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

Huiting Liu[1], Han Gao[1], Mingce Long[2], Heyun Fu[1], Pedro J.J. Alvarez[3], Qilin Li[3], Shourong Zheng[1], Xiaolei Qu[1]*, Dongqiang Zhu[4]

[1]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu 210023, China

[2]School of Environment Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

[3]Department of Civil and Environmental Engineering, Rice University, Houston TX 77005, United States

[4]School of Urban and Environmental Sciences, Peking University, Beijing 100871, China

* Corresponding author Xiaolei Qu, phone: +86-025-8968-0256; email: xiaoleiqu@nju.edu.cn

Abstract

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

Introduction

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

environment.[1, 2] Cadmium ion (Cd^{2+}) is known to cause acute toxicity based on short-term animal tests, and is a probable human carcinogen.[3] Thus the dissolution of cadmium pigments and consequent release of hazardous Cd^{2+} are key processes that control their potential environmental impacts. Previous risk assessments suggested that the use of cadmium pigments poses little risk to humans and the environment (except in occupational settings) due to their extremely low solubility ($K_{sp,CdS} = 7.94\times10^{-27}$ and $K_{sp,CdSe} = 6.31\times10^{-36}$),[4] and consequently low bioavailability.[5-8] Because of insufficient fate, transport, and toxicological studies, current cadmium pigment regulations are based on the precautionary principle.[1] For example, the European Union (EU) prohibits the use of cadmium pigments in 16 plastics with exemptions (see Regulation No. 494/2011). In China and EU, cadmium pigments are recommended to pass extraction tests for Cd^{2+}, < 0.1 wt % (Standards ISO 4620:1986, BS 6857-1987, and HG 2351-1992). However, these presumably conservative regulations may still underestimate associated risks by overlooking photochemical processes that enhance Cd^{2+} release.

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

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

induced oxidation over centuries, which yielded $CdSO_4 \bullet xH_2O$ and other cadmium species (e.g., $CdCO_3$) by secondary reactions. Nevertheless, our understanding of the photo-dissolution process of modern commercial cadmium pigments in natural aquatic systems is still limited, which hinders risk assessment and science-based regulation of these pigments and related colored consumer products.

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

Materials and Methods

Commercial cadmium sulfoselenide pigment powder (cadmium red) was purchased from Kela Co., Ltd., China. Dimethyl sulfoxide (DMSO, ≥ 99.0 %), sodium chloride (NaCl, ≥ 99.5 %), sodium carbonate (Na_2CO_3, ≥ 99.8 %), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \bullet 5H_2O$, ≥ 99 %) and sodium sulfate (Na_2SO_4, ≥ 99 %) were purchased from Nanjing Chemical Reagent Co., Ltd., China. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO, ≥ 97 %) was obtained from J&K Scientific Ltd., USA. Sodium selenite (Na_2SeO_4, ≥ 98 %) was purchased from Chengdu Micxy Chemical Co., Ltd., China. Methyl viologen dichloride hydrate (MV^{2+}, ≥ 98 %), sodium phosphate (Na_3PO_4, 96 %), sodium selenite pentahydrate ($Na_2SeO_3 \bullet 5H_2O$, ≥ 90 %), 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2*H*-tetrazolium-5-carboxanilide (XTT, > 90 %), terephthalic acid (TPA, 98 %), *N,N*-diethyl-p-phenylenediamine sulfate salt (DPD, ≥ 99 %), and horseradish peroxidase (HRP, ≥ 250 units/mg) were purchased from Sigma-

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

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

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

glass plate (Huanan Xiangcheng Co. Ltd., China, 2.5 cm × 2.5 cm, 1.1 mm thick, sheet resistance of 6-8 Ω/in^2). The electrode was then dried at 60 °C for 2 h. The electrolyte was 0.5 M Na_2SO_4 aqueous solution with pH of 5.5. The ac amplitude and frequency were set to be 5 mV and 1.5 KHz, respectively. The ζ-potential of the pigment particles was measured by phase analysis light scattering (PALS) using a ZEN 3500 Zetasizer Nano ZS (Malvern, Worcestershire, UK). Each sample was measured five times at 25 °C in a folded capillary cell (Malvern, Worcestershire, UK).

