

Supplementary Online Material for

**Solar-to-hydrogen peroxide energy conversion on resorcinol–formaldehyde resin photocatalysts prepared by acid-catalysed polycondensation**

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**Supplementary Table 1 | Properties of RF resins prepared under different conditions<sup>[a]</sup> and their photocatalytic activity for H<sub>2</sub>O<sub>2</sub> production.**

| entry | sample name                             | temperature<br>/ K | acid<br>(or base)               | resorcinol/formaldehyde/acid (or base)<br>/ mmol/mmol/mmol | pH  | particle diameter /<br>$\mu\text{m}^{[b]}$ | H <sub>2</sub> O <sub>2</sub><br>/ $\mu\text{mol}^{[c,d]}$ |
|-------|-----------------------------------------|--------------------|---------------------------------|------------------------------------------------------------|-----|--------------------------------------------|------------------------------------------------------------|
| 1     | RF-Na <sub>2</sub> CO <sub>3</sub> -523 | 523                | Na <sub>2</sub> CO <sub>3</sub> | 3.6/7.2/2.0                                                | 9.3 |                                            | 61.0                                                       |
| 2     | RF-NH <sub>3</sub> -523                 | 523                | NH <sub>3</sub>                 | 3.6/7.2/3.0                                                | 7.8 | 0.57 ± 0.08                                | 60.2                                                       |
| 3     | RF-(COOH) <sub>2</sub> -523             | 523                | (COOH) <sub>2</sub>             | 3.6/7.2/0.18                                               | 3.0 | 3.09 ± 1.67                                | 84.7                                                       |
| 4     | RF-HCl-523                              | 523                | HCl                             | 3.6/7.2/0.15                                               | 3.1 | 3.10 ± 0.63                                | 86.0                                                       |
| 5     | RF-H <sub>2</sub> SO <sub>4</sub> -523  | 523                | H <sub>2</sub> SO <sub>4</sub>  | 3.6/7.2/0.11                                               | 3.1 | 2.54 ± 0.64                                | 81.0                                                       |
| 6     | RF-HNO <sub>3</sub> -523                | 523                | HNO <sub>3</sub>                | 3.6/7.2/0.16                                               | 3.0 | 2.52 ± 0.39                                | 78.9                                                       |
| 7     | RF-CH <sub>3</sub> COOH-523             | 523                | CH <sub>3</sub> COOH            | 3.6/7.2/0.50                                               | 3.8 | 2.58 ± 0.31                                | 82.7                                                       |
| 8     |                                         | 523                |                                 | 3.6/7.2/–                                                  | 6.3 | 2.21 ± 0.87                                | 56.0                                                       |
| 9     | RF-(COOH) <sub>2</sub> -473             | 473                | (COOH) <sub>2</sub>             | 3.6/7.2/0.18                                               | 3.0 | 4.45 ± 1.29                                | 69.1                                                       |
| 10    | RF-(COOH) <sub>2</sub> -423             | 423                | (COOH) <sub>2</sub>             | 3.6/7.2/0.18                                               | 3.0 | 7.52 ± 1.08                                | 39.8                                                       |
| 11    |                                         | 373                | (COOH) <sub>2</sub>             | 3.6/7.2/0.18                                               | 3.0 | no solid formed                            |                                                            |
| 12    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/1.2/0.18                                               | 3.2 |                                            | 67.9                                                       |
| 13    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/1.8/0.18                                               | 3.2 |                                            | 80.5                                                       |
| 14    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/3.6/0.18                                               | 3.2 |                                            | 86.0                                                       |
| 15    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/10.8/0.18                                              | 3.2 |                                            | 80.2                                                       |
| 16    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/7.2/0.002                                              | 5.6 |                                            | 66.1                                                       |
| 17    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/7.2/0.018                                              | 4.4 |                                            | 86.7                                                       |
| 18    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/7.2/0.09                                               | 3.5 |                                            | 85.9                                                       |
| 19    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/7.2/0.9                                                | 2.4 | 3.35 ± 1.23                                | 91.0                                                       |
| 20    |                                         | 523                | (COOH) <sub>2</sub>             | 3.6/7.2/1.8                                                | 1.7 | 3.90 ± 1.36                                | 86.0                                                       |

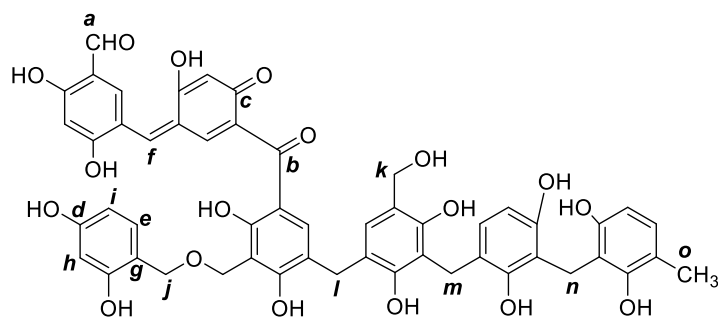
[a] All resins were prepared in water under hydrothermal conditions for 24 h.

[b] Determined by DLS.

[c] Reaction conditions: water (30 mL), catalyst (50 mg), O<sub>2</sub> (1 bar),  $\lambda$  >420 nm (Xe lamp, light intensity at 420–800 nm: 171.3 W m<sup>-2</sup>), temperature (298 K), photoirradiation time (24 h).

[d] All of the data are the mean values determined by three independent experiments and contains ±6% deviations.

**Supplementary Table 2 | The C=O and C–O compositions of the RF resins determined by DD/MAS/<sup>13</sup>C NMR and XPS analysis.**



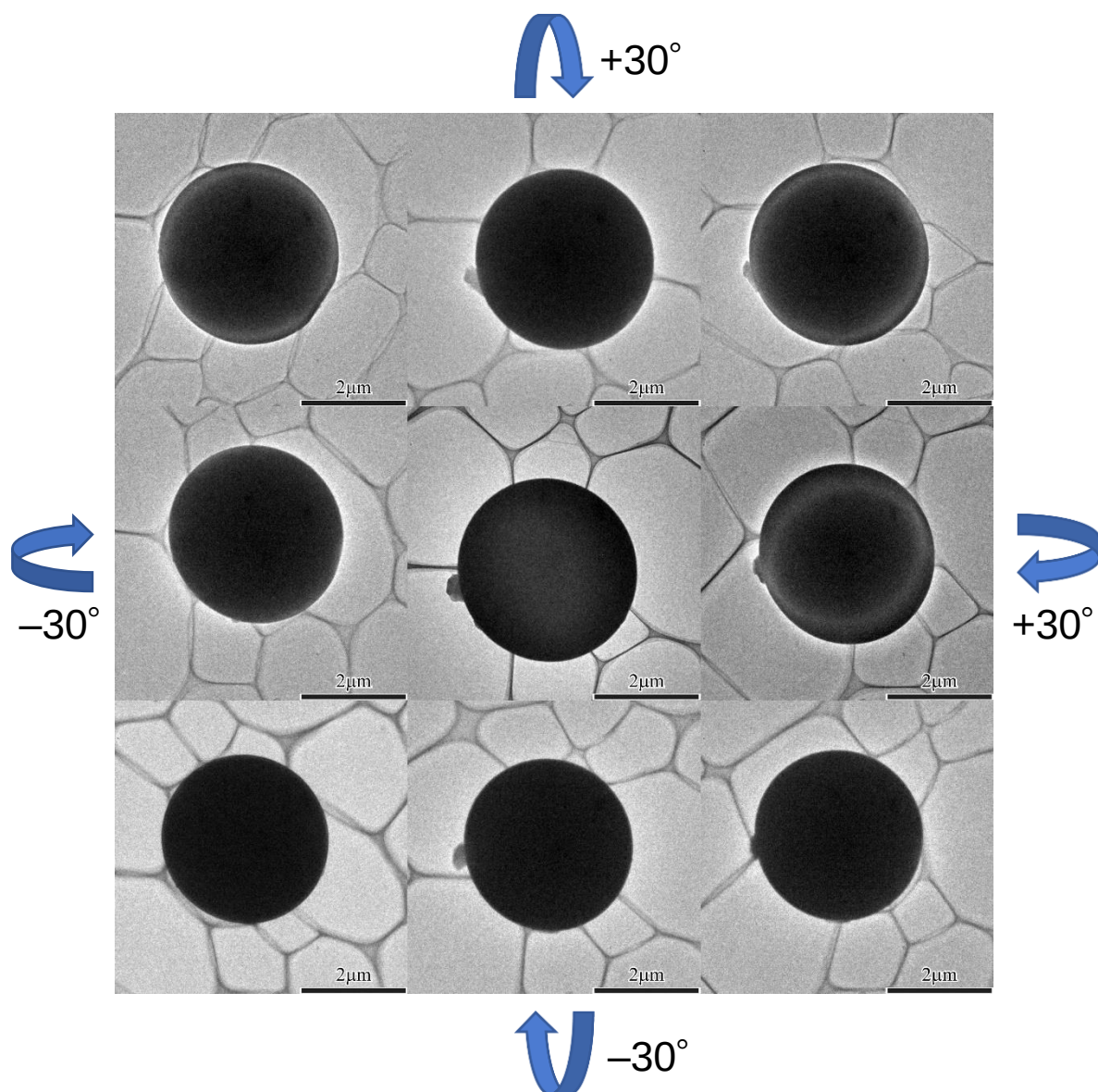
| resins                                     | DD/MAS/ <sup>13</sup> C NMR <sup>[a]</sup> / % |                                 | XPS (O 1s) <sup>[b]</sup> / % |      |
|--------------------------------------------|------------------------------------------------|---------------------------------|-------------------------------|------|
|                                            | C=O<br>(a, b, c) <sup>[c]</sup>                | C–O<br>(d, j, k) <sup>[c]</sup> | C=O                           | C–O  |
| RF-NH <sub>3</sub> -523                    | 28.3                                           | 71.7                            | 28.2                          | 71.8 |
| RF-(COOH) <sub>2</sub> -523                | 30.1                                           | 69.9                            | 30.1                          | 69.9 |
| RF-(COOH) <sub>2</sub> -523 <sup>[d]</sup> | 34.7                                           | 65.3                            | 34.7                          | 65.3 |
| RF-(COOH) <sub>2</sub> -473                | 28.8                                           | 71.2                            | 29.0                          | 71.0 |
| RF-(COOH) <sub>2</sub> -423                | 30.2                                           | 69.8                            | 30.3                          | 69.7 |

[a] The data are from Fig. 5 and Supplementary Fig. 7.

