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# Photoelectrochemical water-splitting over a surface modified p-type Cr<sub>2</sub>O<sub>3</sub> photocathode†

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 $Cr_2O_3$  is a p-type semiconductor with a negative conduction band minimum position suitable for photocathodic  $H_2$  generation. Therefore,  $Cr_2O_3$  is a candidate photocathode material for photoelectrochemical (PEC) water-splitting. However,  $Cr_2O_3$  has not yet been applied for the purpose of  $H_2$  generation because the efficiency and stability of the photocurrent generated by a  $Cr_2O_3$  electrode are poor, due to high defect and vacancy concentrations. In the present work, the  $Cr_2O_3$  surface was modified with n-type  $TiO_2$  after which Pt particles were deposited to catalyse  $H_2$  production. The  $TiO_2$  overlayer passivated the  $Cr_2O_3$  surface states that otherwise cause deleterious interactions with the Pt particles. This layer also improved charge separation from the conduction band of  $Cr_2O_3$  to the Pt co-catalyst, by forming a p-n junction. As a result of the  $TiO_2$  insertion, the cathodic photocurrent resulting from light absorption by  $Cr_2O_3$  was enhanced and stabilized. This represents the first-ever use of  $Cr_2O_3$  as a light-absorbing material in a multi-layered electrode to accomplish PEC water-splitting for  $H_2$  generation.

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## Introduction

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H<sub>2</sub> has attracted considerable interest as a clean energy carrier that does not produce CO2, and is expected to play an important role in meeting growing worldwide energy requirements. 1-3 Photoelectrochemical (PEC) water-splitting into H<sub>2</sub> and O<sub>2</sub> using semiconductor electrodes is a promising approach to the direct conversion of solar energy into H<sub>2</sub>. 4-6 In 1972, Honda and Fujishima first reported the PEC decomposition of water to H2, utilizing an n-type TiO2 electrode in conjunction with UV illumination and the application of an external electrical bias.<sup>7</sup> After this pioneering work, numerous semiconductor photocatalysts and photoelectrodes were developed.8-17 It is widely recognized that most semiconductors require the addition of a sacrificial electron donor or the application of an external voltage, as the edges of the conduction band and valence band typically do not straddle the water reduction and oxidation potentials. As a means of promoting water splitting without an external electrical bias while separately generating H2 and O2 at different electrodes, PEC devices containing electrically connected p-type and semiconductor photoelectrodes have been designed. 18-22 Metal oxides are suitable semiconductor materials because they are abundant and relatively in-

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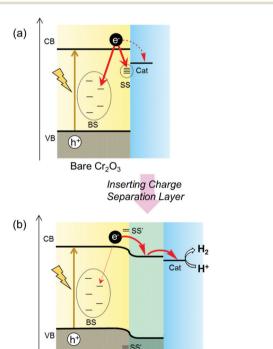
† Electronic supplementary information (ESI) available: An image of the crystal structure, UV/visible absorption spectra, STEM-EDX images and PEC properties. See DOI: 10.1039/C9DT04296B

expensive. Since metal oxide semiconductors predominantly exhibit n-type characteristics, because they readily form oxygen vacancies, there have been many reports regarding the use of n-type semiconductor photoanodes to generate oxygen. In contrast, there are only a few native p-type semiconductor oxides, because the cation vacancies or oxygen interstitials that produce p-type conductivity are not easily generated. <sup>23,24</sup> Moreover, utilizing photocathodes for  $\rm H_2$  evolution requires that the conduction band minimum of the cathode material be more negative than the  $\rm H^+/H_2$  reduction potential (0 V  $\nu s$ . reversible hydrogen electrode; RHE). The oxide p-type semiconductors meeting this requirement are limited, with examples being copper oxides<sup>25,26</sup> and iron oxides. <sup>27–29</sup>

