photo-dissolution process of commercial cadmium  
365 sulfoselenide pigment, we carried out a solar irradiation experiment with a river water sample on the  
366 campus of Nanjing University from 11 a.m. to 3 p.m. on 11/04/2016. The solar irradiance was in the  
367 range of 35.8 to 56.1 mW/cm<sup>2</sup> (Figure S7). The natural river water had pH of  $7.70 \pm 0.20$  and total  
368 organic carbon of  $3.99 \pm 0.32$  mg/L. The concentrations of phosphate and carbonate ions in the river  
369 water were  $0.65 \pm 0.04$  mg/L and  $271.87 \pm 9.34$  mg/L, respectively. Fast release kinetics of Cd<sup>2+</sup> was  
370 observed in this river water sample under natural solar irradiation, with  $38.6 \pm 0.1$  % of the cadmium in  
371 the pigment being released within 4 h (Figure S8). Thus, we provide unequivocal evidence of fast and  
372 significant cadmium release from commercial cadmium sulfoselenide pigments under natural conditions.

### 373 **Environmental implications**

374 The commercial cadmium sulfoselenide pigment is photoactive under solar irradiation and is  
375 susceptible to photo-dissolution, which is the key environmental process controlling its release of Cd<sup>2+</sup>.  
376 The release can be mitigated by an increase in pH and the presence of anions that can form insoluble  
377 and photo-stable salts with Cd<sup>2+</sup>. Once released into aquatic systems, commercial cadmium pigment will  
378 undergo significant photo-dissolution within short period of time. The majority part of it will not persist

379 in the particulate form in natural settings, but will convert to highly toxic and bioavailable Cd<sup>2+</sup>. Thus,  
380 current risk assessments and regulations of cadmium pigments and other semiconductor pigments with  
381 hazardous metals need to consider their photochemistry. Our ongoing field investigation and a previous  
382 study<sup>59</sup> show extensive use and potential discharge of cadmium pigments in several Chinese cities with  
383 a booming ceramic industry.<sup>59</sup> We postulate that photo-dissolution is one of the environmental processes  
384 that lead to the significant accumulation of cadmium in soils at several sites in these cities. Furthermore,  
385 sunlight exposure of materials containing cadmium pigments could lead to potential environmental risks  
386 and health concerns. Little is known about the extent to which the matrix such as polymers and ceramics  
387 can inhibit the photo-dissolution of cadmium pigments and the subsequent release of metals. Future  
388 research is needed to quantify the photo-induced release of toxic Cd<sup>2+</sup> from colored products containing  
389 cadmium pigments.

390

## 391 **ASSOCIATED CONTENT**

### 392 **Supporting Information**

393 The experimental setup for irradiation experiments, the spectrum of the Xeon lamp used in this study  
394 and solar irradiation, the photo-dissolution kinetics of commercial cadmium sulfoselenide pigments  
395 from different vendors, the  $\zeta$ -potential of the commercial cadmium sulfoselenide pigment as a function  
396 of irradiation time, the detection of O<sub>2</sub><sup>•-</sup>, •OH, and H<sub>2</sub>O<sub>2</sub> using probe molecules, the XPS spectrum of  
397 the O1s peak of the pigment at different conditions, the variation of solar light power density during the  
398 natural light exposure, the dissolution kinetics of commercial cadmium sulfoselenide pigment in natural  
399 river water sample under solar irradiation, the cadmium release kinetics of the pigment under dark  
400 condition at initial pH of 4.92, and the determination of pseudo-second-order reaction rate constant can  
401 be found in the Supporting Information. This material is available free of charge via Internet at  
402 <http://pubs.acs.org/>.

403

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407

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415

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