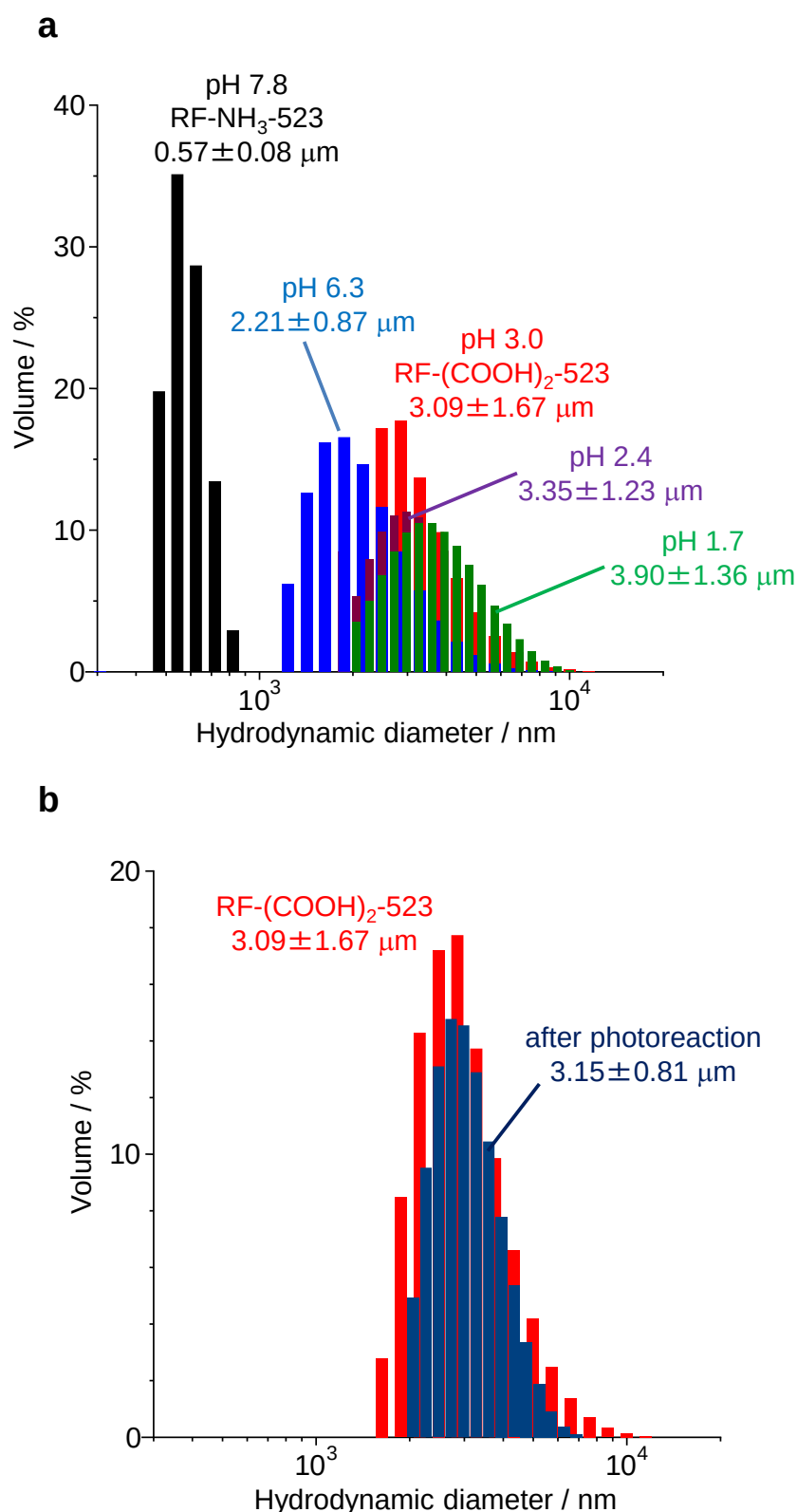
[b] The data are from Supplementary Fig. 9.

[c] Determined by sum of the peak areas for the respective carbon components shown in the round brackets.

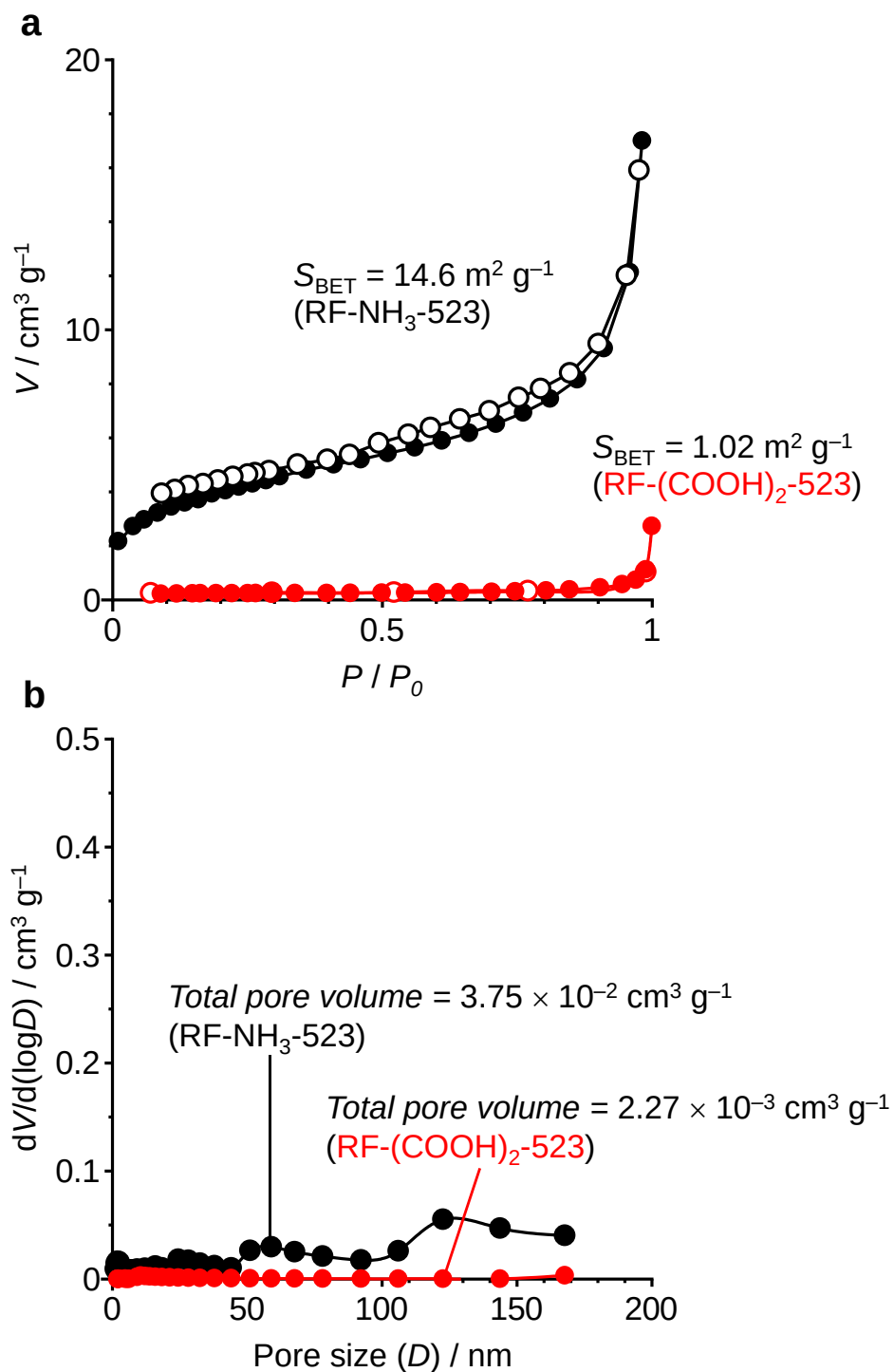
[d] The RF-(COOH)<sub>2</sub>-523 resin recovered after photoreaction for 5 h by a solar simulator (Fig. 4d).



**Supplementary Fig. 1 | TEM images of a RF-(COOH)<sub>2</sub>-523 resin particle observed at different angles.**

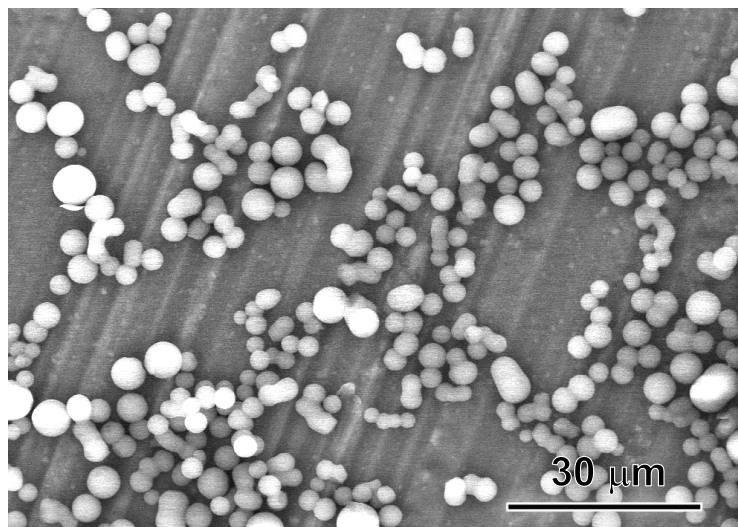


**Supplementary Fig. 2 | DLS analysis of (a) the fresh resins prepared at different pH and (b) the RF-(COOH)<sub>2</sub>-523 resin after photoreaction for 5 h by a solar simulator for 5 h (Fig. 4d). All resins were prepared at 523 K. In (a), the pH 6.3 sample was prepared in pure water, and the pH 2.4 and 1.7 samples were prepared by changing the amounts of (COOH)<sub>2</sub> added (see Supplementary Table 1).**

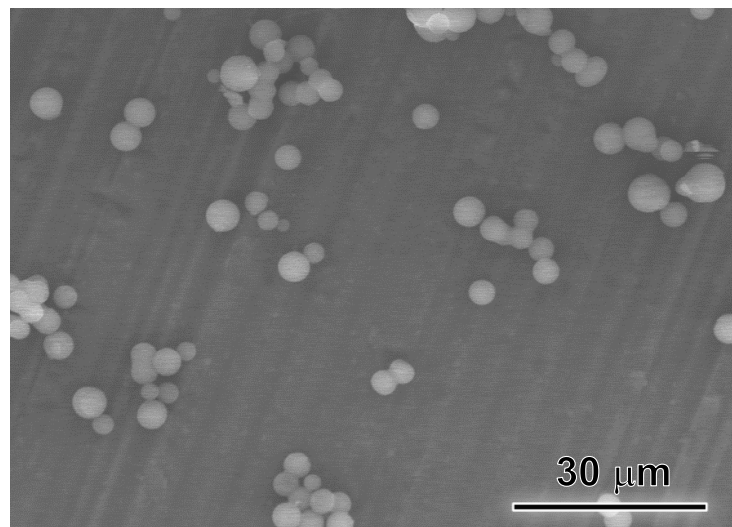


Supplementary Fig. 3 | (a) N<sub>2</sub> adsorption/desorption isotherms of the resins and (b) their pore size distributions determined by the BJH method.