Cr<sub>2</sub>O<sub>3</sub> is one of the few oxides exhibiting p-type conductivity.30,31 Standard Cr2O3 has a hexagonal corundum structure.32,33 In the unit cell of non-defective Cr2O3, twothirds of the octahedral oxygen sites are occupied by Cr while remaining one-third are unoccupied (Fig. S1†). Consequently, removing Cr atoms from the cell generates vacancies. Moreover, the migration of Cr to the pre-existing empty sites (typically interstitial sites in nearby locations) results in Cr Frenkel defects, while the diffusion of O atoms generates O vacancies. These defects and vacancies are known to determine the appearance of p-type and n-type characteristics.34-38 The defect formation energy values calculated using first-principles DFT+U by Diawara et al.38 suggest that the stability of defects follows the order: Cr Frenkel defect > Cr vacancy > O vacancy. Therefore, native Cr<sub>2</sub>O<sub>3</sub> tends to form metal-deficient sites that result in p-type conductivity. The p-type conductivity of Cr<sub>2</sub>O<sub>3</sub> has been applied to produce Paper **Dalton Transactions** 

hole transfer layers inserted between a back contact and a semiconductor photoabsorber, such as CuO<sup>26</sup> or Fe<sub>2</sub>O<sub>3</sub>.<sup>39</sup> Moreover, the conduction band minimum of Cr<sub>2</sub>O<sub>3</sub> is located at a much more negative level than the redox potential for water reduction. 40,41 Even so, to the best of our knowledge, there have been no reports of the application of Cr<sub>2</sub>O<sub>3</sub> as a photoabsorber in photocathodes for H2 generation. This may be due to the ready formation of various defects and vacancies in Cr<sub>2</sub>O<sub>3</sub>. Defects, vacancies and surface dangling bonds form states within the bandgap that can serve as recombination centres for photogenerated charges (Scheme 1a). In addition, a high density of bandgap states will transition Cr2O3 into a conductor. 42,43 However, if photogenerated charges can be prevented from transferring to such bandgap states, it may be possible to apply Cr<sub>2</sub>O<sub>3</sub> as a photocathode for H<sub>2</sub> evolution. Furthermore, since band gap narrowing via doping with specific ions has already been realized, 44-47 Cr<sub>2</sub>O<sub>3</sub> also has the potential to become a visible-light responsive photocathode.

Recently, it has been reported that various benefits can be obtained by the surface treatment of photoelectrodes. 48,49 Specifically, such processing can protect the unstable surface of the photoabsorber from photocorrosion by preventing contact with the electrolyte. Furthermore, this treatment can passivate surface states. When the atomic orbitals of surface states couple with those of deposits, the coupled surface states can be moved away from the band gap because of the for-



Scheme 1 Schematic diagram of the expected electron transfer process in (a) bare  $Cr_2O_3$  and (b)  $TiO_2$ -coated  $Cr_2O_3$  photocathodes. BS and SS indicate bulk states and surface states, respectively. The former are generated by defects and vacancies, while the latter result from surface dangling bonds.

TiO<sub>2</sub>-coated Cr<sub>2</sub>O<sub>3</sub>

mation of bonding and antibonding states<sup>49</sup> (shown as SS' in Scheme 1b). Moreover, the formation of a heterojunction by surface treatment is expected to modify band bending due to the diffusion of charge carriers between two semiconductors having different Fermi levels. This modification should enhance both photogenerated electron-hole separation and carrier transfer. Therefore, in the present work, the Cr<sub>2</sub>O<sub>3</sub> surface was modified with n-type TiO<sub>2</sub> to ensure both charge separation and passivation. Subsequently, Pt particles were deposited on the TiO<sub>2</sub> layer to catalyse H<sub>2</sub> production<sup>50</sup> (Scheme 1b).

## Results and discussion

### Structural and optical properties of Cr<sub>2</sub>O<sub>3</sub>

Cr<sub>2</sub>O<sub>3</sub> electrodes were prepared by the radio frequency (RF) reactive magnetron sputtering of Cr targets in an Ar/O<sub>2</sub> (9:1) plasma to give a thickness of 60 nm on a transparent conductive oxide (TCO; SnO<sub>2</sub>-coated indium tin oxide (ITO)), followed by annealing at 823 K. As shown in Fig. 1 (blue line), the X-ray diffraction (XRD) patterns of the resulting Cr<sub>2</sub>O<sub>3</sub> on TCO exhibit peaks at 33.8°, 36.4° and 55.3°, which are assignable to the (104), (110) and (116) diffractions of Cr<sub>2</sub>O<sub>3</sub> (eskolaite), respectively. All other peaks are attributed to SnO2 or ITO, while there are no peaks due to impurities. The X-ray photoelectron spectroscopy (XPS) data obtained from the resulting Cr<sub>2</sub>O<sub>3</sub> layer are presented in Fig. 2a, and are similar to those produced by the reference Cr<sub>2</sub>O<sub>3</sub> (Fig. 2c). The peaks at binding energies of 576.5 and 586.1 eV are ascribed to the Cr 2p<sub>3/2</sub> and 2p<sub>1/2</sub> signals of Cr(III) oxide, respectively. Although the Cr 2p<sub>3/2</sub> peak includes a shoulder, this peak shape is typical of Cr<sub>2</sub>O<sub>3</sub> and is attributed to the multiplet structure of Cr(III) oxide.<sup>51</sup> Pt was subsequently deposited on the electrodes as a co-catalyst for H<sub>2</sub> evolution from water by sputtering, to a nominal thickness of 1 nm. Scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDX) for elemental mapping was used to assess cross-sections of the Pt/Cr<sub>2</sub>O<sub>3</sub> sample, as shown in Fig. 3a. In