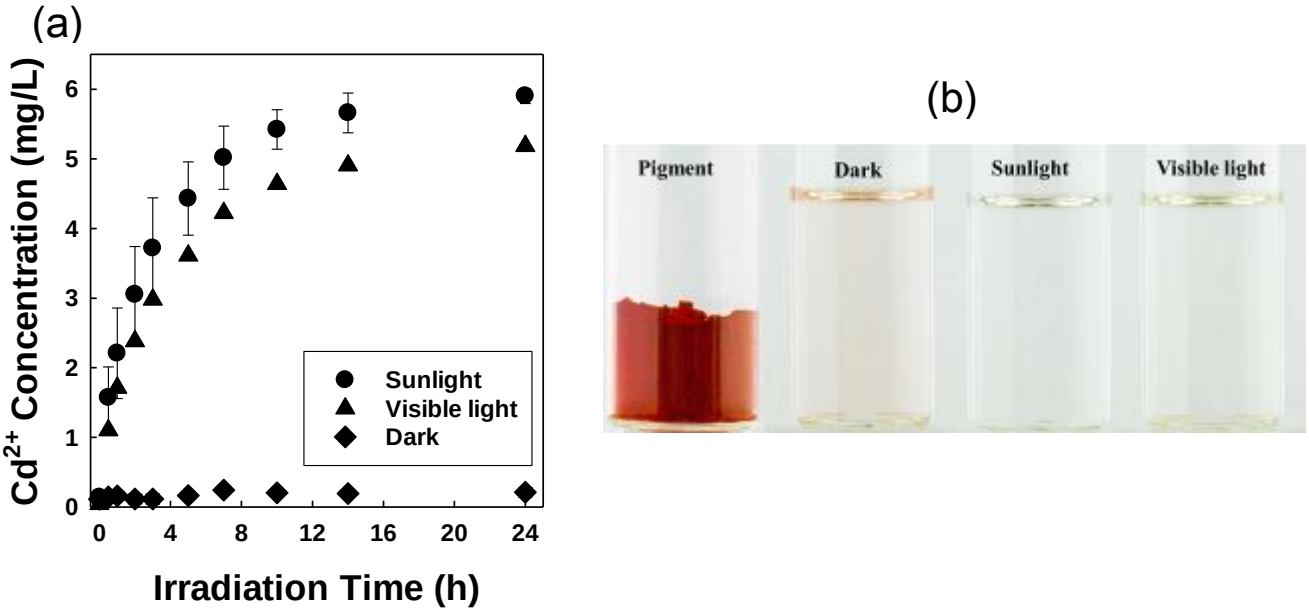
ROS determination. The production of superoxide ($O_2^{\bullet-}$), hydroxyl radical (•OH), and hydrogen peroxide (H_2O_2) by pigment suspensions was measured using probe molecules as described previously.[31-35] Superoxide generation was quantified by the formation of XTT formazan from XTT at an initial concentration of 0.05 mM. XTT formazan was quantified by its absorption at 475 nm using a UV-vis spectra. The extinction coefficient of XTT formazan is 21600 $M^{-1}cm^{-1}$.[31, 34] Hydroxyl radical production was quantified by monitoring the degradation of *p*CBA.[32-34] The *p*CBA concentration was measured at a detection wavelength of 254 nm using a high performance liquid chromatography (HPLC, Agilent 1100, Agilent Technologies, USA) with a Zorbax Eclipse XDB-C18 column (Agilent). The mobile phase was 30 % acetonitrile and 70 % 0.1 wt% phosphoric acid at a flow rate of 1 mL/min. H_2O_2 generation was measured by the HRP (5 mg/L) catalyzed oxidation of DPD (1mM).[35] The stable oxidation product, $DPD^{\bullet+}$, was measured by the UV-vis absorbance at 551 nm. The spin-trapping electron spin resonance (ESR) spectra were recorded on a Bruker EMX-10/12 spectrometer (Germany) at room temperature with X-band, microwave power of 20 mW, sweep width of 200 G, modulation width of 1 G, modulation frequency of 100 kHz.

Results and Discussion

Simulated sunlight exposure results in rapid release of Cd^{2+} from commercial cadmium sulfoselenide pigment

The dissolution kinetics of a representative cadmium pigment, cadmium sulfoselenide (CdS_xSe_{1-x}) was examined to assess its ability to release hazardous Cd^{2+}. The commercial cadmium sulfoselenide

pigment used here was a fine powder with brilliant red color (Figure 1). The SEM and TEM micrographs showed that pigment particles were quasi-spherical with a number average diameter of 186.1 ± 95.8 nm based on TEM micrographs (Figure 2). The commercial pigment can be readily dispersed in water (Figure 1b). The observed colloidal stability can be attributed to the small size and negative surface charge of the pigment particles with a ζ-potential of -24.37 ± 1.48 mV (electrophoretic mobility of -1.91 ± 0.12 μm•cm/Vs), which facilitates their colloidal stability through electrostatic repulsion as suggested by the Derjaguin-Landau-Verwey-Overbeek theory.[36, 37] The XRD pattern of the commercial pigment is shown in Figure 1c. The XRD spectrum has sharp peaks corresponding to the crystal structure of cadmium sulfoselenide, including 2θ at 24.66° (100), 26.28° (002), 27.99° (101), 36.34° (102), 43.30° (110), 47.28° (103), 50.38° (200), 51.28° (112), and 52.19° (201).[12, 38] ICP-MS measurements suggested the atomic ratio of S:Se of the pigment was 1.9 ± 0.1.