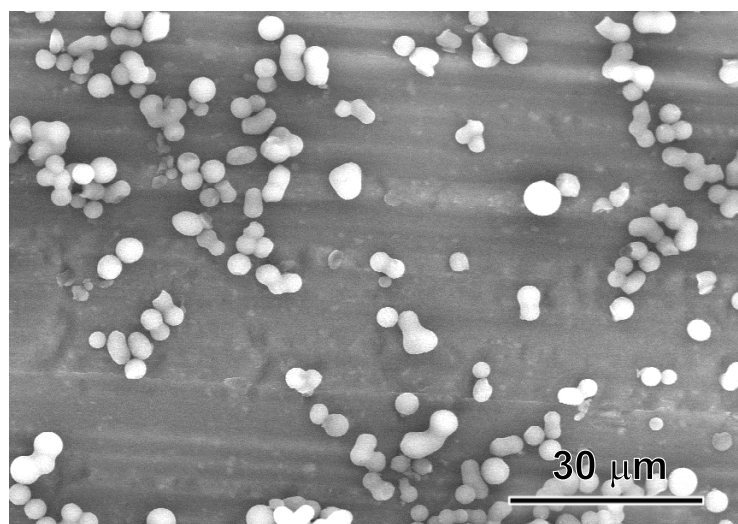
RF-HCl-523



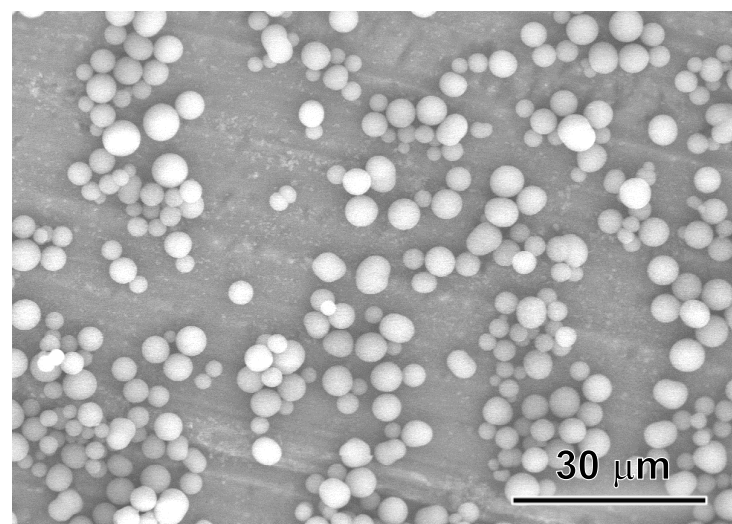
RF-H<sub>2</sub>SO<sub>4</sub>-523



RF-HNO<sub>3</sub>-523

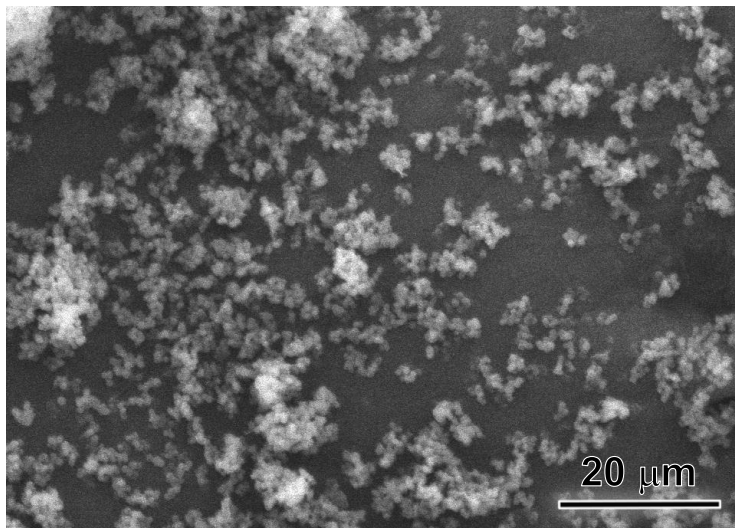


RF-CH<sub>3</sub>COOH-523

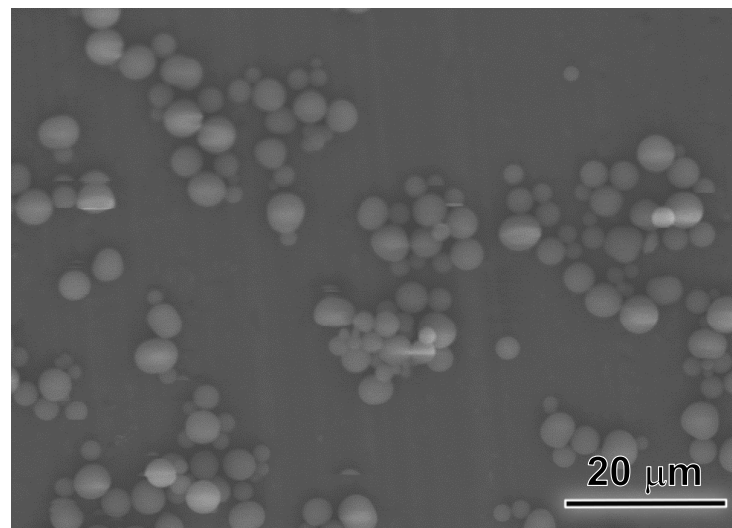


**Supplementary Fig. 4 | SEM images of RF-acid-523 resins.** The size of the particles determined by DLS is summarized in Supplementary Table 1.

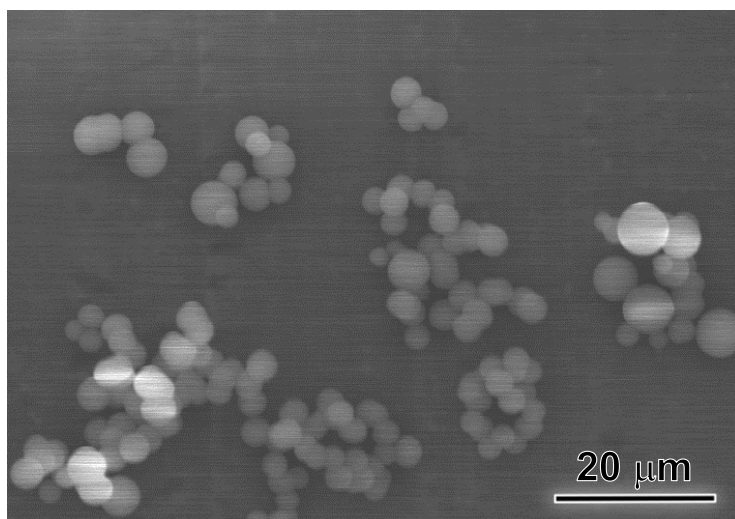
pH 7.8 (RF-NH<sub>3</sub>-573)



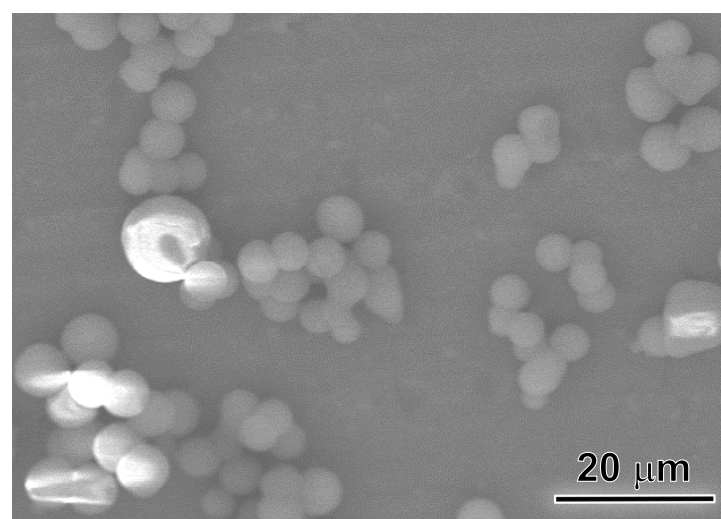
pH 6.3 (prepared in pure water)



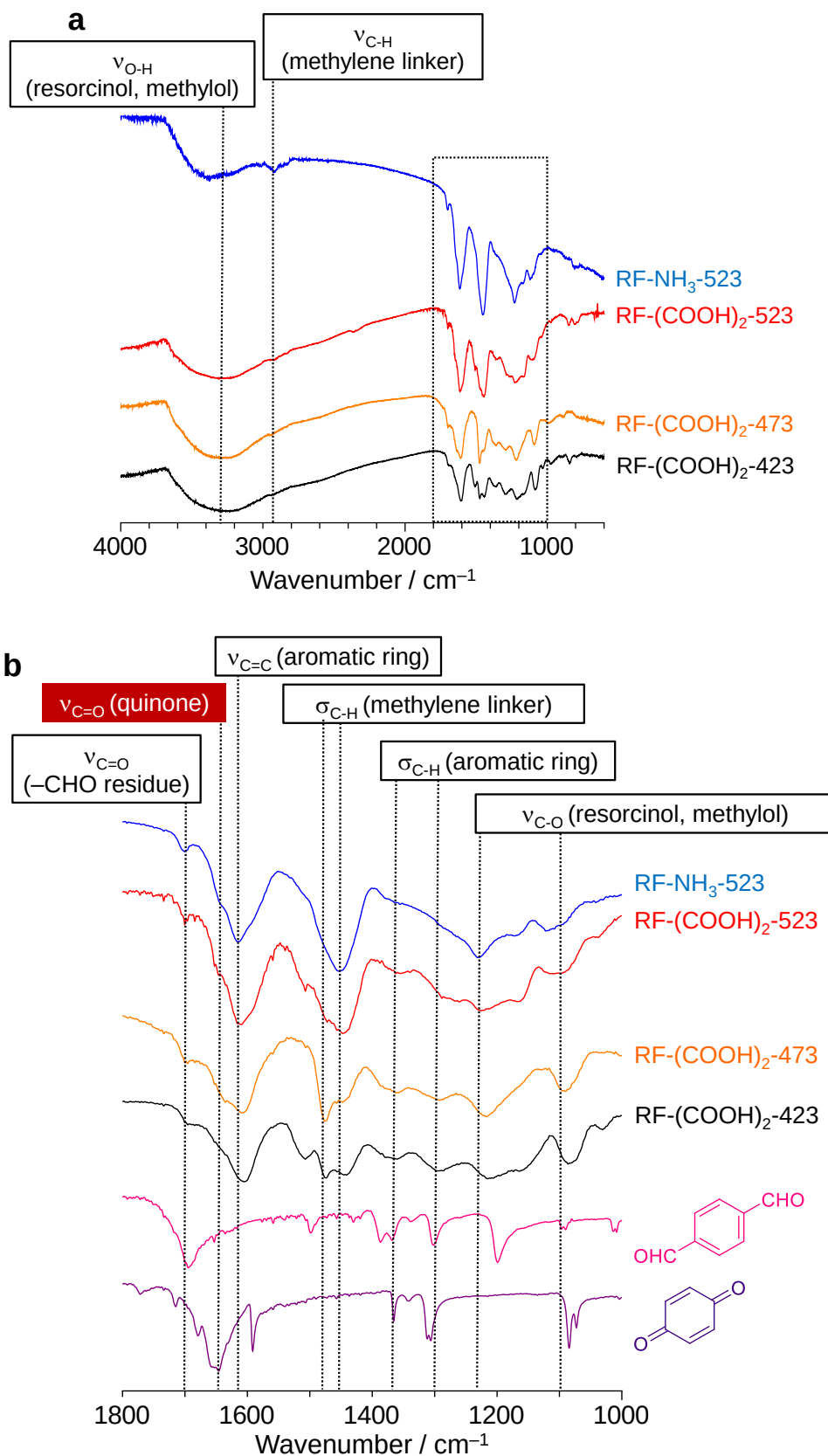
pH 2.4 (prepared with (COOH)<sub>2</sub>)