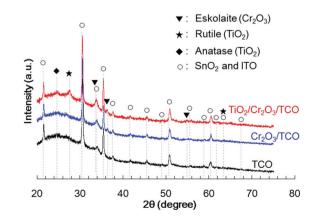


Fig. 1 XRD patterns obtained from TCO (black line), Cr<sub>2</sub>O<sub>3</sub>/TCO (blue line) and TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub>/TCO (red line).

**Dalton Transactions** Paper

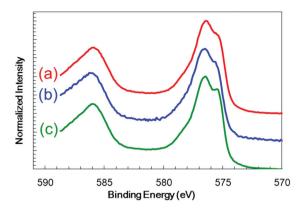


Fig. 2 XPS spectra obtained from a Cr<sub>2</sub>O<sub>3</sub> electrode (a) before and (b) after photoelectrolysis for 1 h and from (c) the reference Cr<sub>2</sub>O<sub>3</sub>.

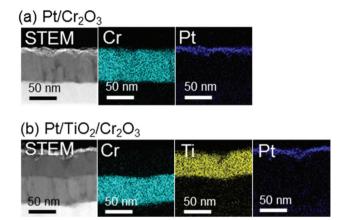


Fig. 3 Cross-sectional STEM images and STEM-EDX elemental maps for (a) Pt/Cr<sub>2</sub>O<sub>3</sub> and (b) Pt/TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub>.

both electrodes, a flat Cr<sub>2</sub>O<sub>3</sub> layer was observed on the TCO film.

UV/visible absorption spectra were acquired by a transmission method for this electrode and are shown in Fig. 4 as a blue line. Although an interference spectrum was included in the original spectrum, the absorption edge is evident at 410 nm, in agreement with a Cr<sub>2</sub>O<sub>3</sub> reference bulk powder (Fig. S2†) and previous reports<sup>52-54</sup>

#### PEC properties of the Cr<sub>2</sub>O<sub>3</sub> electrodes

Fig. 5a and b present the current-potential curves obtained from the Cr<sub>2</sub>O<sub>3</sub>-based electrodes and from a TiO<sub>2</sub> electrode in a 0.5 M Na<sub>2</sub>CO<sub>3</sub>: NaHCO<sub>3</sub> (1:1) buffer electrolyte (pH 9.7) under chopped AM 1.5 irradiation (1 Sun; 100 mW cm<sup>-2</sup>), with irradiation of the deposited semiconductor side. The bare Cr<sub>2</sub>O<sub>3</sub> electrode (Fig. 5a, black line) generated a cathodic photocurrent in the negative voltage range below +1.1 V vs. RHE, although it also produced a dark current. The photocurrent density of this sample at +0.1 V, after removing the dark current density from the current density produced during light irradiation, was –15 μA cm<sup>-2</sup>. This cathodic photocurrent indicates that the Cr<sub>2</sub>O<sub>3</sub> electrode exhibited p-type conductivity

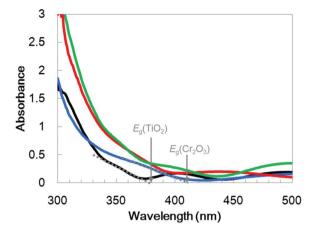


Fig. 4 UV/visible absorption spectra for TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> (red line), Cr<sub>2</sub>O<sub>3</sub> (blue line) and  $TiO_2$  (black line) on TCO and the sum of the  $Cr_2O_3$  and  $TiO_2$  spectra (green line).  $E_g$  indicates the absorption edges for the band-gap excitation.

