Highly Active Water Oxidation on Nanostructured Biomimetic Calcium Manganese Oxides Catalysts

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Turnover frequency (TOF) calculation of the catalysts:

1. TOFs for water oxidation reaction using Ce (IV) as oxidant:

   TOFs are calculated in the initial 600 s with assumption that all Mn atoms are the active sites, which are calculated from the equation:

   \[
   \text{TOF (mmol}_O_2/(mol Mn * h)) = \frac{n_{O_2} \times 3600}{n_{Mn} \times 600}
   \]

   \(n_{O_2}\) is the number of moles of the oxygen evolution after chemical water oxidation reaction for 600 s. \(n_{Mn}\) is the number of moles of Mn that are used in the water oxidation reaction.

   TOFs of chemical water oxidation reaction are normalized by the surface area, which are calculated from the equation:

   \[
   \text{TOF (mmol}_O_2/(m^2 * h)) = \frac{n_{O_2} \times 3600}{S_{BET} \times m \times 600}
   \]

   \(n_{O_2}\) is the number of moles of the oxygen evolution after chemical water oxidation reaction for 600 s. \(S_{BET}\) is the area of the material. \(m\) is mass of the material that are used in the chemical water oxidation reaction.

2. TOFs for water oxidation reaction from visible-light-driven in a reactor – gas chromatography combination system:

   TOFs are calculated in the initial 600 s with assumption that all Mn atoms are the active sites, which are calculated from the equation:

   \[
   \text{TOF (mmol}_O_2/(mol Mn * h)) = \frac{n_{O_2} \times 3600}{n_{Mn} \times 600}
   \]

   \(n_{O_2}\) is the number of moles of the oxygen evolution after photocatalytic water oxidation reaction for 600 s. \(n_{Mn}\) is the number of moles of Mn that are used in the photocatalytic water oxidation reaction.

   TOFs of photocatalytic water oxidation reaction are normalized by the surface area, which are calculated from the equation:

   \[
   \text{TOF (mmol}_O_2/(m^2 * h)) = \frac{n_{O_2} \times 3600}{S_{BET} \times m \times 600}
   \]

   \(n_{O_2}\) is the number of moles of the oxygen evolution after photocatalytic water oxidation reaction for 600 s. \(S_{BET}\) is the area of the material. \(m\) is mass of the material that are used in the photocatalytic water oxidation reaction.
Figure S1. SEM image of MnO$_y$-30, and the table shows the EDX result.

<table>
<thead>
<tr>
<th>Element</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>69.72</td>
</tr>
<tr>
<td>K</td>
<td>05.87</td>
</tr>
<tr>
<td>Mn</td>
<td>24.40</td>
</tr>
</tbody>
</table>

Figure S2. TG of (A) Ca$_x$MnO$_y$-30 with different Ca/Mn molar ratio, and (B) Ca$_{0.46}$MnO$_y$-n with different amount of H$_2$O$_2$ in the synthesis system.

The observed weight loss in the temperature range from 25 °C to 250 °C is most probably caused by the loss of water, and at higher temperature the change of weight may be due to the phase transition.
Figure S3. The relative catalytic activity of Ca$_{0.33}$MnO$_{0.7}$-30 for oxygen evolution reaction utilizing visible-light-driven [Ru(bpy)$_3$]$^{2+}$-persulfate system, measured by a reactor-gas chromatography system (the activity of the first run was set to 100%).