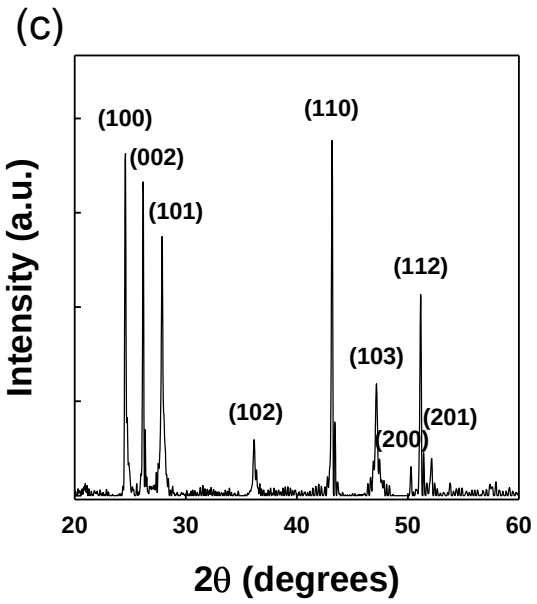


Figure 1. (a) Cadmium release kinetics of 10 mg/L commercial cadmium sulfoselenide pigment in 1 mM NaCl solution at initial pH of 6.77 ± 0.33 under dark, simulated sunlight (202 mW/cm^2), and visible light irradiation (152 mW/cm^2). Error bars represent ± one standard deviation from the average of triplicate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