and could possibly be utilized as a photocathode for water splitting. However, a large cathodic dark current was apparent between +1.1 and +1.5 V, including a peak of -240 μA cm<sup>-2</sup> at +1.08 V. This significant dark current indicates that electrons leaked to defect states and surface states in the band gap. Upon applying a constant potential of +0.11 V vs. RHE, the dark current was decreased due to electron charging, while the cathodic photocurrent was observed to decay from 8.1 to 0.9 μA cm<sup>-2</sup> during 1 sun irradiation for 3 min (Fig. 5c, black line). After 1 h of photoelectrolysis, the dark current was slightly increased but the difference in the photocurrent in the current-potential curve was negligible (Fig. S3†). In addition, when the chemical state of the Cr<sub>2</sub>O<sub>3</sub> surface was examined by XPS, there were almost no differences before and after the photoelectrolysis (Fig. 2a and b, respectively), suggesting no self-reduction of Cr<sub>2</sub>O<sub>3</sub> by the photogenerated electrons. Therefore, Cr<sub>2</sub>O<sub>3</sub> itself was stable during photoelectrolysis but photoelectrons could be trapped in defects and surface states, resulting in photocurrent decay.

Pt was deposited on Cr<sub>2</sub>O<sub>3</sub> as a co-catalyst for H<sub>2</sub> evolution, by sputtering. The current-potential curve produced by the resulting Pt/Cr<sub>2</sub>O<sub>3</sub> exhibited a new and significant dark current between 0.5 and 0.9 V, including a peak of  $-700 \mu A \text{ cm}^{-2}$  at +0.63 V. Moreover, the photocurrent was negligible after Pt loading (Fig. 5a, green line). Although the dark current was reduced by applying a constant potential of +0.11 V vs. RHE under dark conditions, the photocurrent was smaller than that obtained from pure Cr2O3 (Fig. 5c, green line). The large dark current in the current-potential curve suggests that new bandgap states were generated within the bandgap of Cr<sub>2</sub>O<sub>3</sub> following Pt deposition. The appearance of these deleterious band gap states can possibly be ascribed to the coupling of the atomic orbitals of dangling atoms at the Cr2O3 surface with those of deposited Pt atoms. The resulting bonding and antibonding orbitals would generate deleterious band-gap states,55 leading to electron leakage and recombination of photo-gener-

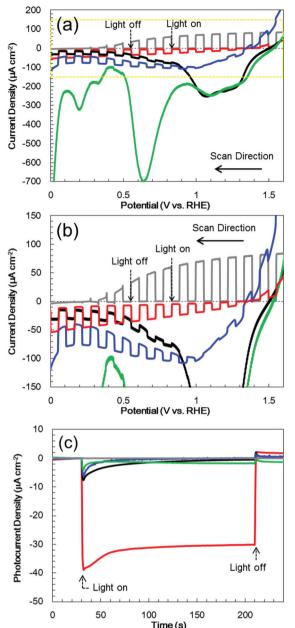


Fig. 5 (a) Photocurrent–potential characteristics under chopped light irradiation, (b) enlargement of the area in the yellow dotted line in (a), and (c) photocurrent transients at +0.11 V vs. RHE in a 0.5 M  $\rm Na_2CO_3:NaHCO_3~(1:1)$  buffer electrolyte (pH 9.7) under one sun (100 mW cm $^{-2}$ , AM 1.5) illumination for the bare  $\rm Cr_2O_3~(black~line),~Pt/Cr_2O_3~(green~line),~TiO_2~(grey~line),~TiO_2/Cr_2O_3~(blue~line)~and~Pt/TiO_2/Cr_2O_3~(red~line).$ 

ated electrons and holes. As a result, the addition of Pt nanoparticles to the  $\rm Cr_2O_3$  surface diminished the photocurrent without acting as a co-catalyst for  $\rm H_2$  evolution.

