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# Treatment of electrochemical plating wastewater by heterogeneous photocatalysis: the simultaneous removal of 6:2 fluorotelomer sulfonate and hexavalent chromium†

 Hak-Hyeon Kim, Seyfollah Gilak Hakimabadi and Anh Le-Tuan Pham \*

6:2 fluorotelomer sulfonate (6:2 FtS) is being widely used as a mist suppressant in the chromate (Cr(vi)) plating process. As a result, it is often present alongside Cr(vi) in the chromate plating wastewater (CPW). While the removal of Cr(vi) from CPW has been studied for decades, little attention has been paid to the treatment of 6:2 FtS. In this study, the removal of Cr(vi) and 6:2 FtS by Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> photocatalysts was investigated. In the Ga<sub>2</sub>O<sub>3</sub>/UVC system, over 95% of Cr(vi) was reduced into Cr(III) after only 5 min. Simultaneously, 6:2 FtS was degraded into F<sup>-</sup> and several perfluorocarboxylates. The predominant reactive species responsible for the degradation of 6:2 FtS in the Ga<sub>2</sub>O<sub>3</sub> system were identified to be h<sub>VB</sub><sup>+</sup> and O<sub>2</sub><sup>•-</sup>. In addition, it was observed that the presence of Cr(vi) helped accelerate the degradation of 6:2 FtS. This synergy between Cr(vi) and 6:2 FtS was attributable to the scavenging of e<sub>CB</sub><sup>-</sup> by Cr(vi), which retarded the recombination of e<sub>CB</sub><sup>-</sup> and h<sub>VB</sub><sup>+</sup>. The In<sub>2</sub>O<sub>3</sub>/UVC system was also capable of removing Cr(vi) and 6:2 FtS, although at significantly slower rates. In contrast, poor removal of 6:2 FtS was achieved with the TiO<sub>2</sub>/UVC system, because Cr(III) adsorbed on TiO<sub>2</sub> and inhibited its reactivity. Based on the results of this study, it is proposed that CPW can be treated by a treatment train that consists of an oxidation–reduction step driven by Ga<sub>2</sub>O<sub>3</sub>/UVC, followed by a neutralization step that converts dissolved Cr(III) into Cr(OH)<sub>3(S)</sub>.

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## 1 Introduction

Owing to their simultaneous lipophobicity and hydrophobicity, high chemical and thermal stability, and surfactant property, per- and polyfluorinated alkyl substances (PFAS) are being used in a wide variety of industrial and commercial products, including in fire-fighting foams, flame retardants, mist suppressants, adhesives, and surface coatings, among others.<sup>1</sup> The extensive use of PFAS and the release of PFAS-containing wastes into the environment have led to their detection in air,<sup>2,3</sup> surface water,<sup>4,5</sup> groundwater,<sup>6–9</sup> drinking water,<sup>10,11</sup> soils<sup>6,8</sup> and biosolids.<sup>12–14</sup> Exposure to PFAS has been linked to various health problems, such as increased blood cholesterol, liver damage, kidney and testicular cancer, and thyroid dysfunction.<sup>15–18</sup> Therefore, guidelines and cleanup criteria in the low part-per-trillion levels are being proposed by jurisdictions around the world. For example, the US Environmental Protection Agency has recently established a health advisory level of 70 ng L<sup>-1</sup> for perfluorooctanoate (PFOA) and perfluorooctane

sulfonate (PFOS).<sup>19</sup> Health Canada has proposed drinking water screening values of 200–600 ng L<sup>-1</sup> for several PFAS compounds.<sup>20,21</sup> As our knowledge about the occurrence, fate, and toxicity of PFAS continues to grow, the guidelines for these compounds may become increasingly more stringent. Therefore, there is an urgent need to develop effective technologies for the treatment of PFAS-containing wastes to meet these future guidelines and to protect ecosystem and human health.

This study concerns the treatment of PFAS in chromate plating wastewater (CPW). During electrochemical plating, the evolution and burst of gas bubbles produced by electrolysis generates chromic acid mists, which pose significant health risks to workers on site. Therefore, a surfactant is usually added to the plating bath to suppress mist formation as well as to decrease surface wettability. Certain PFAS compounds are uniquely suited as mist suppressants in electrochemical plating because of their high aqueous solubility and resistance to electrochemical degradation. PFOS was traditionally the most popular mist suppressant in the electroplating industry, but this compound has been gradually replaced by 6:2 fluorotelomer sulfonate (6:2 FtS),<sup>22</sup> a less recalcitrant and bio-accumulative compound.<sup>23,24</sup> The concentration of 6:2 FtS in electrochemical plating baths is typically tens of mg L<sup>-1</sup>,

Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada. E-mail: [anh.pham@uwaterloo.ca](mailto:anh.pham@uwaterloo.ca); Tel: +1-519-888-4567 ext. 30337

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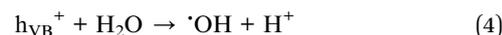
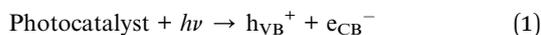


resulting in a concentration of 6:2 FtS in CPW ranging up to hundreds of  $\mu\text{g L}^{-1}$ .<sup>22</sup>

While the treatment of CPW has been investigated for decades, previous efforts focused primarily on removing hexavalent chromium ( $\text{Cr}(\text{VI})$ ) and other metals,<sup>25</sup> with little/no attention being paid to the removal of 6:2 FtS. However, it can be expected that conventional CPW treatment processes such as chemical reduction and coprecipitation are unlikely effective at removing 6:2 FtS. This is because like most PFAS, 6:2 FtS does not adsorb to metal hydroxides to an appreciable extent. Also, 6:2 FtS is generally resistant to chemical degradation; recent studies have shown that PFAS can only be degraded by harsh treatment processes such as thermal treatment,<sup>26–28</sup> plasma-based oxidation and reduction,<sup>29</sup> and reduction by hydrated electrons.<sup>30–32</sup>

Several studies have reported that PFAS can be degraded by heterogeneous photocatalysis. For example, it has been shown that PFOA was destroyed by photogenerated valence band holes ( $h_{\text{VB}}^+$ ) produced when wide-bandgap semiconductors such as  $\text{In}_2\text{O}_3$ ,<sup>33,34</sup>  $\text{Ga}_2\text{O}_3$ ,<sup>35</sup> and In modified- $\text{Ga}_2\text{O}_3$ <sup>36</sup> were irradiated with ultraviolet (UV) light. It has also been shown that PFOA could be degraded by the widely used  $\text{TiO}_2$  photocatalyst,<sup>33,34</sup> although the degradation rate was relatively slow since PFOA did not react appreciably with hydroxyl radical ( $\cdot\text{OH}$ ) (*i.e.*, the predominant reactive species in the  $\text{TiO}_2/\text{UV}$  system). In a recent study, an excellent removal of PFOA was achieved with a commercial boron nitride (BN) photocatalyst.<sup>37</sup> The degradation of PFOA in this system was attributable to multiple reactive species, including  $h_{\text{VB}}^+$ ,  $\cdot\text{OH}$ , and superoxide ( $\text{O}_2^{\cdot-}$ ). In addition to oxidative degradation, it appears that PFOA can also be reductively destroyed *via* reactions with photogenerated conduction band electrons ( $e_{\text{CB}}^-$ )<sup>38</sup> or by surface hydrogen.<sup>39</sup> While the generation of a suite of different reactive species capable of destroying PFAS makes heterogeneous photocatalysis appealing, a major drawback of this approach is that  $h_{\text{VB}}^+$  and  $e_{\text{CB}}^-$  usually recombine rapidly, resulting in inefficient production of reactive species. This limitation can be overcome by the addition of a scavenger (*e.g.*,  $\text{H}_2\text{O}_2$ ,  $\text{IO}_4^-$ ,  $\text{HS}^-$ ,  $\text{I}^-$ ) that react with either  $h_{\text{VB}}^+$  or  $e_{\text{CB}}^-$ , thereby extending the lifetime of the other species.<sup>40</sup>