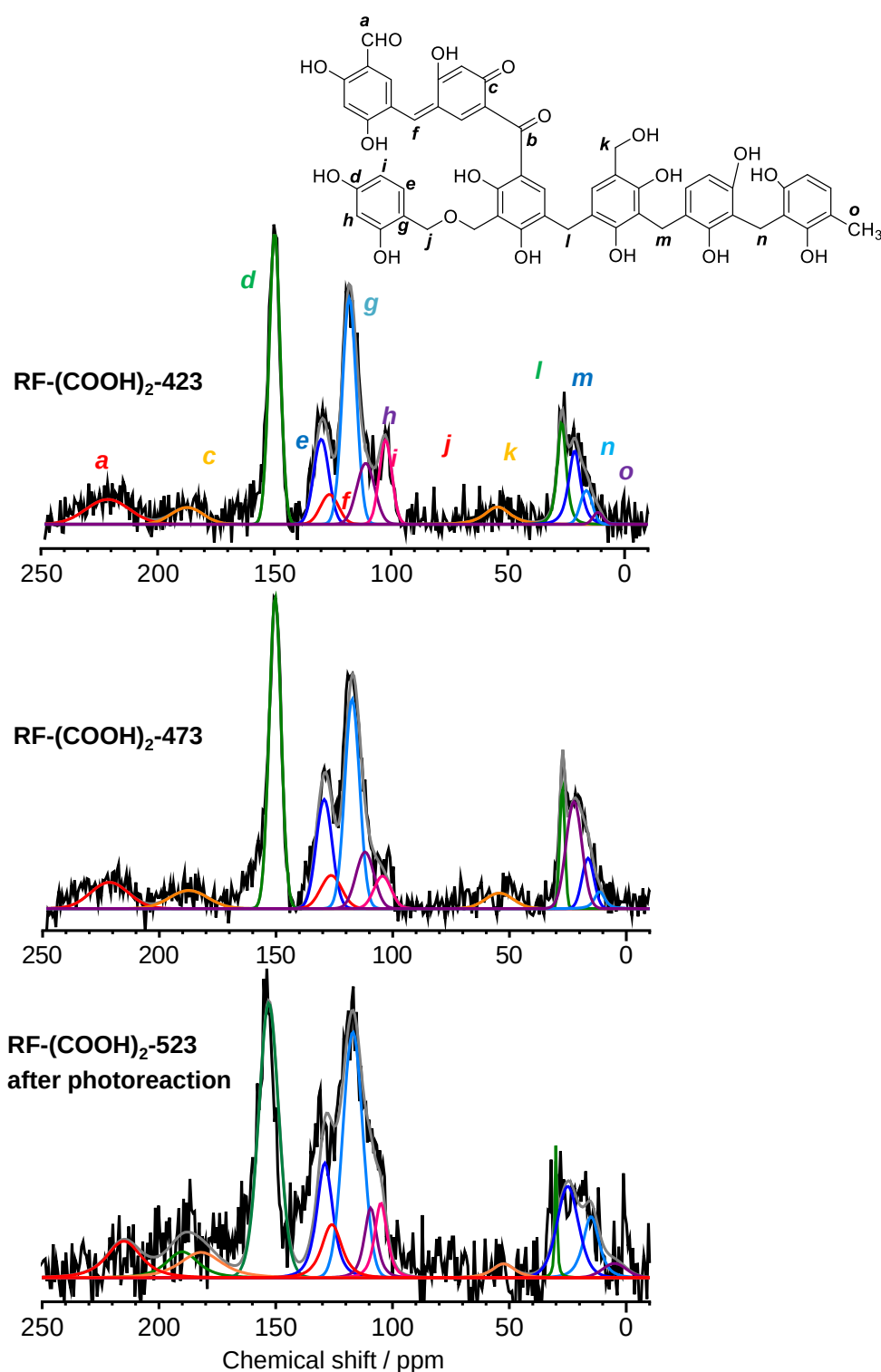
pH 1.7 (prepared with (COOH)<sub>2</sub>)



**Supplementary Fig. 5 | SEM images of RF-NH<sub>3</sub>-523 and the resins prepared at different pH.**

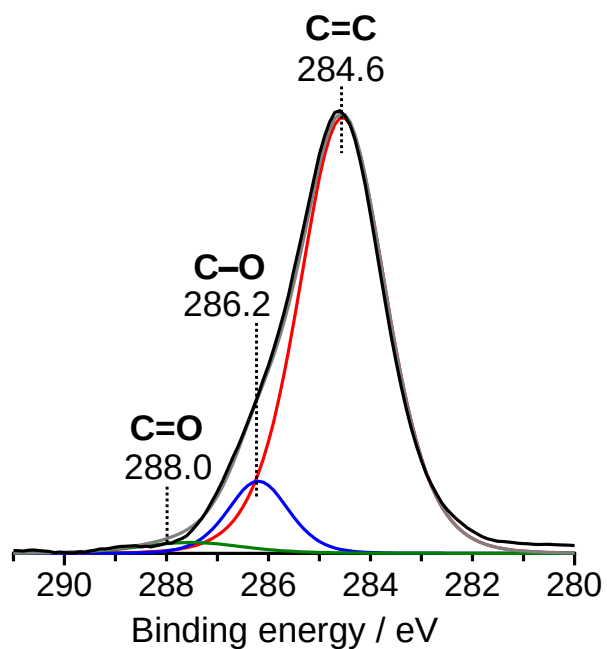


**Supplementary Fig. 6 | Fourier-transformed infrared spectra of RF resins in (a) 1000–4000 cm<sup>-1</sup> and (b) 1000–1800 cm<sup>-1</sup> regions. Peak assignments: 3300 cm<sup>-1</sup> ( $\nu_{\text{O-H}}$  of resorcinol or methylol), 2925 cm<sup>-1</sup> ( $\nu_{\text{C-H}}$  of methylene linker), 1700 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$  of -CHO residue), 1650 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$  of quinone), 1620 cm<sup>-1</sup> ( $\nu_{\text{C=C}}$  of aromatic ring), 1490, 1450 cm<sup>-1</sup> ( $\sigma_{\text{C-H}}$  of methylene linker), 1370, 1300 cm<sup>-1</sup> ( $\sigma_{\text{C-H}}$  of aromatic ring), 1240, 1100 cm<sup>-1</sup> ( $\nu_{\text{C-O}}$  of resorcinol and methylol).**

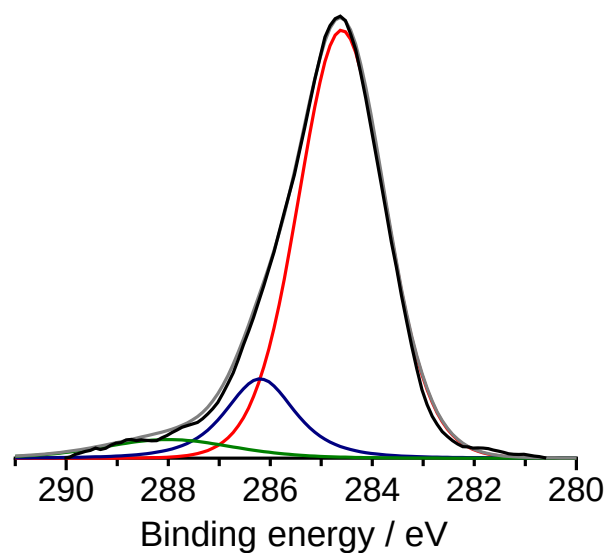


**Supplementary Fig. 7 | Solid-state DD/MAS/<sup>13</sup>C NMR charts of the fresh resins and the RF-(COOH)<sub>2</sub>-523 resin recovered after photoreaction for 5 h by a solar simulator (Fig. 4d, red).** The assignments of the respective carbon components: aldehyde –CHO (210 ppm: **a**), ketone C=O (190 ppm: **b**), quinone C=O (182 ppm: **c**), resorcinol C–OH (153 ppm: **d**), nonsubstituted resorcinol C at the *meta* position (130 ppm: **e**), methine linker –C= (126 ppm: **f**), substituted resorcinol C (117 ppm: **g**), nonsubstituted resorcinol C at the *para* and *ortho* positions (110 ppm: **h**, 105 ppm: **i**), methylene ether linker –C–O–C– (70 ppm: **j**), methylol C–OH (55 ppm: **k**), methylene linker –C–substituted to 4,4′-, 2,4′-, and 2,2′-positions of resorcinols (30 ppm: **l**, 20 ppm: **m**, 10 ppm: **n**), and methyl –CH<sub>3</sub> (5 ppm: **o**).