#### Coating with TiO2 as passivation and charge-separation layer

 $TiO_2$  overlayers with thicknesses ranging from 10 to 120 nm were subsequently deposited by sputtering a  $TiO_2$  target in an  $Ar/O_2$  (4:1) plasma onto  $Cr_2O_3$ . This was followed by post-

annealing at 748 K. The XRD patterns generated by  $TiO_2/Cr_2O_3/TCO$  (Fig. 1, red line) exhibit peaks attributable to anatase (101), and rutile (110) and (310) diffractions at 24.8°, 27.8° and 63.4°, respectively. In the STEM-EDX images for the  $Pt/TiO_2/Cr_2O_3$  electrode (Fig. 3b), the  $TiO_2$  layer completely covered the  $Cr_2O_3$  surface, preventing contact with both the Pt and the electrolyte. The UV/visible absorption spectrum of the  $TiO_2/Cr_2O_3$  electrode was essentially consistent with the sum of the spectra of the  $TiO_2$  and  $Cr_2O_3$  electrodes (Fig. 4, grey dotted line). The absorption edge of the  $TiO_2$  electrode (Fig. 4, black line) was observed at 380 nm, consistent with a  $TiO_2$  reference bulk powder (Fig. S2†) and the previous report. <sup>56</sup> These data indicate that simulated solar radiation imparted to the  $TiO_2$  side should be absorbed by both  $TiO_2$  and  $Cr_2O_3$ .

In photocurrent-potential curves, the surface of Cr<sub>2</sub>O<sub>3</sub> was subsequently coated with a 60 nm thick TiO2 layer. The resulting TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> photocathode generated a cathodic photocurrent below +1.1 V (Fig. 5b, blue line). The photocurrent at +0.1 V was  $-35 \mu A \text{ cm}^{-2}$ , and so exceeded that obtained from the bare  $Cr_2O_3$  (-15  $\mu A$  cm<sup>-2</sup>). Although the  $TiO_2$  electrode (without Cr2O3) exhibited an anodic photocurrent at values more positive than +0.3 V (Fig. 5b, grey line), the photocurrent of TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> cannot be explained as a combination of those for TiO2 and Cr2O3. The cathodic photocurrent produced by TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> was also larger than that for Cr<sub>2</sub>O<sub>3</sub>. The anodic photocurrent produced by TiO2/Cr2O3 was smaller and appeared at a more positive potential than that for TiO<sub>2</sub>. This positive shift of the onset potential for the anodic photocurrent can be explained by the formation of a p-n junction. The Fermi level of the n-type TiO<sub>2</sub> would be expected to be shifted positively following the formation of a junction with the p-type Cr<sub>2</sub>O<sub>3</sub> because the Fermi levels of TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> would be equalized by carrier diffusion. Moreover, the Cr2O3 layer would be expected to inhibit photogenerated electron transfer from TiO2 to TCO, because the conduction band minimum of Cr<sub>2</sub>O<sub>3</sub> is higher than that of TiO<sub>2</sub>. Hence, TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> generated a cathodic photocurrent. Moreover, the dark current produced by  $TiO_2/Cr_2O_3$  decreased, from -240 to  $-100 \mu A$  cm<sup>-2</sup>, by the TiO2 coating, indicating a decrease in the electron transfer to the band-gap states. Since the recombination of photo-generated electrons and holes at the band-gap states was suppressed, the photocurrent was enhanced by the TiO2 coating. However, at a constant potential of +0.11 V vs. RHE, the photocurrent also decayed after irradiation (Fig. 5c, blue line).

Following the above trials, Pt nanoparticles were deposited on  ${\rm TiO_2/Cr_2O_3}$  as a co-catalyst. The resulting  ${\rm Pt/TiO_2/Cr_2O_3}$  specimen exhibited a cathodic photocurrent below +1.4 V (Fig. 5b, red line), with an onset potential more positive than that of  ${\rm TiO_2/Cr_2O_3}$ . In addition, the dark current was diminished by the Pt loading. At a constant potential of +0.11 V  $\nu s$ . RHE, the cathodic photocurrent was larger and more stable than those of the other electrodes (Fig. 5c, red line). Thus, in contrast to the results obtained from the direct deposition of Pt on  ${\rm Cr_2O_3}$  (Fig. 5a, green and black lines), there was no decrease in the photocurrent and an increase in the dark current. These results demonstrate that the  ${\rm TiO_2}$  overlayer pas-

**Dalton Transactions** Paper

sivated the Cr<sub>2</sub>O<sub>3</sub> surface states to prevent the generation of new band-gap states via the coupling of Cr<sub>2</sub>O<sub>3</sub> and Pt. As a result, the dark current due to electron leakage to band-gap states was decreased. The photocurrent was also enhanced, because the photoelectrons generated in Cr<sub>2</sub>O<sub>3</sub> were able to flow to the Pt nanoparticles via the TiO2 layer, after which they were consumed for H2 evolution.