We hypothesize that heterogeneous photocatalysis is a promising approach for the treatment of CPW, owing to its potential to remove both  $\text{Cr}(\text{VI})$  and 6:2 FtS in a single treatment step. Specifically, we envision that in heterogeneous photocatalysis  $\text{Cr}(\text{VI})$  will be reduced by  $e_{\text{CB}}^-$  into  $\text{Cr}(\text{III})$ , which then can be separated as  $\text{Cr}(\text{OH})_3(\text{s})$  by precipitation. Simultaneously, 6:2 FtS will be oxidized by  $h_{\text{VB}}^+$  and/or  $\cdot\text{OH}$ . Moreover, we hypothesize that there could be a synergistic effect between the removals of  $\text{Cr}(\text{VI})$  and 6:2 FtS—that is the removal of each contaminant will be enhanced in the presence of the other. This is because the scavenging of  $e_{\text{CB}}^-$  by  $\text{Cr}(\text{VI})$ , and of  $h_{\text{VB}}^+$  by 6:2 FtS could potentially mitigate the recombination of  $h_{\text{VB}}^+$  and  $e_{\text{CB}}^-$  as discussed above.



To test the hypotheses above, the removals of  $\text{Cr}(\text{VI})$  and 6:2 FtS were investigated using three commercially available photocatalysts, namely  $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ , and  $\text{TiO}_2$ . A series of experiments with probe compounds were conducted to gain insights into the reactive species responsible for degradation of 6:2 FtS. In addition, the 6:2 FtS degradation byproducts were measured throughout the experiment to close mass balance and elucidate the degradation pathway. Finally, the reusability of  $\text{Ga}_2\text{O}_3$  (which turned out to be the most promising among the studied materials) was investigated through a repeated contaminant removal experiment.

## 2 Materials and methods

### 2.1 Materials

The photocatalysts  $\text{Ga}_2\text{O}_3$  ( $\geq 99.99\%$ ),  $\text{In}_2\text{O}_3$  (99.9%), and  $\text{TiO}_2$  (Degussa P25, 99.5%) were purchased from Sigma Aldrich and were used as received. The surface morphology and elemental composition of these materials were characterized by scanning electron microscopy (SEM)/energy dispersive X-ray spectrometry (EDS), while their surface area was determined using the Brunauer–Emmett–Teller (BET)  $\text{N}_2$  physisorption method. The results of these characterizations are available in the ESI (Table S1 and Fig. S1†). 6:2 FtS (2-(perfluorohexyl)ethane-1-sulfonic acid sodium salt,  $>98\%$ ) was purchased from Toronto Research Chemicals (Toronto, ON), while PFAS analytical native and mass-labelled standards were purchased from Wellington Laboratories (Guelph, ON). All other chemicals were purchased at the highest purity available from Sigma Aldrich or Fisher Scientific. A stock solution of  $5 \text{ mg L}^{-1}$  6:2 FtS was prepared by dissolving 6:2 FtS in an aqueous solution consisting of 15 mM methanol. Other stock solutions, namely  $\text{Cr}(\text{VI})$  ( $100 \text{ mg L}^{-1}$  as Cr),  $\text{Cr}(\text{III})$  ( $100 \text{ mg L}^{-1}$  as Cr), *p*-benzoquinone (BQ, 100 mM) and bromate ( $\text{BrO}_3^-$ , 500 mM), were prepared by dissolving  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , BQ, and  $\text{KBrO}_3$  in  $18.2 \text{ M}\Omega \text{ cm}$  MilliQ water (Millipore).

### 2.2 Photolysis experiments

All experiments were carried out in a reactor chamber that was equipped with  $6 \times 4 \text{ W}$  UVC lamps (Fig. S2 in the ESI†). A quartz container, which held the reaction suspension, was placed at the center of the chamber. In most experiments, the reaction suspension was prepared by adding a photocatalyst and aliquots containing 6:2 FtS and  $\text{Cr}(\text{VI})$  from their respective stock solutions to MilliQ water such that  $[\text{catalyst}] = 0.5 \text{ g L}^{-1}$ ,  $[6:2 \text{ FtS}]_0 = 100$  or  $500 \mu\text{g L}^{-1}$ , and  $[\text{Cr}(\text{VI})]_0 = 0$  or  $1 \text{ mg L}^{-1}$ . Although the concentration of  $\text{Cr}(\text{VI})$  in chromium plating wastewaters can be in the order of tens of  $\text{mg L}^{-1}$ , the concentration of  $\text{Cr}(\text{VI})$  employed in most experiments was kept low to avoid damaging the liquid chromatograph mass spectrometer (LC/MS/MS). However, in one experiment, the initial concentrations of



Cr(VI) and 6:2 FtS were  $20 \text{ mg L}^{-1}$  and  $2 \text{ mg L}^{-1}$ , respectively. The samples collected from this experiment were diluted 400 times prior to LC/MS/MS analysis. In some experiments, the reaction suspension also contained formic acid (HCOOH, a  $h_{\text{VB}}^+$  scavenger),<sup>40</sup> *tert*-butyl alcohol (*t*-BuOH, an  $\cdot\text{OH}$  scavenger),<sup>41</sup> BQ (a  $\text{O}_2^{\cdot-}$  scavenger),<sup>42</sup> or  $\text{BrO}_3^-$  (a  $e_{\text{CB}}^-$  scavenger).<sup>43</sup> The initial pH of the reaction suspension was adjusted to  $\text{pH} = 3 \pm 0.1$  using either  $1 \text{ M H}_2\text{SO}_4$  or  $1 \text{ M NaOH}$ . The pH of the suspension varied by less than 0.1 unit throughout the entire course of each experiment.

Preliminary experiments showed that approximately 10% of the initial 6:2 FtS was lost by adsorption on the photocatalysts, and that adsorption equilibrium was attained within 30 min. As such, the suspension was vigorously mixed in the dark for 1 hour. Subsequently, photochemical reactions were initiated by turning the UVC lamps on. At predetermined time intervals, aliquots of suspension were withdrawn and subjected to analyses for dissolved Cr, fluoride ( $\text{F}^-$ ), as well as 6:2 FtS and its degradation products.