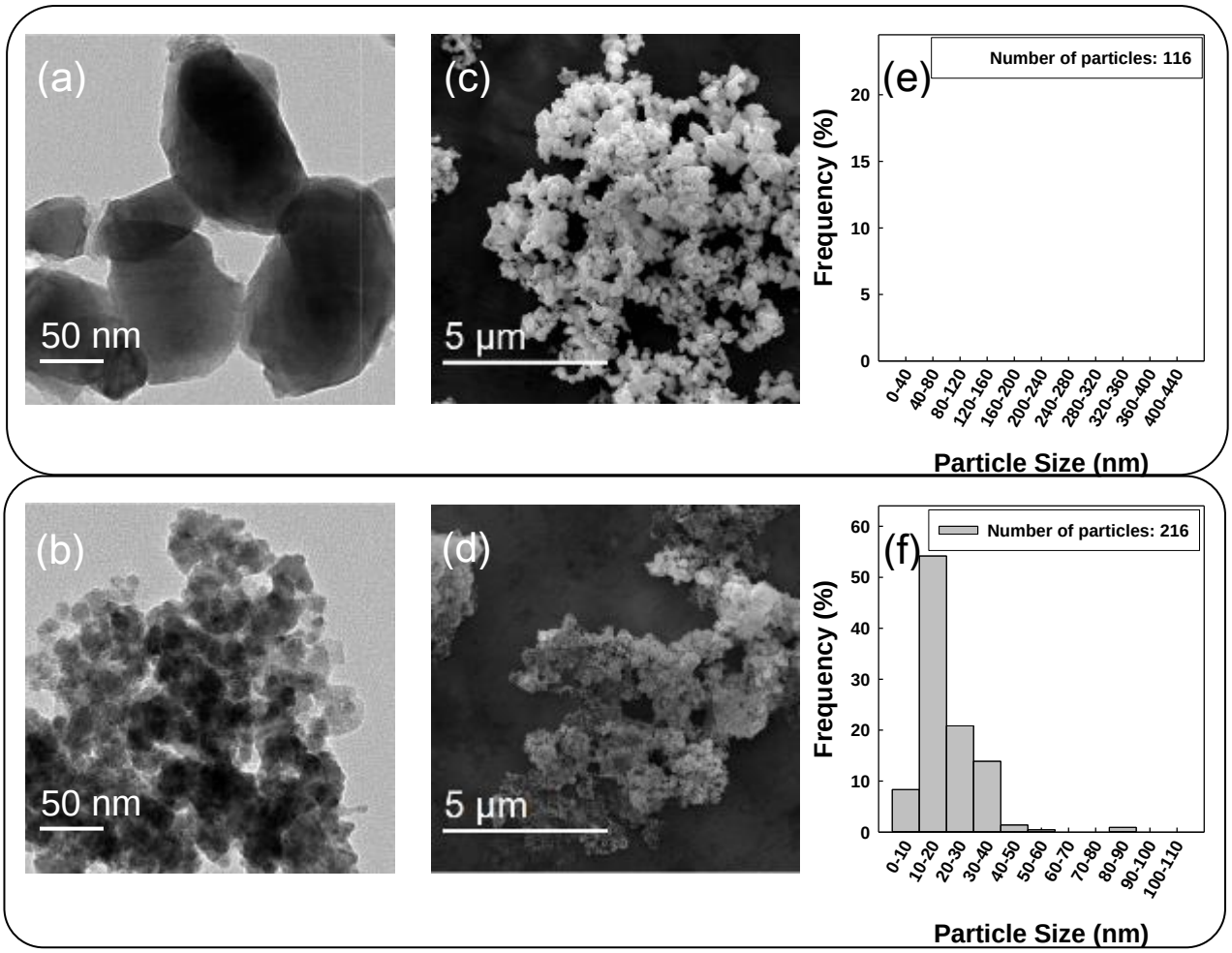


Figure 2. Morphology and size distribution of commercial cadmium sulfoselenide pigment particles before and after 7-h simulated sunlight exposure. TEM micrographs of commercial cadmium sulfoselenide pigment particles (a) before and (b) after sunlight exposure; SEM micrographs of commercial cadmium sulfoselenide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

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

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

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

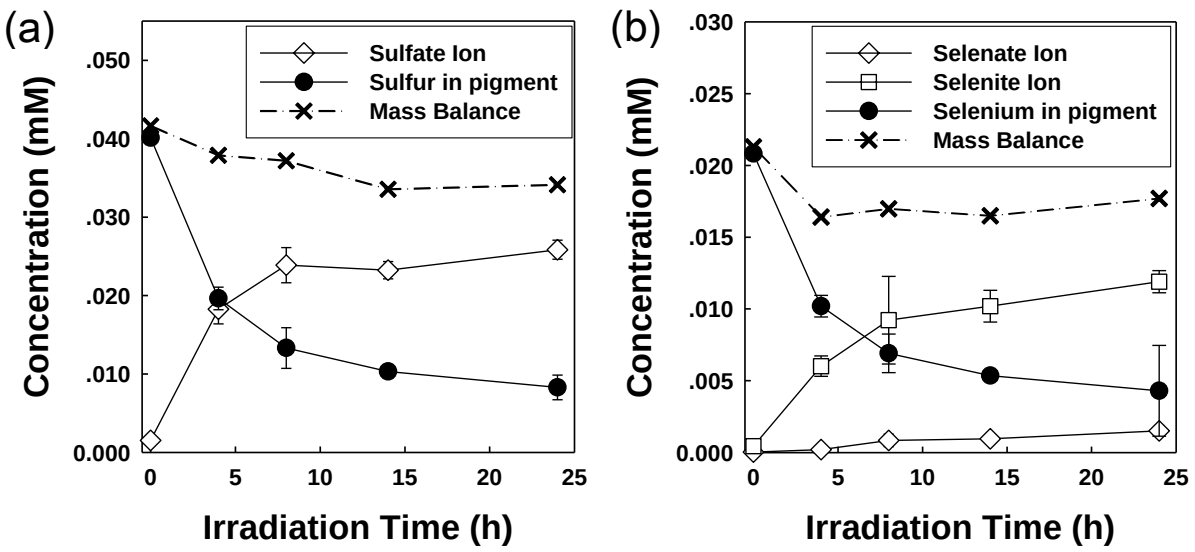


Figure 3. (a) The concentrations and mass balance of sulfur species, including sulfur in the pigment and sulfate ion (SO_4^{2-}), as a function of simulated sunlight irradiation time at initial pH of 6.77 ± 0.33. (b) The concentrations and mass balance of selenium species, including selenium in the pigment, selenite ion (SeO_3^{2-}), and selenate ion (SeO_4^{2-}), as a function of simulated sunlight irradiation time.

The release of sulfur and selenium species and their mass balance were examined during the photo-dissolution of commercial cadmium sulfoselenide pigment (Figure 3). The solution concentration of SO_4^{2-} increased with decreasing sulfur remaining in the pigment (Figure 3a). No SO_3^{2-} or S was detected using ion chromatography and HPLC, respectively. The mass balance of sulfur species was 81.8 % at 24 h. Similar analysis was applied to selenium species (Figure 3b). Both SeO_3^{2-} and SeO_4^{2-} were detected as reaction products, with SeO_4^{2-} being the major product and SeO_3^{2-} being the intermediate product. The mass balance of selenium species was 83.1 % at 24 h.