### Effect of the TiO2 overlayer thickness

In order to optimize the thickness of the TiO<sub>2</sub> layer on the Cr<sub>2</sub>O<sub>3</sub> electrode, Pt/TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> electrodes having TiO<sub>2</sub> thicknesses of 10, 30, 60, 80 and 120 nm were prepared by adjusting the deposition time in the TiO<sub>2</sub> sputtering. UV/visible absorption spectra acquired by a transmission method for these electrodes are shown in Fig. S4.† It can be seen that the absorptions in  $\lambda$  < 380 nm increase in proportion to the thickness of TiO<sub>2</sub> because the absorption edge of TiO<sub>2</sub> is 380 nm (Fig. 4). The photocurrent transients of these specimens were assessed under irradiation with simulated solar radiation (100 mW cm<sup>-2</sup>, AM 1.5) for 3 min while applying a potential of +0.11 V vs. RHE (Fig. 6). Although the photoelectrode with a 10 nmthick TiO2 layer underwent a rapid decay, the other photoelectrodes showed stable photocurrents. The highest photocurrent value was observed for a thickness of 30 nm, and the photocurrents decreased with increases in the TiO2 thickness.

To investigate the effect of the TiO2 thickness in more detail, incident photon to current conversion efficiency (IPCE) spectra were obtained by irradiation with monochromatic light using band pass filters. Fig. 7 shows the IPCE spectra acquired from Pt/TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> specimens with various TiO<sub>2</sub> layer thicknesses. The IPCE spectra of the electrodes with more than 30 nm thick TiO<sub>2</sub> layers increased in intensity at 400 nm, showing a good correlation with the absorption spectrum of Cr<sub>2</sub>O<sub>3</sub> (Fig. 4, blue line). Although the IPCE values at wave-

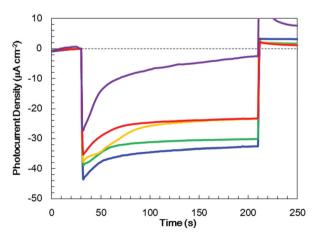


Fig. 6 Photocurrent transients for Pt/TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> specimens with various TiO<sub>2</sub> layer thicknesses (10 nm; purple line, 30 nm; blue line, 60 nm; green line, 80 nm; yellow line and 120 nm; red line) at +0.11 V vs. RHE in a 0.5 M Na<sub>2</sub>CO<sub>3</sub>: NaHCO<sub>3</sub> (1:1) buffer electrolyte (pH 9.7) under one sun (100 mW cm $^{-2}$ , AM 1.5) illumination. The thickness of the Cr<sub>2</sub>O<sub>3</sub> layer was fixed at 60 nm.

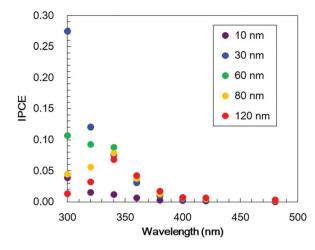


Fig. 7 IPCE spectra obtained from Pt/TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> electrodes at various wavelengths using different TiO2 layer thicknesses (10 nm; purple, 30 nm; blue, 60 nm; green, 80 nm; yellow and 120 nm; red) at +0.11 V vs. RHE in a 0.5 M Na<sub>2</sub>CO<sub>3</sub>: NaHCO<sub>3</sub> (1:1) buffer electrolyte (pH 9.7) under monochromatic illumination. The thickness of the Cr<sub>2</sub>O<sub>3</sub> layer was fixed at 60 nm.

lengths longer than 340 nm were similar for each electrode, the IPCE values below this point became smaller as the TiO<sub>2</sub> layer thickness exceeded 30 nm. These results suggest that light absorption by Cr<sub>2</sub>O<sub>3</sub> was inhibited by the TiO<sub>2</sub> overlayer. As an example, as shown by the black line in the absorption spectrum in Fig. 4, a TiO<sub>2</sub> layer having a thickness of 60 nm had an absorbance greater than 1 below 320 nm. Thus, more than 90% of the light below this wavelength could not reach Cr<sub>2</sub>O<sub>3</sub>. The observation that the IPCE spectra were affected by the TiO<sub>2</sub> thickness clearly indicates that the cathodic photocurrent originated from the photoexcitation of Cr2O3, and that light absorption by TiO<sub>2</sub> decreased the photocurrent. However, the IPCE values for the photoelectrode with a 10 nm-thick TiO2 layer were lower than those of the other electrodes at almost all wavelengths. Although a 10 nm-thick TiO2 layer covered the surface of Cr<sub>2</sub>O<sub>3</sub> (Fig. S5†), the thickness of TiO<sub>2</sub> may be insufficient for the formation of a p-n junction structure. As a result of the trade-off between the light filtering effect of TiO<sub>2</sub> and the formation of a charge separation structure, the optimal TiO<sub>2</sub> film thickness with regard to generating a large photocurrent is believed to be 30 nm.