As will be presented in the Results and discussion sections,  $\text{Ga}_2\text{O}_3$  was observed to be the photocatalyst most efficient at removing 6:2 FtS and Cr(VI). Therefore, the reusability of  $\text{Ga}_2\text{O}_3$  was evaluated over 3 experimental cycles wherein at the end of each cycle  $\text{Ga}_2\text{O}_3$  particles were separated and added to a fresh reaction solution containing  $100 \mu\text{g L}^{-1}$  6:2 FtS and  $1 \text{ mg L}^{-1}$  Cr(VI). Subsequently, the photolysis experiment was repeated.

All experiments were carried out at least in triplicate, and the average values are presented along with one standard deviation. The evolution of the concentrations of different species in the solution is expressed against energy flux ( $\text{J cm}^{-2}$ ) received by the reaction suspension, which was determined based on ferrioxalate actinometry.

### 2.3 Analytical methods

For the analysis of  $\text{F}^-$ ,  $\text{Ga}_2\text{O}_3$  particles were separated from the suspension by centrifugation, and  $\text{F}^-$  in the supernatant was measured spectrophotometrically using the modified SPADNS method (limit of quantitation of  $50 \mu\text{g L}^{-1}$ ).<sup>44</sup> For the analysis of dissolved Cr, the suspension was first acidified to  $\text{pH} < 2$  to dissolve particulate Cr(III) (which was formed due to the photoreduction of Cr(VI) to Cr(III)). Subsequently,  $\text{Ga}_2\text{O}_3$  particles were separated by centrifugation, and Cr(VI) and total Cr (*i.e.*, Cr(VI) + Cr(III)) in the acidified supernatant were measured spectrophotometrically using the 1,5-diphenylcarbazide method.<sup>45</sup> The limits of quantitation by this method are  $30 \mu\text{g L}^{-1}$  for Cr(VI), and  $50 \mu\text{g L}^{-1}$  for total Cr. The concentration of Cr(III) in the sample was calculated based on the difference between the concentrations of total Cr and Cr(VI).

For the analysis of PFAS by LC/MS/MS, each sub-aliquot was diluted 9 times in a solution consisting of 50 v% methanol and 50 v% 5 mM ammonium acetate in water. The purpose of this dilution was threefold: (a) to desorb PFAS from the catalyst in order to enable closing mass balance, (b) to precipitate Cr(III) from the sample in order to minimize the amount of dissolved Cr introduced into the LC/MS/MS, and (c) to obtain a sample consisting of *ca.* 50/50 v/v methanol/water for analysis by LC/

MS/MS. Following dilution, the suspension was centrifuged to separate  $\text{Ga}_2\text{O}_3$  and  $\text{Cr}(\text{OH})_3$ , and the supernatant was added to an HPLC vial. Prior to LC/MS/MS analysis, mass-labelled PFAS, which served as internal standards, were spiked into each vial. Details about the LC/MS/MS operating condition and the list of PFAS compounds analysed in this study can be found in the ESI (Tables S2 and S3†).

## 3 Results

Photolysis without a catalyst did not result in 6:2 FtS or Cr(VI) removal (data not shown). Also, both contaminants were not removed appreciably by adsorption in the absence of light (Fig. S3†). In contrast, both contaminants were removed when  $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ , or  $\text{TiO}_2$  was present, although the reaction rates varied significantly (Fig. 1). In the  $\text{Ga}_2\text{O}_3$  system, the concentration of Cr(VI) decreased to around the method quantitation limit after only 5 min of irradiation (Fig. 1a). Simultaneously, the concentration of 6:2 FtS gradually decreased throughout the course of the experiment, with 90% 6:2 FtS removed after 2 hours (equivalent to a fluence of  $19 \text{ J cm}^{-2}$ , Fig. 1d). Interestingly, the 6:2 FtS degradation rate was over twice slower when Cr(VI) was absent ( $k_{\text{observed}} = 0.34 \text{ h}^{-1}$ , versus  $k_{\text{observed}} = 0.73 \text{ h}^{-1}$  in the presence of Cr(VI)). Excellent removals of Cr(VI) and 6:2 FtS were also observed in the experiment wherein the initial concentrations of the contaminants were increased by 20 times (*i.e.*,  $[\text{Cr}(\text{VI})]_0 = 20 \text{ mg L}^{-1}$ ,  $[\text{6:2 FtS}] = 2 \text{ mg L}^{-1}$ ; Fig. S4†).

Cr(VI) and 6:2 FtS were also simultaneously removed in the  $\text{In}_2\text{O}_3$  system, although at significantly slower rates. After 8 hours, the concentrations of Cr(VI) and 6:2 FtS decreased by only 50% and 35%, respectively (Fig. 1b and e). As in the  $\text{Ga}_2\text{O}_3$  system, the presence of Cr(VI) enhanced the rate of 6:2 FtS degradation ( $k_{\text{observed}} = 0.12 \text{ h}^{-1}$  and  $0.10 \text{ h}^{-1}$  in the presence and absence of Cr(VI), respectively). On the contrary, the presence of Cr(VI) inhibited the degradation of 6:2 FtS in the  $\text{TiO}_2$  system: whereas 80% of 6:2 FtS was removed within the first 20 min in the absence of Cr(VI), only 30% removal was achieved in the presence of Cr(VI) even after 8 hours ( $k_{\text{observed}} = 0.04 \text{ h}^{-1}$ ) (Fig. 1f). If the 6:2 FtS degradation was very slow, the reduction of Cr(VI) in the  $\text{TiO}_2$  system was slightly faster than that in the  $\text{In}_2\text{O}_3$  system (Fig. 1c).

The varying reactivity among the materials discussed above is attributable to their inherent photocatalytic reactivity rather than to the difference in their surface area. In the absence of Cr(VI), the 6:2 FtS degradation rate with  $\text{TiO}_2$  ( $k_{\text{observed}} = 2.39 \text{ h}^{-1}$ ) was over seven times faster than that with  $\text{Ga}_2\text{O}_3$  ( $k_{\text{observed}} = 0.34 \text{ h}^{-1}$ ), although the surface area of  $\text{TiO}_2$  ( $51.9 \text{ m}^2 \text{ g}^{-1}$ ) is only three times greater than that of  $\text{Ga}_2\text{O}_3$  ( $19.5 \text{ m}^2 \text{ g}^{-1}$ ). In the presence of Cr(VI), the 6:2 FtS degradation rate with  $\text{Ga}_2\text{O}_3$  ( $k_{\text{observed}} = 0.73 \text{ h}^{-1}$ ) was over six times greater than that of  $\text{In}_2\text{O}_3$  ( $k_{\text{observed}} = 0.12 \text{ h}^{-1}$ ), even though the surface area of the latter ( $7.1 \text{ m}^2 \text{ g}^{-1}$ ) is only 2.7 times less than that of the former.

Not only did the contaminant removal rates vary but also the reactive species responsible for the degradation of 6:2 FtS appeared to be significantly different in the three photocatalyst systems. With  $\text{In}_2\text{O}_3$ , 6:2 FtS did not degrade appreciably in the presence of either 10 mM HCOOH or 10 mM *t*-BuOH (Fig. S5a†).