Mechanisms of the photo-dissolution of commercial cadmium sulfoselenide pigments

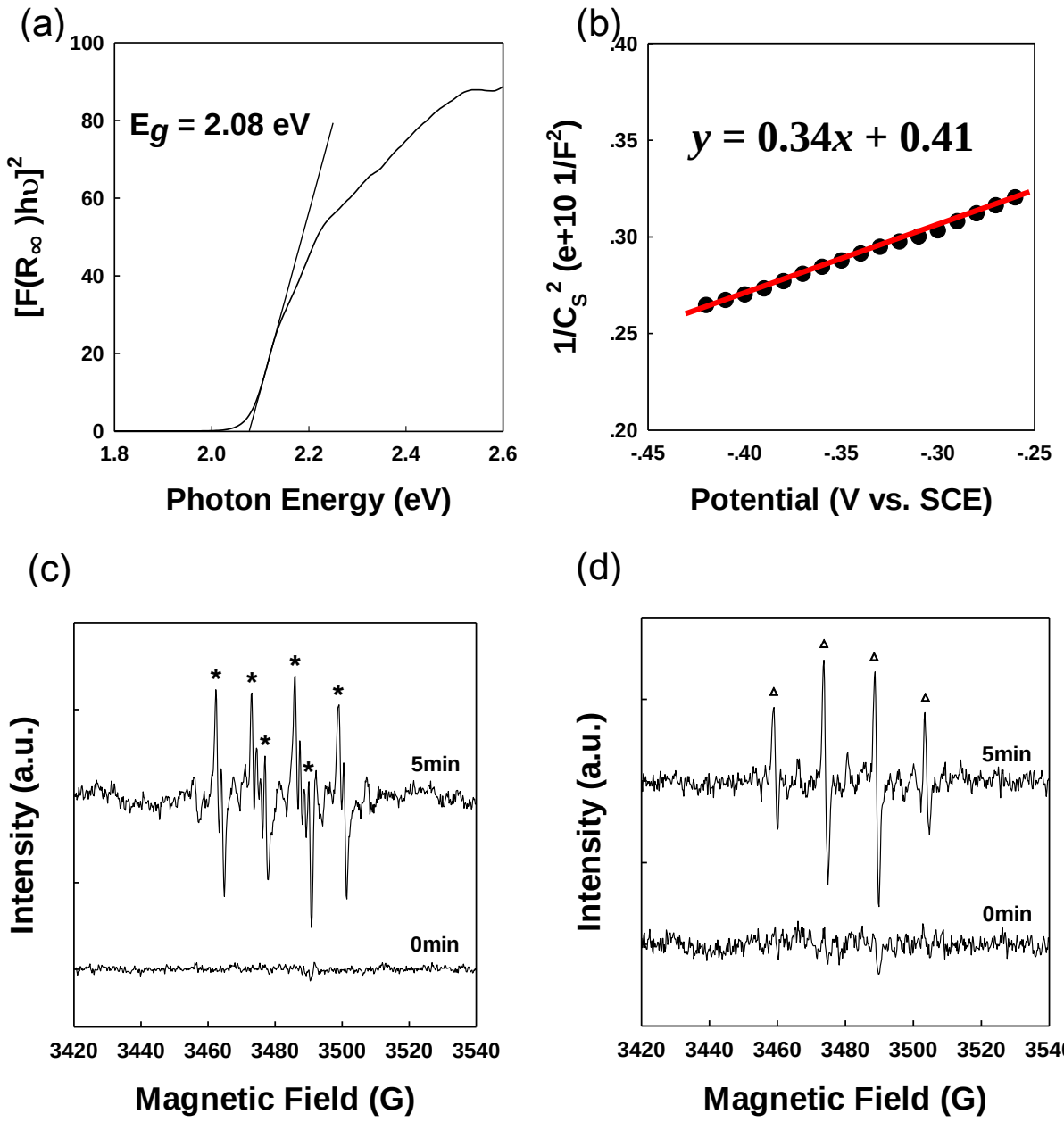


Figure 4. (a) Kubelka-Munk function, $(F(R_\infty)h\upsilon)^2$, as a function of photon energy. (b) Mott-Schottky plot of the commercial cadmium sulfoselenide pigment. (c) ESR spectra recorded under simulated sunlight irradiation with 10 mg/L commercial cadmium sulfoselenide pigment and 100 mM spin trap DMPO in 80 % DMSO, indicating the generation of superoxide ($O_2^{\bullet-}$). (d) ESR spectra recorded during simulated sunlight irradiation with 10 mg/L commercial cadmium sulfoselenide pigment and 100 mM spin trap DMPO in water, indicating the generation of hydroxyl radicals (•OH).