#### PEC water splitting

To confirm PEC H2 evolution, the gaseous products were analysed by gas chromatography after 1 h of irradiation with AM 1.5 light while applying a bias of +0.11 V vs. RHE (Table 1). The Pt/TiO<sub>2</sub>(60 nm)/Cr<sub>2</sub>O<sub>3</sub> specimen generated a stable photocurrent over this time span (Fig. S6†), with a charge flow of 110 mC cm<sup>-2</sup>. During this trial, 510 nmol cm<sup>-2</sup> of H<sub>2</sub> was produced (entry 1 in Table 1), equivalent to 89% faradaic efficiency. Control experiments without Pt or without both Pt and TiO<sub>2</sub> did not produce H<sub>2</sub> (entries 2 and 4, Table 1), while a test without TiO2 gave only a very small amount of this product (entry 3 in Table 1). Thus, even if light is absorbed by Cr<sub>2</sub>O<sub>3</sub>,

Paper

Table 1 The amounts of charge and H2 obtained from a 1 h PEC reactiona

Entry	Photoelectrode	Charge mC cm <sup>-2</sup>	${ m H_2} \\ { m nmol~cm}^{-2}$
$1^b$	Pt/TiO <sub>2</sub> /Cr <sub>2</sub> O <sub>3</sub>	109.8	510
2	$Cr_2O_3$	13.3	nd
$3^b$	$TiO_2/Cr_2O_3$	1.7	nd
4	Pt/Cr <sub>2</sub> O <sub>3</sub>	10.5	2

<sup>a</sup> AM 1.5 light irradiation with applying bias at +0.11 V vs. RHE. <sup>b</sup> The thickness of TiO2 layers was 60 nm.

PEC water splitting does not proceed without TiO2 and Pt. Therefore, it is considered that PEC water splitting progresses due to the generation of photoexcited electrons in Cr<sub>2</sub>O<sub>3</sub> in response to light absorption. These electrons are transferred to the Pt via the TiO2 charge-separation layer.

## Conclusion

The generation of H<sub>2</sub> via solar PEC water-splitting by Cr<sub>2</sub>O<sub>3</sub> was successfully realized following surface modification of the oxide. Bare Cr<sub>2</sub>O<sub>3</sub> was found to produce a significant dark current but a minimal photocurrent. The addition of Pt further deteriorated the performance of this material. Therefore, neither bare Cr<sub>2</sub>O<sub>3</sub> nor Pt/Cr<sub>2</sub>O<sub>3</sub> provided H<sub>2</sub> by PEC water-splitting. Applying a TiO2 overlayer with subsequent Pt deposition to fabricate a Pt/TiO<sub>2</sub>/Cr<sub>2</sub>O<sub>3</sub> electrode resulted in an enhanced photocurrent and realized solar PEC H2 generation. The dark current almost disappeared following this surface treatment, suggesting that TiO2 passivated the Cr2O3 surface. In this layered electrode, a photocathode current was induced in response to light absorption by Cr<sub>2</sub>O<sub>3</sub>, while the TiO<sub>2</sub> layer acted as a filter to inhibit this light absorption. Nevertheless, since the photocurrent was enhanced by the presence of a TiO<sub>2</sub> coating, it is evident that TiO<sub>2</sub> also acted as a charge separation layer. Thus, within the Pt/TiO2/Cr2O3 electrode, TiO2 accumulated photoexcited electrons generated by light absorption by Cr<sub>2</sub>O<sub>3</sub> while blocking undesired interactions between Cr<sub>2</sub>O<sub>3</sub> and Pt. As a result, H<sub>2</sub> generation was realized through water-splitting. In future, the use of this TiO2 layering technique with a doped Cr2O3 could lead to practical visible-lightdriven PEC water-splitting systems.