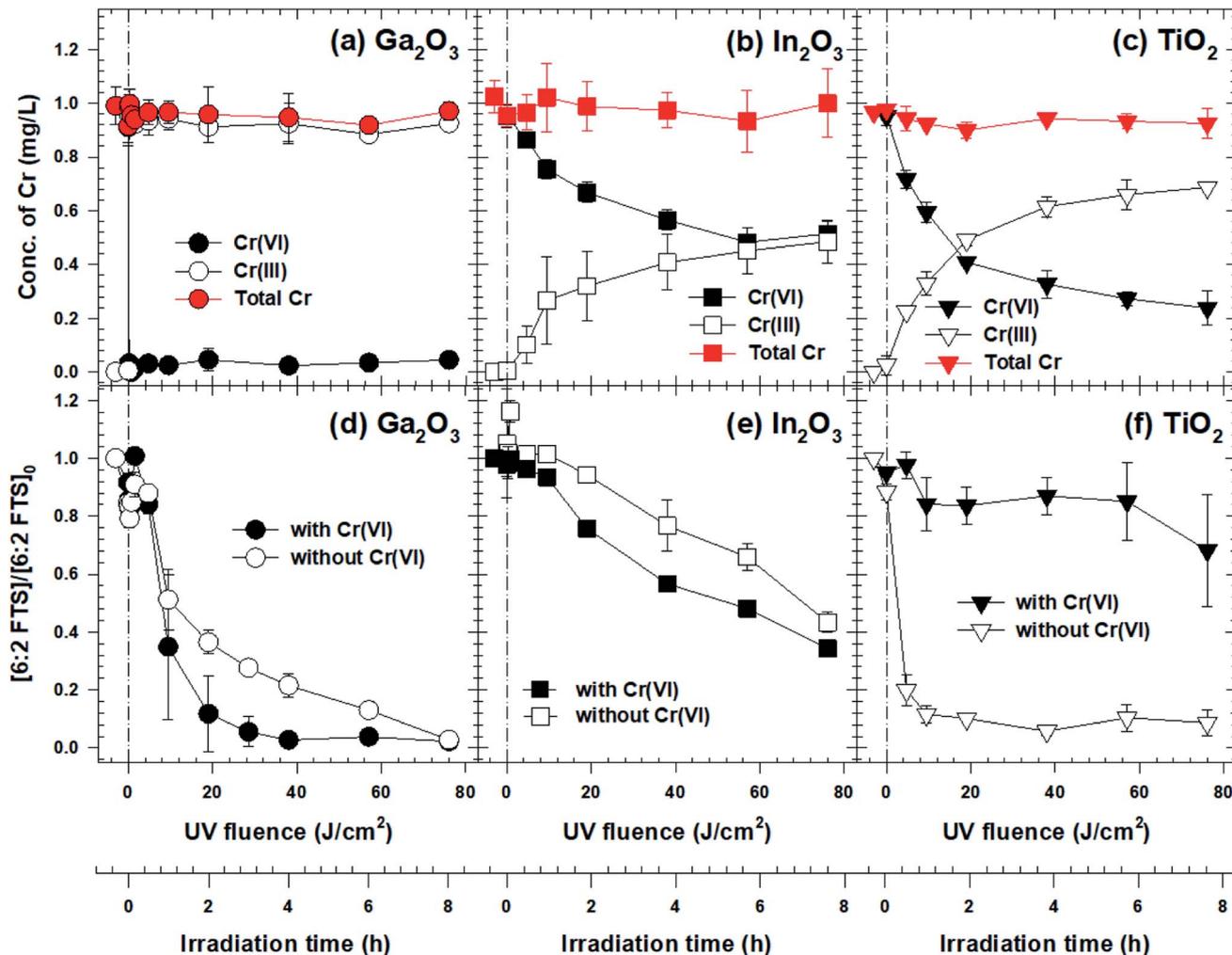


Fig. 1 Removals of Cr(vi) and 6:2 Fts by  $\text{Ga}_2\text{O}_3$  (a) and (d),  $\text{In}_2\text{O}_3$  (b) and (e) and  $\text{TiO}_2$  (c) and (f) photocatalysts. [Catalyst] =  $0.5 \text{ g L}^{-1}$ ,  $[\text{6:2 Fts}]_0 = 100 \mu\text{g L}^{-1}$ ,  $[\text{Cr(vi)}]_0 = 1 \text{ mg L}^{-1}$ ,  $\text{pH} = 3.0 \pm 1$ . The solution was vigorously mixed in the dark for 1 hour. Subsequently, photolysis was initiated by turning UV-C lamps on at  $t = 0$  h.

With  $\text{TiO}_2$ , the degradation of 6:2 Fts was also significantly inhibited by  $\text{HCOOH}$ , but was only partially inhibited by  $t\text{-BuOH}$  (Fig. S5b<sup>†</sup>). Somewhat surprisingly, neither of these two scavengers had any effect on the degradation of 6:2 Fts by  $\text{Ga}_2\text{O}_3$  (Fig. 2a). However, the degradation was partially inhibited when  $\text{BrO}_3^-$  was present, and was completely inhibited in the presence of  $\text{HCOOH}$  and  $\text{BrO}_3^-$ , or  $\text{HCOOH}$  and BQ (Fig. 2a).

Because  $\text{Ga}_2\text{O}_3/\text{UVC}$  was effective at removing both Cr(vi) and 6:2 Fts, the evolution of the 6:2 Fts degradation byproducts in this system was further investigated to gain insight into the reaction pathway. Besides  $\text{F}^-$ , a total of 5 byproducts, *i.e.*, 6:2 fluorotelomer carboxylate (6:2 FtCA), perfluoroheptanoate (PFHpA), perfluorohexanoate (PFHxA), perfluoropentanoate (PFPeA), perfluorobutanoate (PFBA), were observed as 6:2 Fts was degraded (Fig. 2b). The fluorine mass balance indicates that the sum of  $\text{F}^-$ , the F in the 5 byproducts, and the F in the remaining 6:2 Fts accounted for 80% of the total F initially added as 6:2 Fts (Fig. 2c). This result suggests that there must be other byproducts that were not detected by the LCMS analytical

method used in this study. Among the measured byproducts, 6:2 FtCA exhibited a two-phase concentration–time profile wherein its concentration first increased and subsequently decreased (Fig. 2b). For the other 4 byproducts, their concentrations increased gradually (Fig. 2b). By the end of the experiment, the concentration of  $\text{F}^-$  was  $135 \mu\text{g L}^{-1}$  (equivalent to approximately 50% of the total F added).

In the  $\text{Ga}_2\text{O}_3$  reusability experiment, excellent removals of both Cr(vi) and 6:2 Fts were observed over three cycles (Fig. 3a). In each cycle, more than 95% of Cr(vi) was reduced into Cr(III), 80% of which can be separated by  $\text{Cr}(\text{OH})_{3(\text{s})}$  from the treated stream by raising the solution pH to 7.5 (Fig. 3b). The concentration of dissolved Cr after pH adjustment and  $\text{Cr}(\text{OH})_{3(\text{s})}$  separation (by centrifugation) was  $0.2 \text{ mg L}^{-1}$ , well below the US EPA's discharge limit of  $2\text{--}4 \text{ mg L}^{-1}$ .<sup>46</sup> Meanwhile, the fraction of 6:2 Fts degraded in each cycle ranged between 86 and 92%. The slightly lower 6:2 Fts removal in cycle 3 could be due to the adsorption of Cr species on  $\text{Ga}_2\text{O}_3$ , thereby diminishing its photocatalytic reactivity.