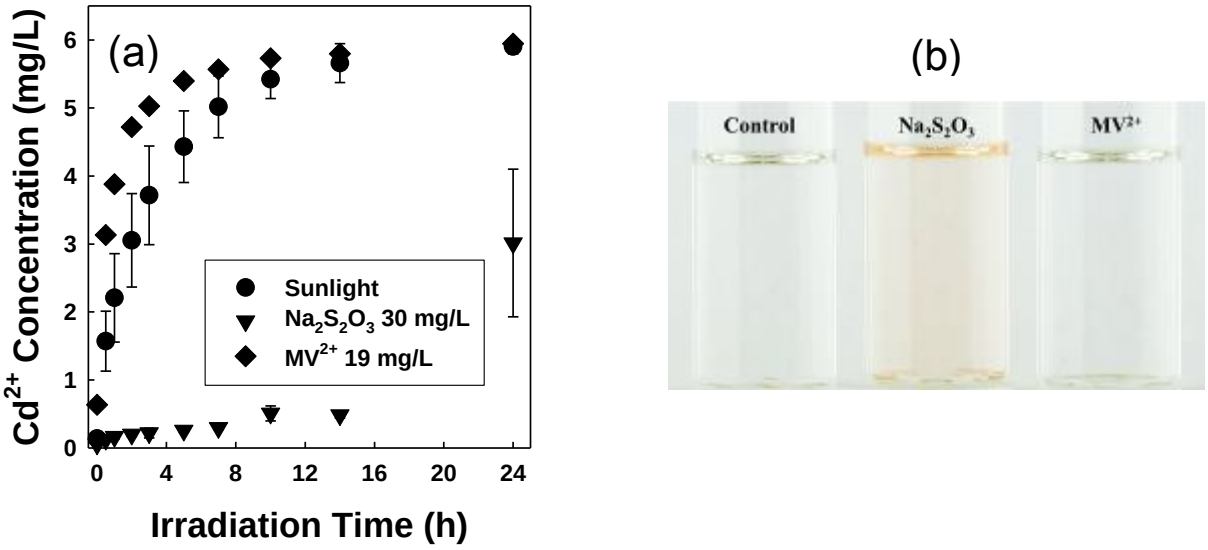


Figure 5. (a) Cadmium release kinetics of 10 mg/L commercial cadmium sulfoselenide pigment in 1 mM NaCl solution at initial pH of 6.86 ± 0.43 in the presence of 30 mg/L $Na_2S_2O_3$ or 19 mg/L methyl viologen (MV^{2+}) under simulated sunlight (202 mW/cm^2). Error bars represent ± one standard deviation from the average of triplicate tests. (b) Photos of 10 mg/L commercial cadmium sulfoselenide pigment in 1 mM NaCl solution in the presence of 30 mg/L $Na_2S_2O_3$ or 19 mg/L MV^{2+} after 24 h simulated sunlight irradiation.

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

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

In which, R is the reflectance, h is Planck's constant, and υ is the light frequency. The E_g was determined to be 2.08 eV by extrapolating the steepest slope to the *x* axis (Figure 4b).[41] This value is generally consistent with the typical range of the E_g of cadmium sulfoselenide nanocrystals.[9] Thus, commercial cadmium sulfoselenide pigment used in this study can be activated by irradiation

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

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

$$CdS_xSe_{1-x} \xrightarrow{(\lambda < 596\ nm)} e^- + h^+ \quad (2)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (3)$$

$$2O_2^{\bullet -} + 2\ H^+ \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + e^- \rightarrow \ \bullet OH + OH^- \quad (5)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow \bullet OH + OH^- + O_2 \quad (6)$$

$$H_2O_2 \xrightarrow{h\nu} 2\ \bullet OH \quad (7)$$

Colloidal semiconductors usually contain a large number of surface defect sites, which can trap charge carriers upon excitation.[44] Some of these charge carriers will react with surrounding molecules to form phototransients. The conduction band potential of the pigment is more negative than the redox potential of O_2/ $O_2^{\bullet -}$ (-0.28 V *vs.* NHE), thus the photogenerated electrons can transfer to O_2 and form $O_2^{\bullet -}$. We carried out ESR experiments under simulated sunlight irradiation using DMPO as a spin trap to detect these phototransients. In the presence of 10 mg/L pigment and 80 % DMSO as the •OH