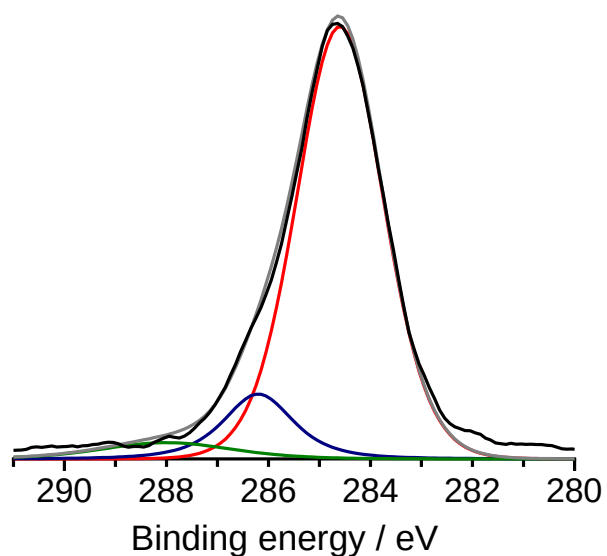
**RF-(COOH)<sub>2</sub>-523**



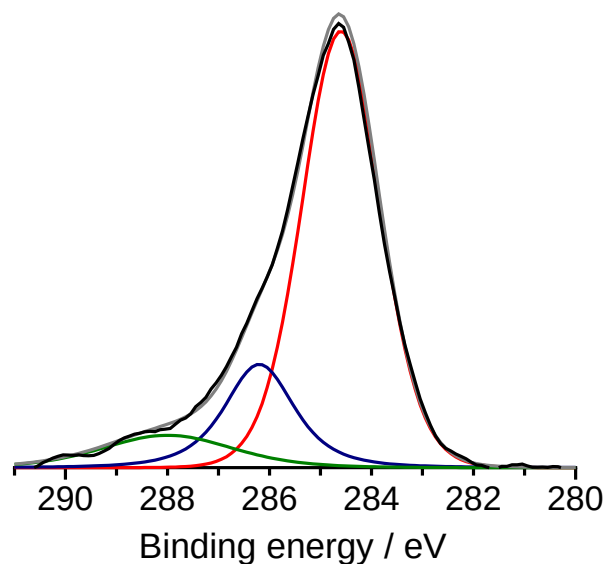
**RF-(COOH)<sub>2</sub>-473**



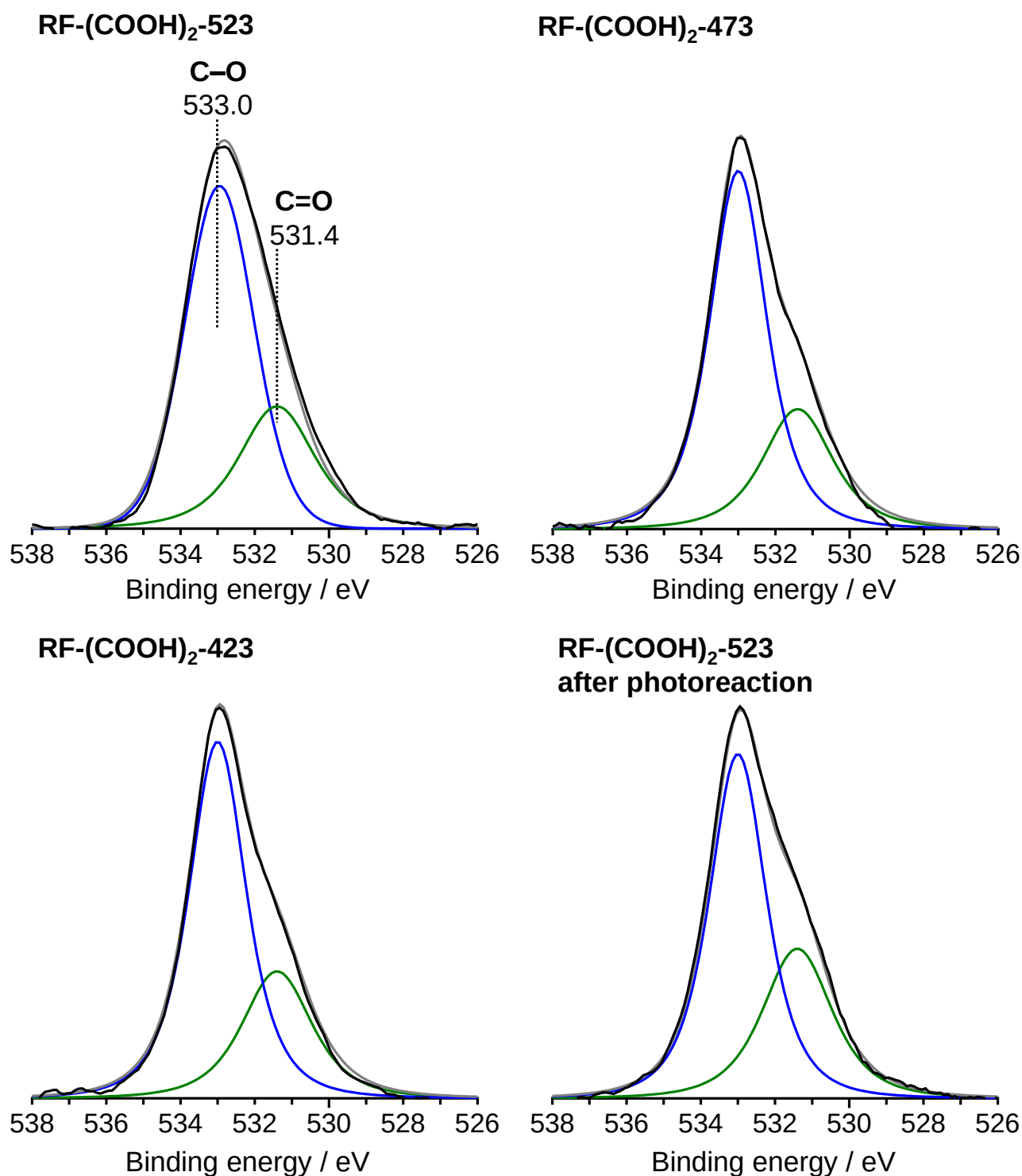
**RF-(COOH)<sub>2</sub>-423**



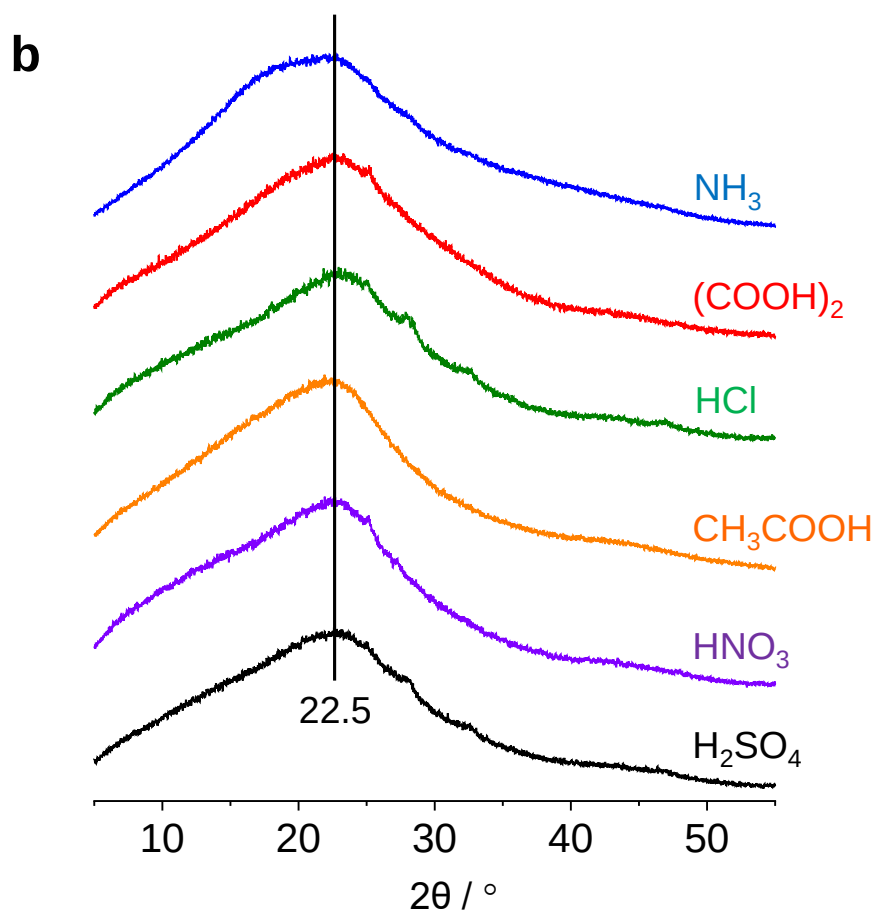
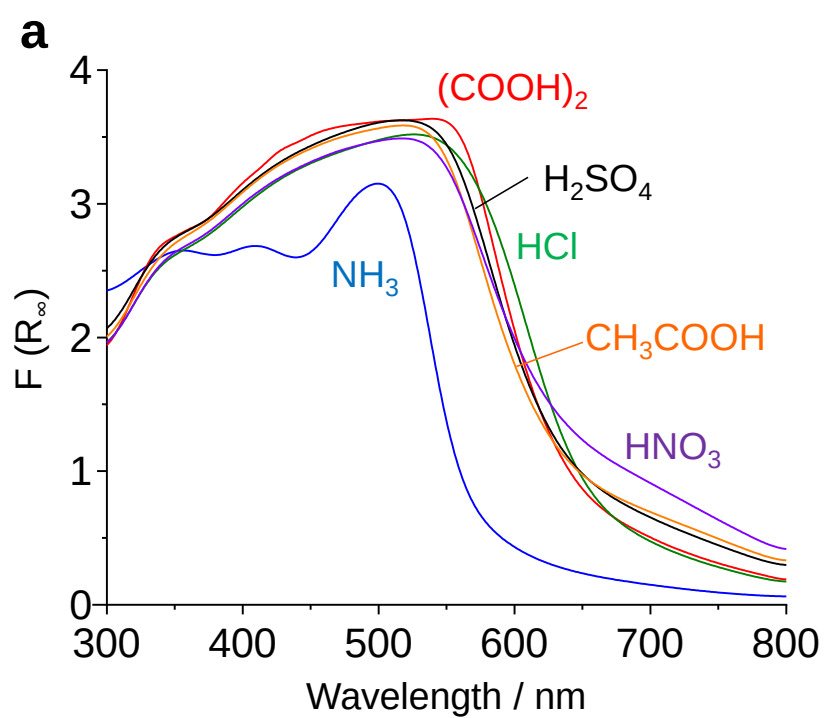
**RF-(COOH)<sub>2</sub>-523  
after photoreaction**



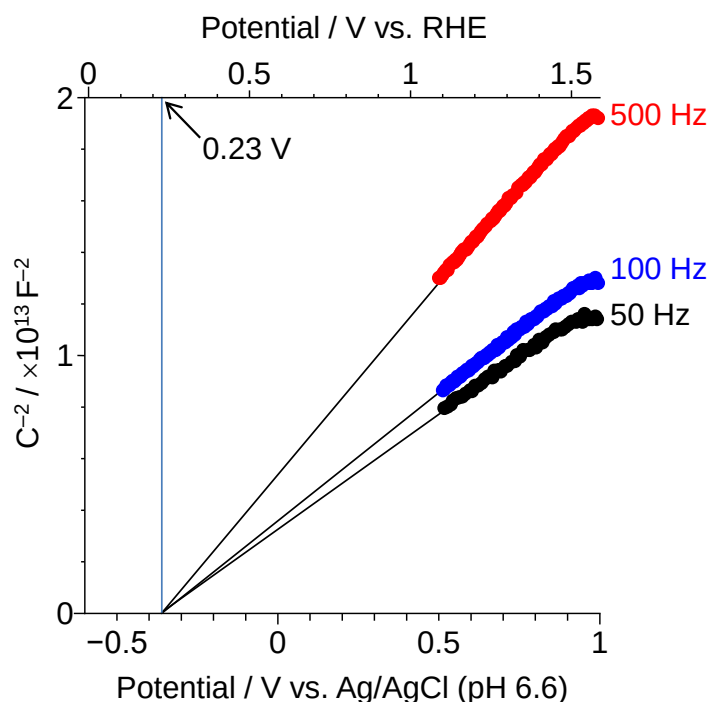
**Supplementary Fig. 8 | XPS charts of RF-(COOH)<sub>2</sub>-523 resin at the C 1s level.** Black line is the observed chart, and gray line is sum of the components.