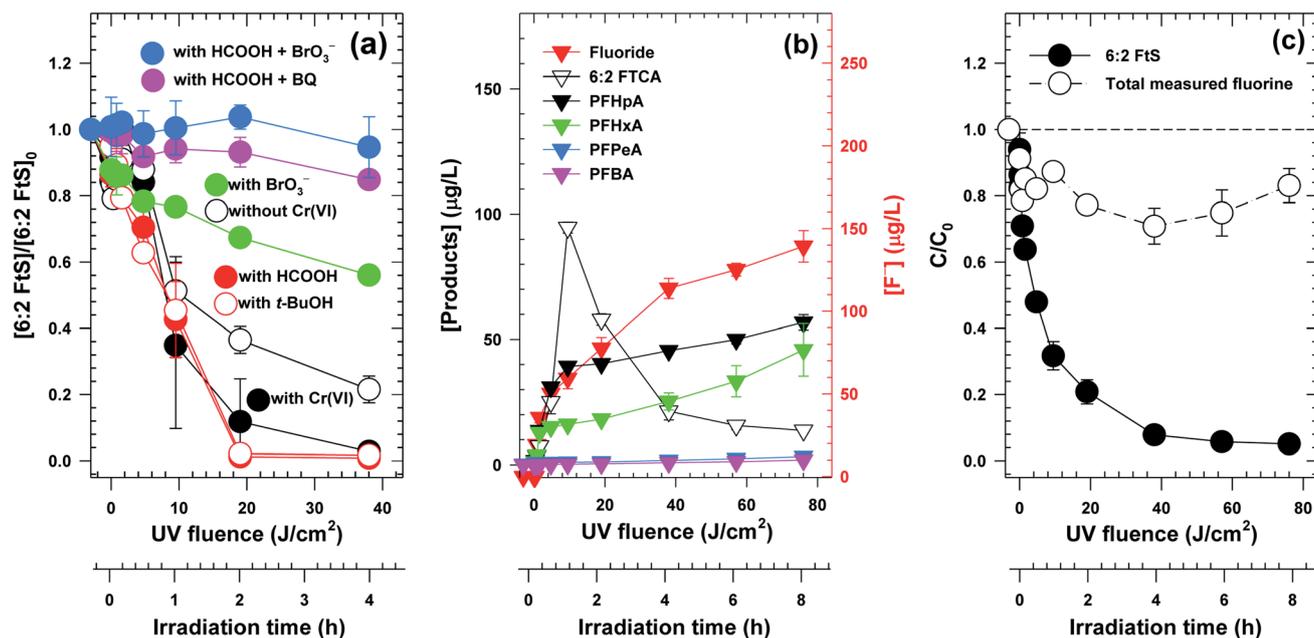


Fig. 2 (a) Effect of various scavengers on the degradation of 6:2 FtS; (b) evolution of byproducts; (c) F mass balance.  $[\text{Ga}_2\text{O}_3]_0 = 0.5 \text{ g L}^{-1}$ ,  $[6:2 \text{ FtS}]_0 = 100 \mu\text{g L}^{-1}$  in (a)  $500 \mu\text{g L}^{-1}$  in (b) and (c),  $[\text{Cr}(\text{vi})] = 1 \text{ mg L}^{-1}$ ,  $[\text{t-BuOH}]_0 = [\text{HCOOH}]_0 = [\text{BrO}_3^-]_0 = 10 \text{ mM}$ ,  $[\text{BQ}]_0 = 1 \text{ mM}$ ,  $\text{pH} = 3.0 \pm 1$ . It is noted that Cr(vi) was not added in the experiments wherein other scavengers (i.e., HCOOH, BQ,  $\text{BrO}_3^-$ , and t-BuOH) were present.

## 4 Discussion

### 4.1 Reactive species responsible for contaminant removal

The Cr mass balance and the stoichiometric production of Cr(III) in all three photocatalytic systems suggest that Cr(vi) was removed *via* reactions with  $e_{\text{CB}}^-$  (reaction (2)). (The reduction of

Cr(vi) *via* direct reactions with 6:2 FtS can be ruled out as Cr(III) was not produced in the absence of photocatalysts. The production of Cr(III) from direct reactions between Cr(vi) and the byproducts of 6:2 FtS can also be ruled out, since 6:2 FtS was not degraded appreciably in the first 5 min in the  $\text{Ga}_2\text{O}_3$  system (Fig. 1a)). The much faster Cr(vi) reduction in the  $\text{Ga}_2\text{O}_3$

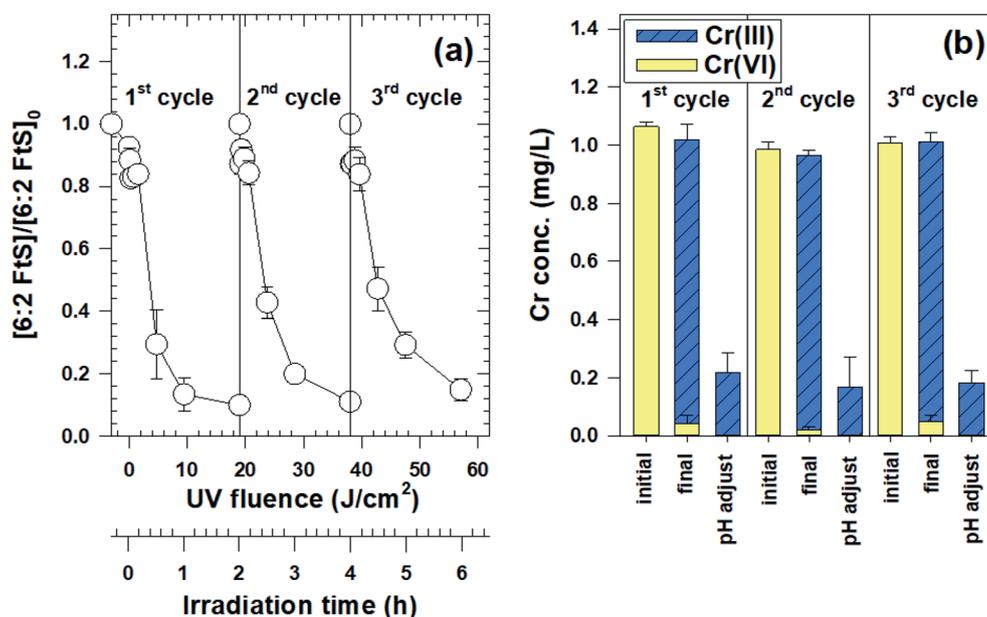


Fig. 3 (a) Degradation of 6:2 FtS by  $\text{Ga}_2\text{O}_3/\text{UV-C}$  over three cycles. The concentration of  $\text{Ga}_2\text{O}_3$  was  $0.5 \text{ g L}^{-1}$ . At the beginning of each cycle, the spent solution was replaced with a fresh solution containing  $[6:2 \text{ FtS}]_0 = 100 \mu\text{g L}^{-1}$  and  $[\text{Cr}(\text{vi})]_0 = 1 \text{ mg L}^{-1}$ ; (b) the concentrations of dissolved Cr(vi) and Cr(III) at the beginning of each cycle (labelled as "initial"), after photolysis (labelled as "final"), and after adjusting pH to 7.5 and separating  $\text{Cr}(\text{OH})_3(\text{s})$  (labelled as "pH adjust").