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

In 10 mg/L pigment water suspension, we observed an ESR pattern consisting of a 1:2:2:1 quartet with $a_N = a_H$ = 14.9 G under simulated sunlight, which is the hallmark for the DMPO•OH adduct (Figure 4d), indicating the generation of •OH.[45] By using molecular probe, *p*CBA, the generation of •OH was confirmed in the illuminated pigment suspension (Figure S5c).[32, 33] The valence band potential of the pigment (+1.02 V *vs.* NHE) is lower than the redox potential of •OH/H_2O (+2.27 V *vs.* NHE) and •OH/OH^- (+1.99 V *vs.* NHE). Thus, the generation of •OH was not caused by the reactions between holes and H_2O or surface-bound OH^-. H_2O_2 was detected in the irradiated pigment suspension as shown in Figure S5d, which was the product of the disproportionation of $O_2^{\bullet-}$ (Equation 4). Therefore, the detected •OH was most likely formed through the H_2O_2 reduction pathway (Equation 5-6).[47]

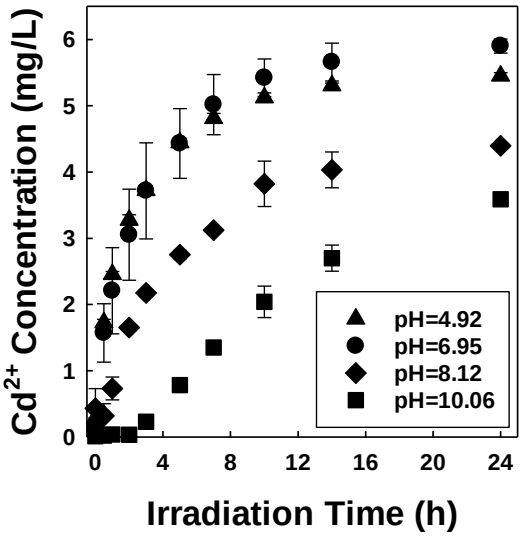
The valence band edge (+1.02 V *vs.* NHE) is higher than the standard potential for anodic dissolution of cadmium chalcogenide, around +0.32 V *vs.* NHE,[48] leading to the corrosion of pigment surface sites by photogenerated holes.[15, 19, 49, 50] To test this hypothesis, we added electron/hole scavengers into the reaction system. The photo-dissolution of the pigment was completely inhibited initially by the addition of 30 mg/L $Na_2S_2O_3$, a hole scavenger,[51] highlighting the predominant role of photogenerated holes (Figure 5). The release of Cd^{2+} was observed after 7-h irradiation likely due to the consumption of $Na_2S_2O_3$. On the other hand, the photo-dissolution of Cd^{2+} was enhanced in the presence of an electron

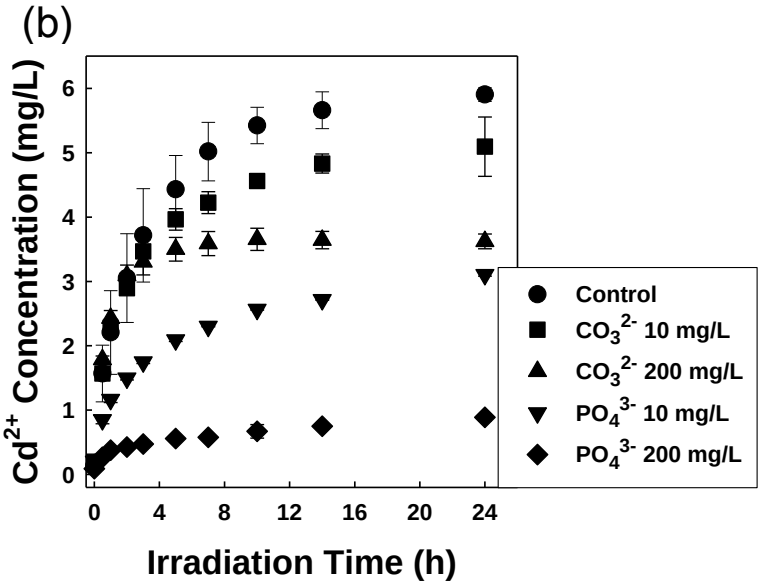
scavenger, MV^{2+}[15] (Figure 5). The MV^{2+} quickly reacted with photogenerated electrons, decreasing the recombination of photogenerated electron-hole pairs and consequently leaving more holes involved in the reactions with pigment lattices.[15, 22] Based on the evidence presented above as well as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

$$CdS_xSe_{1-x} + 4h^+ + O_2 + 2H_2O \xrightarrow{(\lambda < 596\ nm)} Cd^{2+} + xSO_4^{2-} + 4H^+ + (1-x)SeO_4^{2-} \quad (8)$$