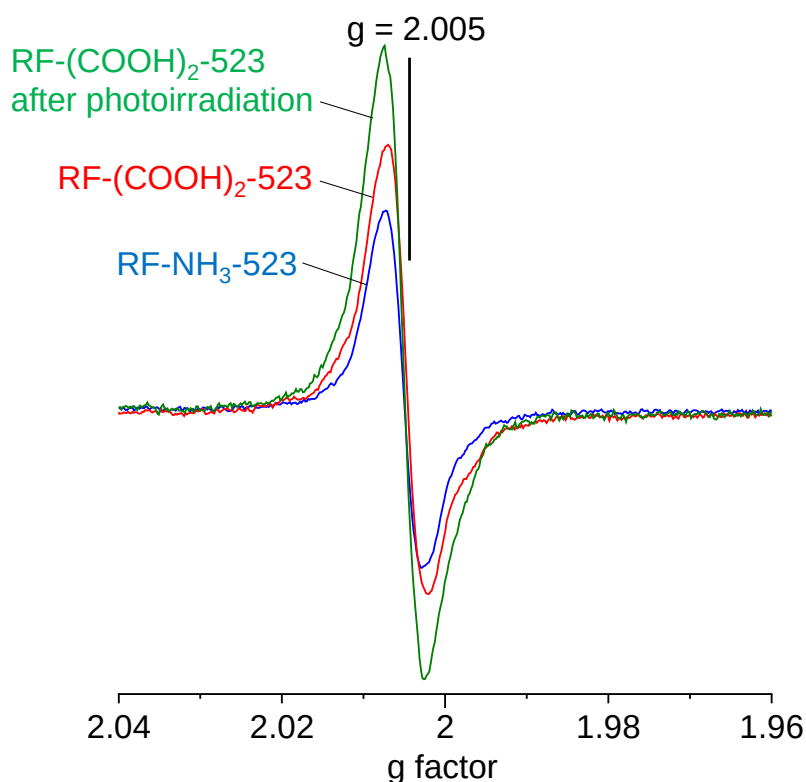
**Supplementary Fig. 9 | XPS charts of RF-(COOH)<sub>2</sub>-523 resin at the O 1s level.** Black line is the observed chart, and gray line is sum of the components.



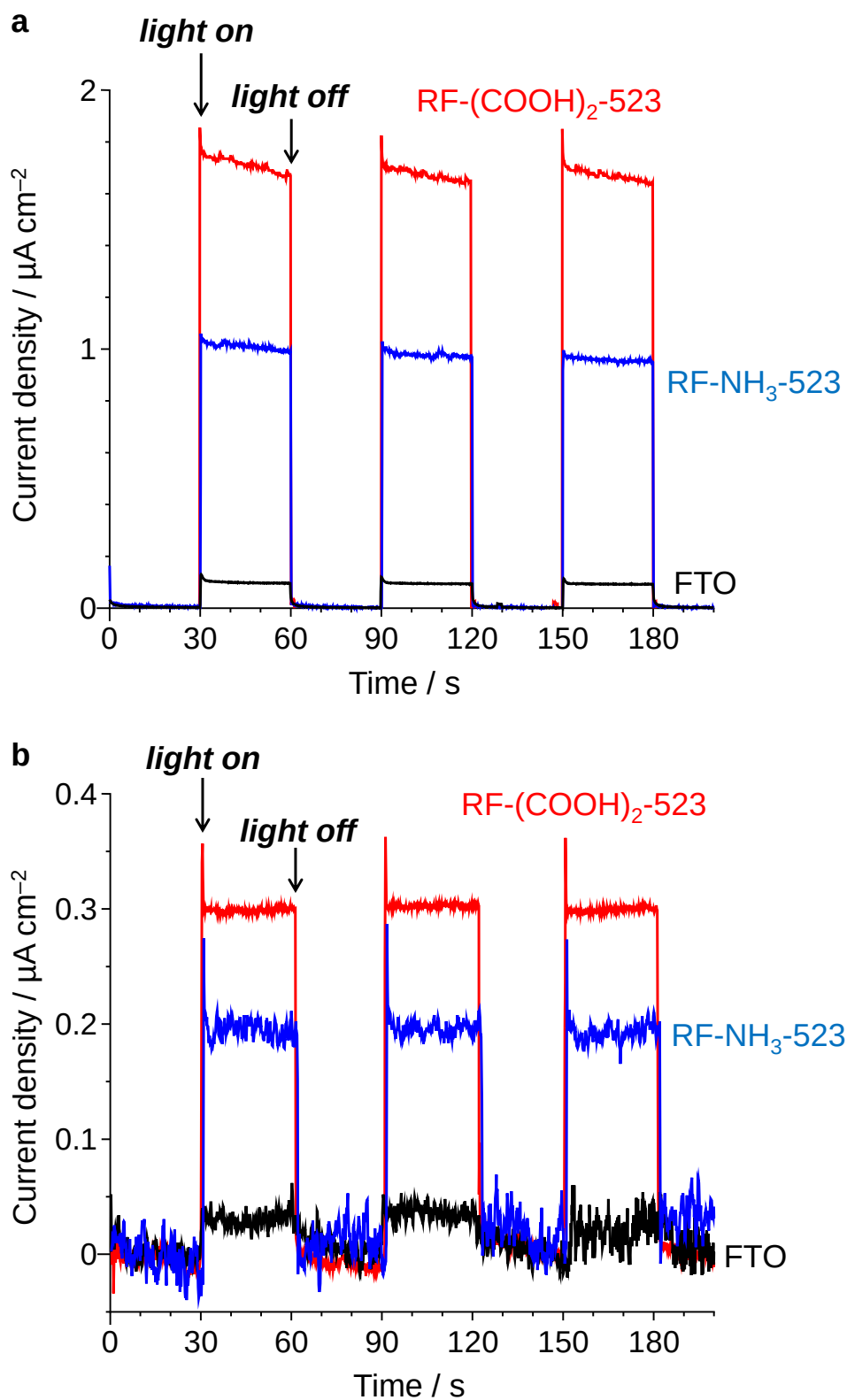
Supplementary Fig. 10 | DR UV-vis and XRD patterns of RF- $\text{NH}_3$ -523 and RF-acid-523 resins.



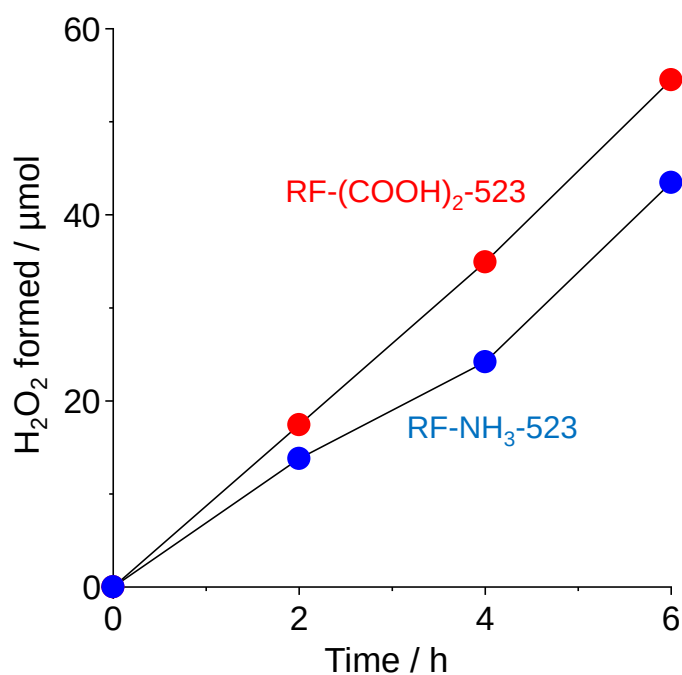
**Supplementary Fig. 11 | Electrochemical Mott-Schottky plots of RF-(COOH)<sub>2</sub>-523.** The measurements were performed in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 6.6). The perturbation signal for the analysis was set at 10 mV.



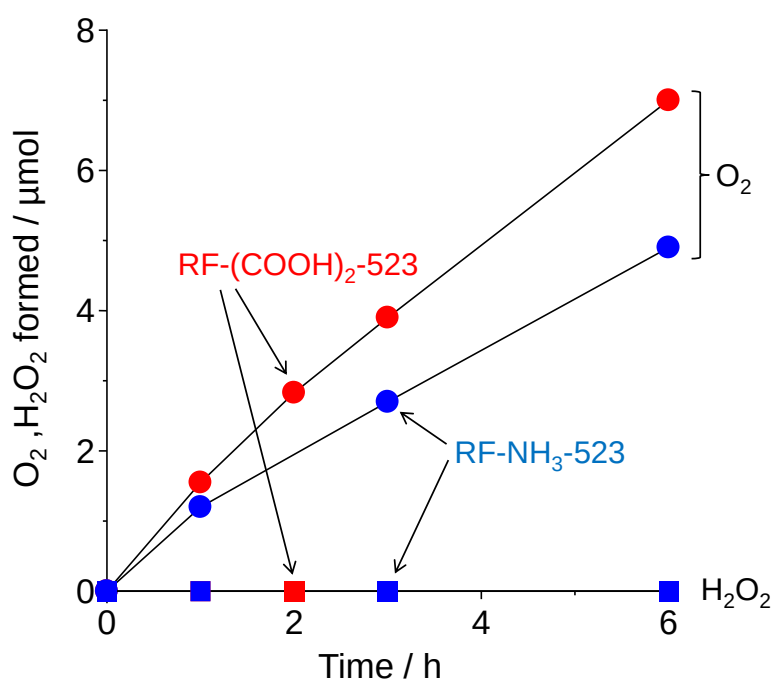
**Supplementary Fig. 12 | ESR spectra of the resins.** The catalyst (20 mg) was placed in a quartz tube, evacuated at 373 K for 6 h, and cooled to room temperature. The tube was then subjected to analysis at room temperature. Visible light was irradiated to the tube for 1 min at room temperature, and the tube was subjected to analysis.