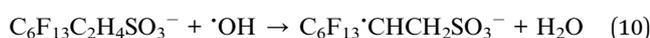


compared to that in the other two systems is attributable to Ga<sub>2</sub>O<sub>3</sub>'s higher conduction band position ( $E_{CB,Ga_2O_3} = -2.95$  eV versus  $E_{CB,TiO_2} = -4.21$  eV and  $E_{CB,In_2O_3} = -4.30$  eV), resulting in  $e_{CB}^-$  that possesses a greater reduction power.<sup>47–49</sup> Despite a rapid removal at the beginning, the concentration of Cr(vi) in the Ga<sub>2</sub>O<sub>3</sub> system never decreased to zero. Instead, a steady state concentration of Cr(vi) of ca. 30 μg L<sup>-1</sup> was maintained in the solution throughout the course of the experiment. As such, it is hypothesized that there was a redox cycle between Cr(vi) and Cr(III) in this system, driven by reaction (2) and the oxidation of Cr(III) back to Cr(vi):



The role of the Cr(vi)–Cr(III) redox cycling toward sustaining the enhanced 6:2 FtS degradation (compared to when Cr was absent) in the Ga<sub>2</sub>O<sub>3</sub> system will be discussed further in Section 4.2.

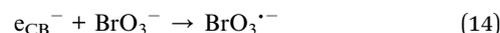
Whereas  $e_{CB}^-$  was the only reactive species responsible for Cr(vi) removal, a few different reactive species appears to be involved in the degradation of 6:2 FtS. In the In<sub>2</sub>O<sub>3</sub> system, the predominant oxidant likely was  $\cdot OH$ , although  $h_{VB}^+$  also could have had a partial contribution, since the 6:2 FtS degradation was somewhat further inhibited by HCOOH (a  $h_{VB}^+$  scavenger, which is also expected to inhibit reaction (4)) (Fig. S5a†). In the TiO<sub>2</sub> system, both  $h_{VB}^+$  and  $\cdot OH$  played an important role because HCOOH and *t*-BuOH appreciably retarded the degradation of 6:2 FtS (Fig. S5b†). Because  $h_{VB}^+$  and  $\cdot OH$  can oxidize substrates *via* hydrogen abstraction,<sup>40</sup> it is proposed that the oxidation of 6:2 FtS proceeded as follows:



Previous studies have reported that  $\cdot OH$  played a minor role in the degradation of PFOA by TiO<sub>2</sub>- and In<sub>2</sub>O<sub>3</sub>-based photocatalysts.<sup>33,34</sup> This is because PFOA, a fully fluorinated compound, does not react with  $\cdot OH$  to an appreciable extent. The second-order rate constant for the reaction between PFOA and  $\cdot OH$  is thought to be  $k_{OH} < 10^6$  M<sup>-1</sup> s<sup>-1</sup>, although the precise value is not available in the literature.<sup>50</sup> For 6:2 FtS, the second-order rate constant with  $\cdot OH$  was estimated by density functional theory to be  $1.0 \times 10^6$  (reaction (9)) and  $3.0 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> (reaction (10)).<sup>51</sup> It is generally agreed that contaminants with a  $k_{OH} < 10^8$  M<sup>-1</sup> s<sup>-1</sup> will not be removed appreciably by  $\cdot OH$ -based processes, due to the  $\cdot OH$  scavenging by HCO<sub>3</sub><sup>-</sup> and other solutes. However, since CPW is acidic (pH < 3), the concentration of HCO<sub>3</sub><sup>-</sup> in CPW should be very small (H<sub>2</sub>CO<sub>3</sub> has a pK<sub>a1</sub> = 6.5). In case where the scavenging of  $\cdot OH$  by other background solutes is significant, 6:2 FtS could still be degraded by  $h_{VB}^+$  (reactions (7) and (8)).

It has been well established that the irradiation of Ga<sub>2</sub>O<sub>3</sub> by UVC generates  $h_{VB}^+$  and  $\cdot OH$ . As mentioned previously,

however, neither HCOOH nor *t*-BuOH had any appreciable effect on the oxidation of 6:2 FtS (Fig. 2a). The rate of 6:2 FtS removal remained the same even when the concentration of HCOOH was increased to 50 mM (Fig. S6†). At a first glance, these results seem to suggest that  $h_{VB}^+$  and  $\cdot OH$  played a minimal role in the degradation of 6:2 FtS in the Ga<sub>2</sub>O<sub>3</sub> system. This hypothesis appears to be further corroborated by the experiment in the presence of BrO<sub>3</sub><sup>-</sup>, which indicates that 6:2 FtS was degraded by reductants such as  $e_{CB}^-$  and/or superoxide radical:<sup>42,52</sup>



However, if  $e_{CB}^-$  and  $O_2^{\cdot -}$  were the only reactive species involved in the degradation of 6:2 FtS, it would not have been possible to explain why the presence of HCOOH together with BrO<sub>3</sub><sup>-</sup> further inhibited the degradation (Fig. 2a). In fact, the inhibitory effect of HCOOH + BrO<sub>3</sub><sup>-</sup> suggests that the involvement of  $h_{VB}^+$  cannot be ruled out. To reconcile these seemingly conflicting experimental observations, the degradation of 6:2 FtS by the Ga<sub>2</sub>O<sub>3</sub>/UVC system is proposed to have occurred as follows. First, both  $h_{VB}^+$  and  $e_{CB}^-$  should be important to the degradation of 6:2 FtS. It is noted that the degradation of 6:2 FtS is determined not only by the rate at which  $h_{VB}^+$  and  $e_{CB}^-$  were produced, but also by the rate at which these species recombined. Thus, although the presence of HCOOH would on the one hand suppress the oxidation of 6:2 FtS, the scavenging of  $h_{VB}^+$  by HCOOH would on the other hand mitigate the recombination of  $h_{VB}^+$  and  $e_{CB}^-$ , thereby extending the lifetime of the latter. As a result, while the removal of 6:2 FtS by reactions (7)–(10) would be retarded, the removal by reactions (12) and (13) would be enhanced, resulting in no net change in the removal rate. On the contrary,  $h_{VB}^+$  and  $e_{CB}^-$  would be scavenged when both HCOOH and BrO<sub>3</sub><sup>-</sup> were present, resulting in the inhibition of reactions (7)–(13). It is further hypothesized that the involvement of  $\cdot OH$  (*i.e.*, reactions (9) and (10)) is likely minimal, since *t*-BuOH (which is not expected to affect the production or recombination of  $h_{VB}^+$  and  $e_{CB}^-$ ) did not influence the rate of 6:2 FtS degradation. Finally, it appears that  $O_2^{\cdot -}$  played a greater role than  $e_{CB}^-$  in the reductive degradation 6:2 FtS. This hypothesis is supported by two lines of evidence. Firstly, the 6:2 FtS degradation profile in the presence of HCOOH + BQ was similar to that in the presence of HCOOH + BrO<sub>3</sub><sup>-</sup>. (BQ only scavenges  $O_2^{\cdot -}$  but not  $e_{CB}^-$ ). Secondly, removing O<sub>2</sub> from the solution (by sparging N<sub>2</sub>) also retarded the degradation to the same extent as BrO<sub>3</sub><sup>-</sup> did (Fig. S7†).