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

(a)





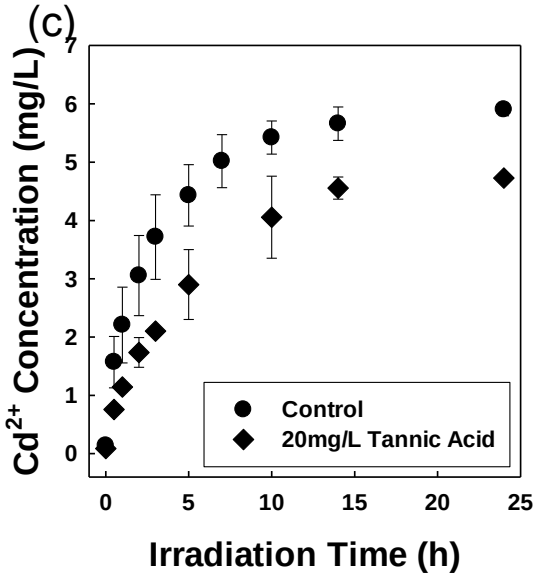


Figure 6. Dissolution kinetics of 10 mg/L commercial cadmium sulfoselenide pigment in 1 mM NaCl solution under simulated sunlight irradiation (a) at various initial pH, (b) in the presence of PO_4^{3-} or CO_3^{2-} species at initial pH of 6.90 ± 0.30, and (c) in the presence of tannic acid at initial pH of 6.51 ± 0.10. Error bars represent ± one standard deviation from the average of triplicate tests.

To better discern the environmentally-relevant release process, the impact of solution chemistry including pH, phosphate, carbonate, and tannic acid on the photo-dissolution kinetics was further 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 ± 0.03 to 6.95 ± 0.02. However, photo-dissolution drastically decreased as the initial pH increased from
331 6.95 ± 0.02 to 10.06 ± 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.[43, 48] Another potential
335 offsetting mechanism is the formation of $Cd(OH)_2$ precipitates (K_{sp}, $Cd(OH)_2 = 7.2\times10^{-15}$)[52] or sorption
336 of OH^- on the particle surfaces under alkaline conditions.[50] 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.[22] 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 ± 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 ± 0.02 was 6.81 ±
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^{2+} 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}, $Cd_3(PO_4)_2 = 2.5\times10^{-33}$, and K_{sp}, $CdCO_3 = 5.7\times10^{-13}$).[53, 54] Meanwhile,
351 the anions in these cadmium salts, PO_4^{3-} and CO_3^{2-}, 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^{2+}.

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

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

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

Environmental implications

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

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

ASSOCIATED CONTENT

Supporting Information

The experimental setup for irradiation experiments, the spectrum of the Xeon lamp used in this study and solar irradiation, the photo-dissolution kinetics of commercial cadmium sulfoselenide pigments from different vendors, the ζ-potential of the commercial cadmium sulfoselenide pigment as a function of irradiation time, the detection of $O_2^{\bullet-}$, •OH, and H_2O_2 using probe molecules, the XPS spectrum of the O1s peak of the pigment at different conditions, the variation of solar light power density during the natural light exposure, the dissolution kinetics of commercial cadmium sulfoselenide pigment in natural river water sample under solar irradiation, the cadmium release kinetics of the pigment under dark condition at initial pH of 4.92, and the determination of pseudo-second-order reaction rate constant can be found in the Supporting Information. This material is available free of charge via Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*Xiaolei Qu; Phone: +86-025-8968-0256; email: xiaoleiqu@nju.edu.cn

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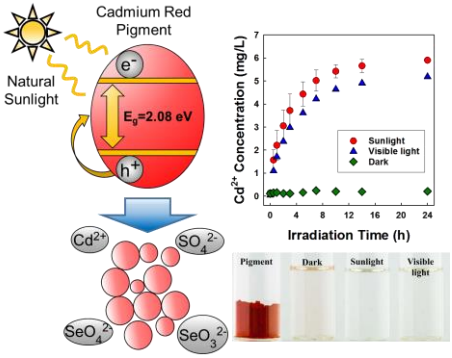
Cadmium Red Pigment
Natural Sunlight
e⁻
h⁺
Eg=2.08 eV
Cd2+
SO4 2-
SeO4 2-
SeO3 2-
Cd2+ Concentration (mg/L)
Irradiation Time (h)
Sunlight
Visible light
Dark
Pigment
Dark
Sunlight
Visible light

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