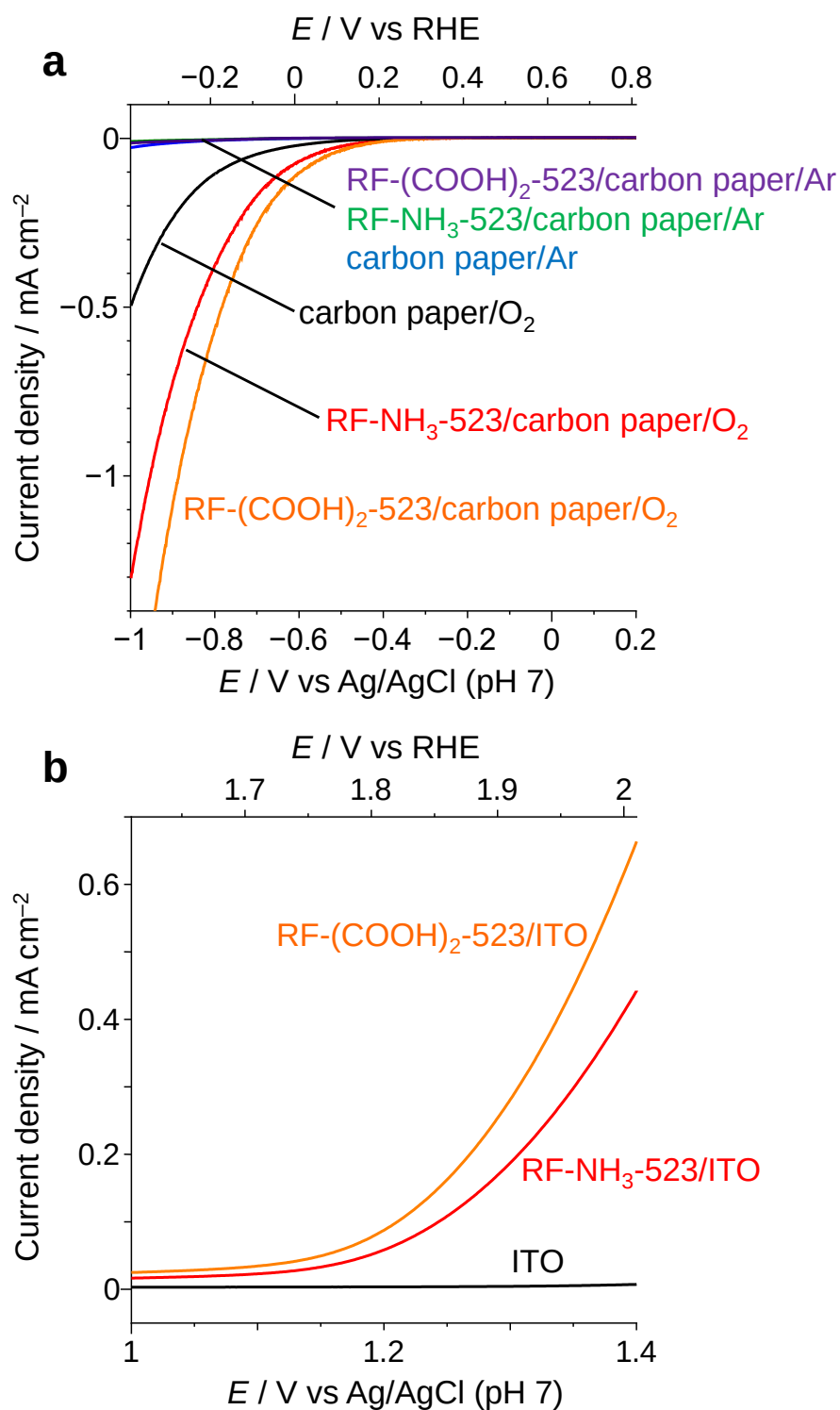
**Supplementary Fig. 13 | Photocurrent response of the resin monitored under (a)  $\lambda > 400$  nm and (b)  $\lambda = 550$  nm monochromatic light irradiation.** The measurements were performed on a FTO electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution under visible light at a bias of 0.5 V (vs Ag/AgCl).



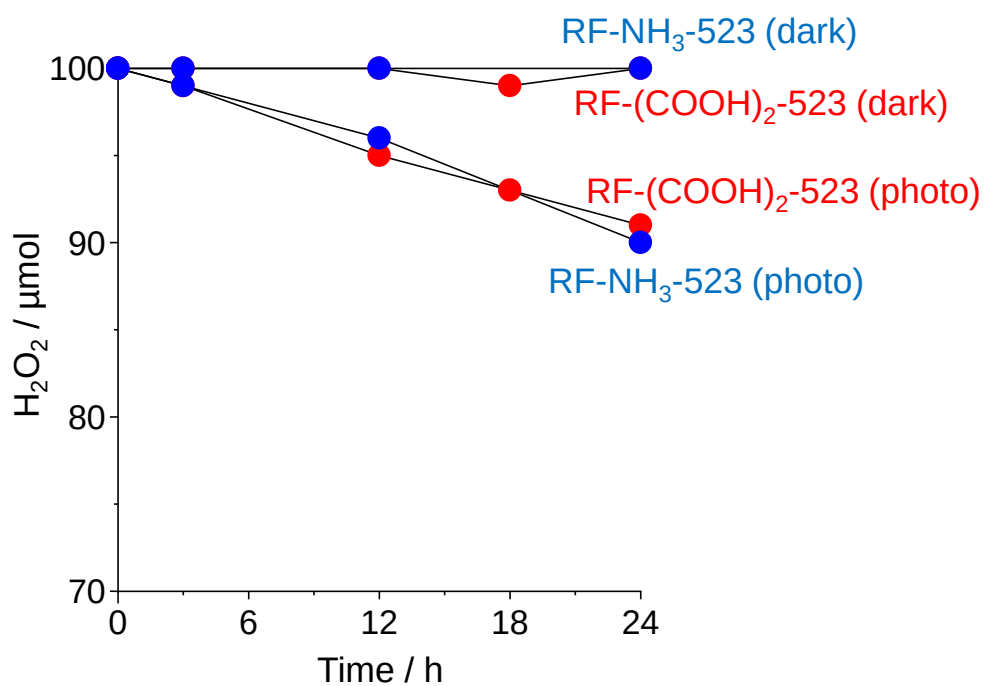
**Supplementary Fig. 14 | Amount of H<sub>2</sub>O<sub>2</sub> formed on the respective resins during the half photoreaction.** Conditions: water (30 mL), resin (50 mg), benzyl alcohol (350 mM), O<sub>2</sub> (1 bar),  $\lambda > 420$  nm (Xe lamp, light intensity at 420–700 nm: 140.3 W m<sup>-2</sup>), 298 K.



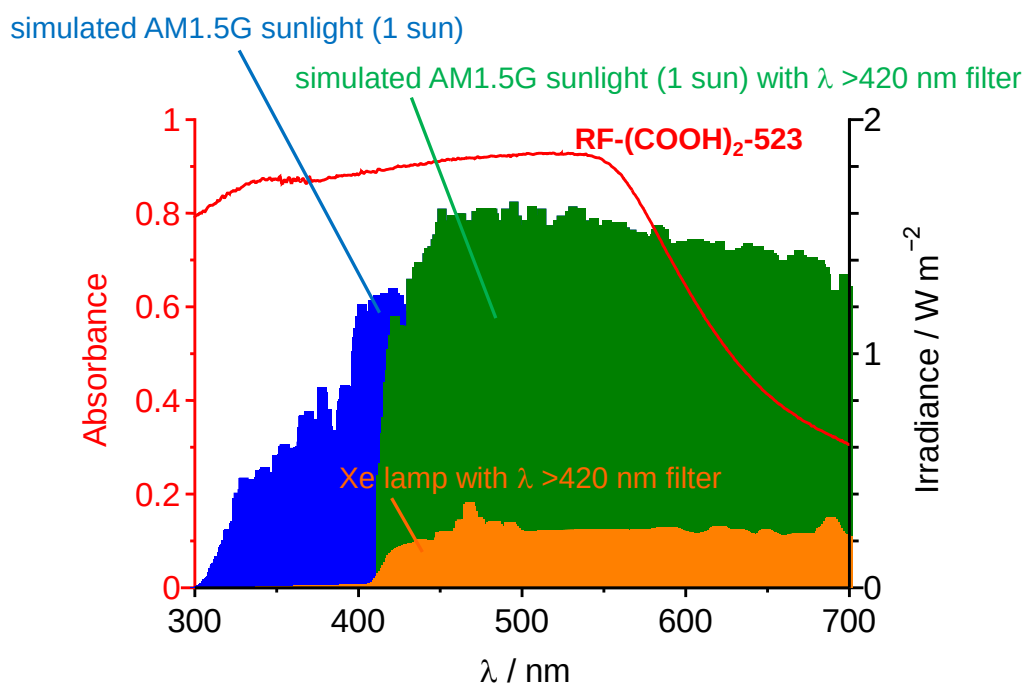
**Supplementary Fig. 15 | Amounts of O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> formed on the respective resins during the half photoreaction.** Conditions: water (30 mL), RF523 catalyst (50 mg), NaIO<sub>3</sub> (2.5 mM), Ar (1 bar),  $\lambda > 420$  nm (Xe lamp, light intensity at 420–700 nm: 140.3 W m<sup>-2</sup>), 298 K.