#### 4.2 The effect of Cr(vi) on 6:2 FtS removal

In agreement with the hypothesis that a synergistic effect may exist between Cr(vi) and 6:2 FtS, the 6:2 FtS degradation rate was enhanced in the Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> systems when Cr(vi) was

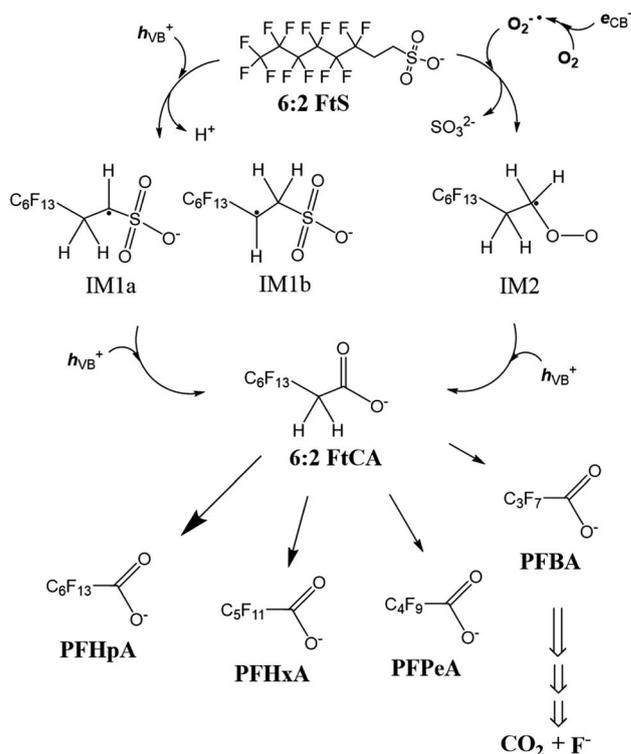


present. In the  $\text{In}_2\text{O}_3$  system, reaction (2) would mitigate the  $h_{\text{VB}}^+/e_{\text{CB}}^-$  recombination, thereby making  $h_{\text{VB}}^+$  more available to  $\text{H}_2\text{O}$ —as discussed above,  $\cdot\text{OH}$ , which is generated from the reaction between  $h_{\text{VB}}^+$  and  $\text{H}_2\text{O}$  (reaction (4)), is likely the primary species involved in the degradation of 6:2 FtS in the  $\text{In}_2\text{O}_3$  system. In the  $\text{Ga}_2\text{O}_3$  system, the presence of  $\text{Cr}(\text{vi})$  can on the one hand enhance reactions (7) and (8) (by retarding the  $h_{\text{VB}}^+/e_{\text{CB}}^-$  recombination), but on the other hand suppress reaction (11) (and thereby suppressing reaction (13)). However, it is hypothesized that the production of  $\text{O}_2^{\cdot-}$  by reaction (11) was not appreciably affected by  $\text{Cr}(\text{vi})$ , since the concentration of dissolved  $\text{O}_2$  (0.25 mM) in the solution were over 400 times greater than that of  $\text{Cr}(\text{vi})$  ( $30 \mu\text{g L}^{-1}$ , or  $0.57 \times 10^{-3}$  mM). (As the rate constants for reactions (2) and (11) are not known, the exact proportions of  $e_{\text{CB}}^-$  that react with  $\text{O}_2$  and  $\text{Cr}(\text{vi})$  cannot be estimated).

Unlike the other two photocatalysts,  $\text{TiO}_2$  was not effective at removing 6:2 FtS when  $\text{Cr}(\text{vi})$  was present (Fig. 1c). As has been established above,  $e_{\text{CB}}^-$  and  $\text{HO}_2^{\cdot}$  are not involved in the degradation of 6:2 FtS in the  $\text{TiO}_2$  system. Therefore, the inhibitory effect of  $\text{Cr}(\text{vi})$  cannot be ascribed to the scavenging of  $e_{\text{CB}}^-$  by reaction (2). Instead, the most plausible explanation could be that the reactivity of  $\text{TiO}_2$  was severely reduced by the deposition of  $\text{Cr}(\text{iii})$  on the surface of  $\text{TiO}_2$ . Whereas the color of  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  did not change throughout the experiment,  $\text{TiO}_2$  rapidly turned grey/black when photolysis started (Fig. S8†). Surface elemental analysis by EDS revealed that the surface of the spent  $\text{TiO}_2$  catalyst consisted of 3.7 wt% of  $\text{Cr}$  (this number was 0.22 wt% and 0.44 wt% for the spent  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$ , respectively) (Fig. S9†). Therefore, it is hypothesized that the  $\text{Cr}(\text{iii})$  adsorbed on  $\text{TiO}_2$  suppressed the degradation of 6:2 FtS by inhibiting the reactive sites on  $\text{TiO}_2$  and/or competing with 6:2 FtS for  $h_{\text{VB}}^+$  (reaction (6)). A similar hypothesis was invoked in several studies to explain for the reactivity decrease of  $\text{TiO}_2$ .<sup>53,54</sup> In the  $\text{Ga}_2\text{O}_3$  system, essentially all  $\text{Cr}$  remained in the solution by the end of the experiment (Fig. 3b), suggesting that the adsorption of  $\text{Cr}$  on  $\text{Ga}_2\text{O}_3$  was minimal, which is consistent with SEM/EDS results (Fig. S9a†).

### 4.3 The transformation pathway of 6:2 FtS in the $\text{Ga}_2\text{O}_3/\text{UV}$ system

According to the discussion above about the reactive species involved and the concentration–time profiles of the byproducts, the transformation of 6:2 FtS in the  $\text{Ga}_2\text{O}_3/\text{UV}$  system is proposed to take place as follows (Scheme 1). Upon reacting with  $h_{\text{VB}}^+$  (reactions (7) and (8)), 6:2 FtS is oxidized into intermediate radicals IM1a and IM1b. 6:2 FtS can also be reduced by  $\text{O}_2^{\cdot-}$  into IM2 (reaction (13))—this nucleophilic substitution reaction is thought to occur in a way similar to the dehalogenation of alkyl halides by  $\text{O}_2^{\cdot-}$ .<sup>42,55</sup> Next, IM1a, IM1b and IM2 are oxidized into 6:2 FtCA. It is noted that the exact mechanism through which 6:2 FtCA is produced is unclear at this point. It is also noted that IM1a, IM1b could also have been converted into other intermediates that were not detected by the LCMS analytical method used in this study. For example, by employing suspected screening-high resolution mass spectrometry,



Scheme 1 Proposed 6:2 FtS degradation pathway.