## Experimental section

## **Materials**

Tin(IV) oxide/ITO double-layered TCO coated glass (Geomatec Co., Ltd) was used as substrates for the preparation of the electrodes. Commercially available Cr, TiO2 and Pt sputtering targets and TiO2 powder were obtained from the Kojundo Chemical Laboratory Co. A reference sample of Cr<sub>2</sub>O<sub>3</sub> for the XPS analysis and UV/Visible diffuse reflectance spectroscopy was obtained from Nacalai Tesque, Inc.

#### **Preparation**

A Cr<sub>2</sub>O<sub>3</sub> film was deposited by RF reactive magnetron sputtering of a Cr target with an Ar/O<sub>2</sub> (9:1 v/v) plasma. After deposition, the electrodes were annealed at 823 K under an N<sub>2</sub>/O<sub>2</sub> (4:1 v/v) gas flow for 2 h. Subsequently, a TiO<sub>2</sub> layer was deposited on the surface of the Cr<sub>2</sub>O<sub>3</sub> thin film by RF reactive magnetron sputtering of a  $TiO_2$  target with an  $Ar/O_2$  (4:1 v/v) plasma. The deposited electrodes were then annealed at 823 K under an O2 gas flow for 2 h. The Pt cocatalyst was loaded onto either TiO2-coated or bare Cr2O3 specimens by RF magnetron sputtering. The amount of Pt applied was adjusted to obtain an average thickness of 1 nm.

#### Characterization

The crystal structures of the films were analysed using XRD (Ultima IV, Rigaku Co.) with Cu Kα radiation, while the optical properties of the films were assessed by using UV/visible absorption spectroscopy (UV-3600, Shimadzu Co.). STEM together with EDX was performed using a JEM-2100F microscope (JEOL Co.). Samples for these observations were cut using a focused ion beam (FIB; NB5000, Hitachi High-Tech Co.). Prior to cutting the samples, the film surfaces were coated with carbon and Pt layers to protect the specimens from the FIB. XPS data were acquired using a PHI5000 VersaProbe (Ulvac-Phi Co.) spectrometer.

#### PEC measurements

The photocurrent density measurements were performed in a three-electrode configuration consisting of a silver-silver chloride (Ag/AgCl) electrode, a platinum wire electrode and a prepared photocathode as the working, reference and counter electrodes, respectively. In these trials, the exposed TCO layer of the photocathode was covered with silicone rubber and all potentials were converted to the RHE reference scale using the equation E (vs. RHE) = E (vs. Ag/AgCl) + 0.20 V + 0.059 V  $\times$  pH. A sealed Pyrex® glass cell was employed as the reactor and Arsaturated aqueous 0.5 M NaHCO<sub>3</sub>: Na<sub>2</sub>CO<sub>3</sub> (1:1; pH 9.7) solutions were employed as the electrolytes. An electrochemical analyser (ALS612E and ALSCHI-614C, ALS Co., Ltd) supplied the potential and frequency to the electrode. The electrode was irradiated with a light intensity equivalent to one sun (AM 1.5; 100 mW cm<sup>-2</sup>) using a solar simulator (HAL-320, Asahi Spectra Co.). Prior to exposure, the light intensity was adjusted with a CS-20 instrument (Asahi Spectra Co.). The sample irradiation was limited to an area of 10 × 10 mm via a slit. Linear sweep voltammetry was conducted at a scan rate of 50 mV s<sup>-1</sup> under chopped light irradiation. The photocurrent densities in the photocurrent transient curves were converted by subtracting the dark current density values determined just prior to photo-irradiation from the current densities. The PEC water-splitting reaction, in conjunction with the application of an electrical bias, was conducted while measuring the photocurrent generated under continuous irradiation at a fixed electrode potential of -0.5 V vs. Ag/AgCl. After incubation for 30 min to allow the gaseous reaction products to equilibrate

Dalton Transactions Paper

between the liquid and gas phases, these products were analysed by gas chromatography (GC-2014, Shimadzu Co.), employing a thermal conductivity detector and an active carbon column (Shincarbon ST, Shinwa Chemical Industries Co.) with Ar as the carrier gas. IPCE spectra were acquired under monochromatic light generated by a 300 W xenon lamp (MAX-303, Asahi Spectra Co.), using band-pass filters to obtain specific wavelengths.

## Conflicts of interest

There are no conflicts to declare.

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Paper **Dalton Transactions** 

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