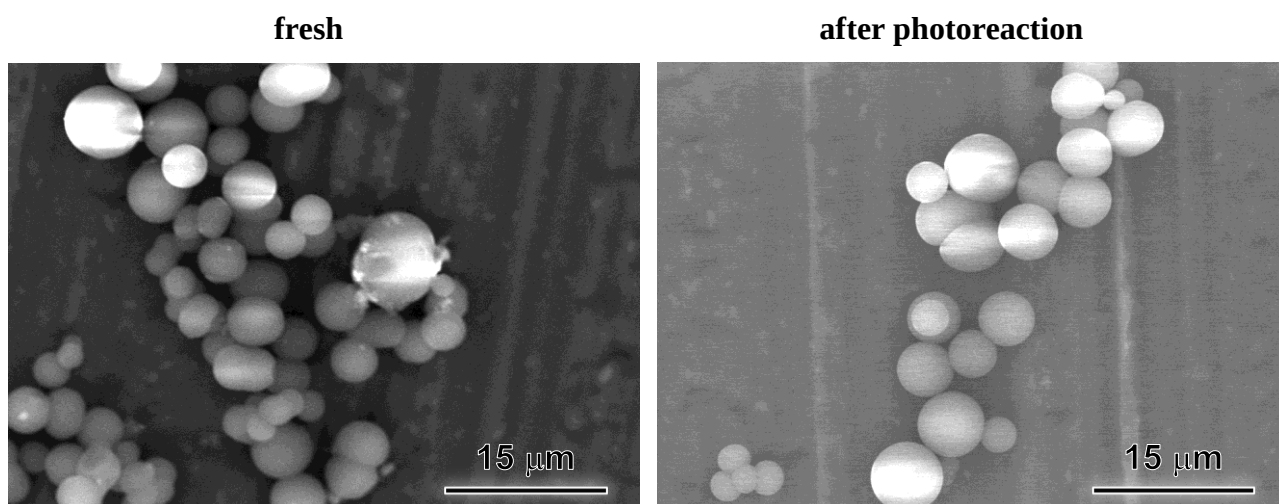
**Supplementary Fig. 16 | Linear sweep voltammograms of the respective resins measured on (a) carbon paper and (b) indium tin oxide (ITO). The measurements were carried out in saturated 0.5 M phosphate buffer solution (pH 7) with scan rate of 10 mV s<sup>-1</sup>.**



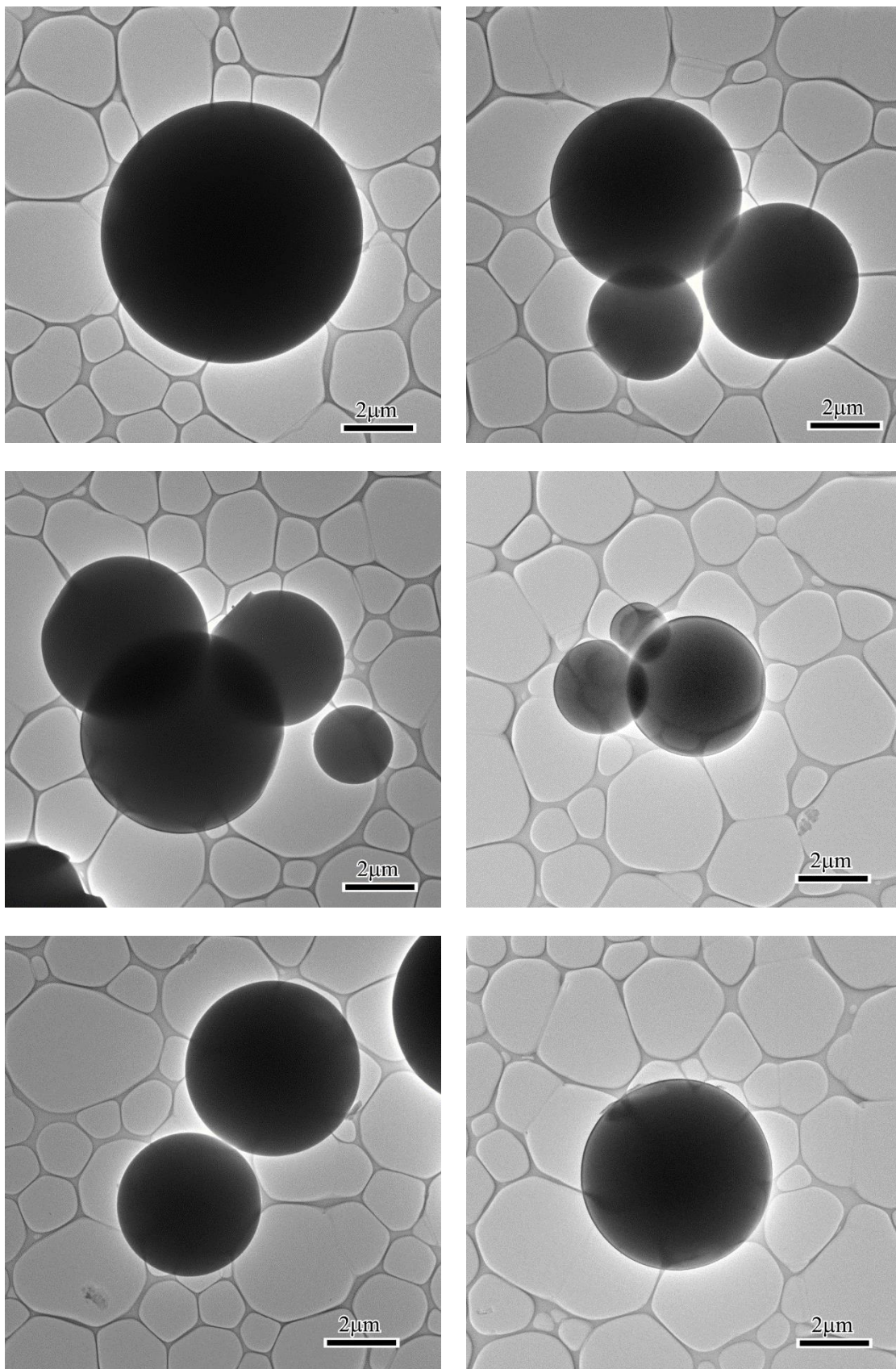
**Supplementary Fig. 17 | Change in the H<sub>2</sub>O<sub>2</sub> amounts during stirring (red) RF-(COOH)<sub>2</sub>-523 or (blue) RF-NH<sub>3</sub>-523 catalyst in a H<sub>2</sub>O<sub>2</sub> solution with NaIO<sub>3</sub> as a sacrificial electron acceptor under the dark or photoirradiation condition.** Conditions: water (30 mL), H<sub>2</sub>O<sub>2</sub> (100 μmol), catalyst (50 mg), NaIO<sub>3</sub> (2.5 mM), Ar (1 bar),  $\lambda > 420$  nm (Xe lamp, light intensity at 420–700 nm: 140.3 W m<sup>-2</sup>), 298 K.



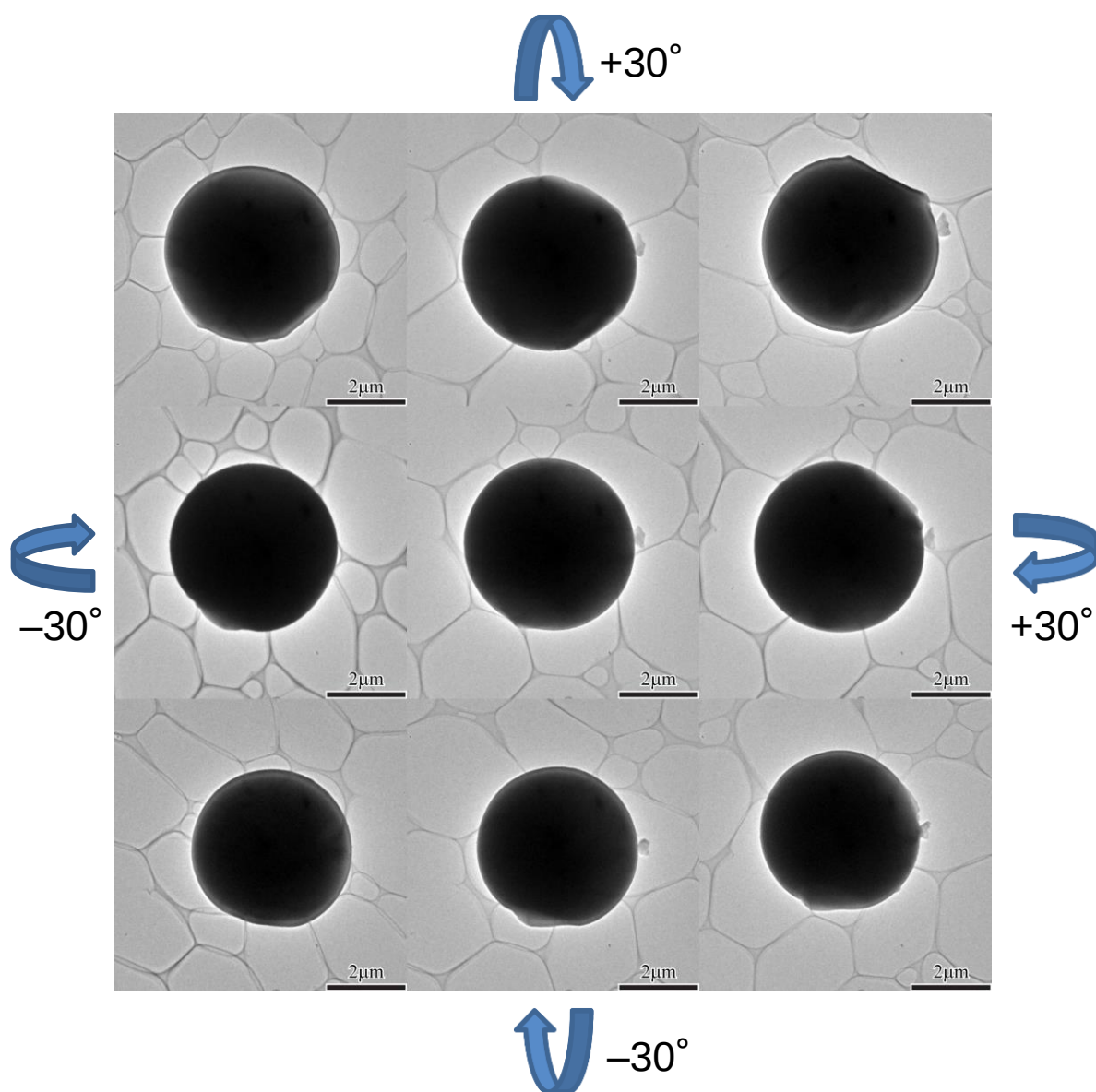
Supplementary Fig. 18 | Absorption spectrum of the RF-(COOH)<sub>2</sub>-523 resin and light emission spectra for Xe lamp with  $\lambda > 420$  nm filter and AM1.5G simulated sunlight (1 sun) with or without  $\lambda > 420$  nm filter.



Supplementary Fig. 19 | SEM images of fresh RF-(COOH)<sub>2</sub>-523 resin and the resin recovered after photoreaction for 5 h by a solar simulator (Fig. 4d).



**Supplementary Fig. 20 | TEM images of the RF-(COOH)<sub>2</sub>-523 resin recovered after photoreaction for 5 h by a solar simulator (Fig. 4d).**



**Supplementary Fig. 21 | TEM images of a RF-(COOH)<sub>2</sub>-523 resin particle recovered after photoreaction for 5 h by a solar simulator (Fig. 4d), observed at different angles.**