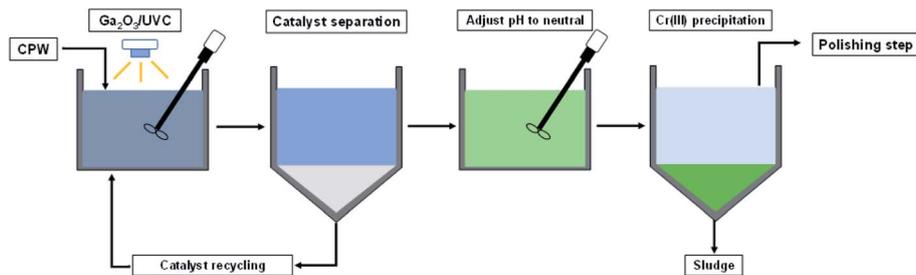
Zhang *et al.*<sup>51</sup> observed that sulfonate byproducts such as  $\text{C}_6\text{F}_{13}\text{C}_2\text{H}_2\text{OSO}_3^-$ ,  $\text{C}_6\text{F}_{13}\text{C}_2\text{H}_2\text{O}_2\text{SO}_3^-$ , and  $\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{O}_2\text{SO}_3^-$  were produced when  $\cdot\text{OH}$  reacted with 6:2 FtS ( $\cdot\text{OH}$  was generated using  $\text{Co}^{2+}$ /peroxymonosulfate). Whether these sulfonate byproducts can be produced *via* reactions with  $h_{\text{VB}}^+$  remains to be explored. However, as was discussed earlier, approximately 20% of  $\text{F}$  was unaccounted for in the fluorine mass balance. This missing  $\text{F}$  fraction could be that associated with sulfonate intermediate products, as well as other short-chain fluorinated compounds such as trifluoroacetic acid.

Most previous studies have proposed that the degradation of PFOA by  $h_{\text{VB}}^+$  and  $\cdot\text{OH}$  takes place *via* a stepwise decarboxylation mechanism  $\text{PFOA} \rightarrow \text{PFHpA} \rightarrow \text{PFHxA} \rightarrow \text{PFPeA} \rightarrow \text{PFBA}$ .<sup>56,57</sup> This stepwise mechanism implies that the concentration of the preceding byproduct will rise and fall before the subsequent byproduct is generated. However, it was observed that PFHpA, PFHxA, PFPeA and PFBA were generated simultaneously, and that none of these byproduct exhibited a two-phase concentration–time profile (Fig. 2b). Therefore, we argue that PFHpA, PFHxA, PFPeA and PFBA were generated directly from 6:2 FtCA. Additional research is needed to investigate the mechanism through which this transformation occurs.

### 4.4 Proposed treatment train for the removal of 6:2 FtS and $\text{Cr}(\text{vi})$ in CPW

Based on the results of this study, it is proposed that  $\text{Cr}(\text{vi})$  and 6:2 FtS in CPW can be removed using a treatment train that consists of an oxidation–reduction step driven by  $\text{Ga}_2\text{O}_3/\text{UVC}$ ,





Scheme 2 Process flow chart for CPW treatment including the oxidation–reduction step using  $\text{Ga}_2\text{O}_3/\text{UVC}$  system.

followed by a neutralization step (Scheme 2). The neutralization step not only will convert dissolved  $\text{Cr}(\text{VI})$  into  $\text{Cr}(\text{OH})_3(\text{s})$ , which can be separated (e.g., by filtration, centrifugation, or sedimentation), but also will raise the pH to the range that would comply with discharge regulations (typically  $\text{pH} = 6\text{--}8$ ). If required, the effluent from this treatment system can be further polished using ion exchange or activated carbon to enhance the removal of Cr species as well as the fluorinated byproducts. Because conventional CPW treatment systems usually already consist of a neutralization step and a polishing step, existing systems can be readily upgraded by placing the  $\text{Ga}_2\text{O}_3/\text{UVC}$  unit in the front. Although existing systems with ion exchange or activated carbon could also remove 6:2 FtS, the upfront degradation by  $\text{Ga}_2\text{O}_3/\text{UVC}$  will significantly reduce the loading of fluorinated compounds on the polishing step. Recall that under the condition employed in this study, 50% of the initial organic fluorine was converted into  $\text{F}^-$ . While  $\text{F}^-$  could be toxic to aquatic life,<sup>58</sup> its concentration in the treated CPW is not expected to exceed discharge limits (which is typically above  $1 \text{ mg L}^{-1}$ ),<sup>59,60</sup> since raw CPW only contains up to a few hundreds  $\mu\text{g L}^{-1}$  of 6:2 FtS.<sup>22</sup>

## 5 Conclusions

Heterogeneous photocatalysis is a promising approach for the treatment of complex waste streams, owing to its ability to generate several types of oxidative and reductive species, namely  $\text{h}_{\text{VB}}^+$ ,  $\cdot\text{OH}$ ,  $\text{e}_{\text{CB}}^-$ , and  $\text{O}_2^{\cdot-}$ . This study showed that the two commercial wide-band gap photocatalysts  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  were capable of simultaneously removing  $\text{Cr}(\text{VI})$  and 6:2 FtS in chromate plating wastewater. With a significantly higher reactivity,  $\text{Ga}_2\text{O}_3$  appeared to be superior to  $\text{In}_2\text{O}_3$ . Through a detailed investigation of how different probe compounds influence 6:2 FtS removal,  $\text{h}_{\text{VB}}^+$  and  $\text{O}_2^{\cdot-}$  were identified to be the primary reactive species involved in the 6:2 FtS degradation in the  $\text{Ga}_2\text{O}_3/\text{UVC}$  system. It was also found that there was a synergistic effect between  $\text{Cr}(\text{VI})$  and 6:2 FtS. The faster degradation of 6:2 FtS in the presence of  $\text{Cr}(\text{VI})$  was attributable to the scavenging of  $\text{e}_{\text{CB}}^-$  by  $\text{Cr}(\text{VI})$ , which prevented the recombination  $\text{h}_{\text{VB}}^+$  and  $\text{e}_{\text{CB}}^-$ .

While this study has successfully demonstrated how  $\text{Cr}(\text{VI})$  and 6:2 FtS can be simultaneously removed using photocatalysis, additional research is needed to improve the efficiency of this approach. For example, a recent study reported

that In-doped  $\text{Ga}_2\text{O}_3$  is significantly more reactive than  $\text{Ga}_2\text{O}_3$ . Future research should explore if In-doped  $\text{Ga}_2\text{O}_3$  as well as other highly reactive catalysts (e.g., BN) can be employed for the treatment of CPW. Future studies should also employ real CPW samples to explore how factors such as the catalyst dosage, the solution pH, the concentration of  $\text{Cr}(\text{VI})$  and 6:2 FtS, and the presence of other contaminants typically present in CPW (e.g., heavy metals) may affect the treatment efficacy. Additionally, future research should investigate if photocatalysis can be used to treat other types of PFAS used in electrochemical plating, such as PFOS and F-53B (i.e.,  $\text{ClC}_6\text{F}_{12}\text{OCF}_2\text{CF}_2\text{SO}_3^-$ ).

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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