An engineered polypeptide around nano-sized manganese-calcium oxide: Copying plants for water oxidation

Mohammad Mahdi Najafpour\textsuperscript{ab*}, Mohadeseh Zarei Ghabadi, \textsuperscript{\dag a} Bahram Sarvi\textsuperscript{\dag a} and Behzad Haghighi\textsuperscript{a-c}

\textsuperscript{a}Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

\textsuperscript{b}Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

\textsuperscript{c}Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

*Corresponding author; Phone: (+98) 24 3315 3201; E-mail: mnnajafpour@iasbs.ac.ir

\textsuperscript{\dag}These authors contributed equally to the work.
Supplementary Figure S1. Mass spectroscopy result for $G_7HV_2(TV_2)_2$. 

Sample Information
Injection Volume: 1.00 μl
Sample Name: EV-16
MW: 1980.13
Lot No.: P130929-XL369359

Probe: ESI
Gas Flow: 1.5 L/min
DL Temp: 250°C
Block Temp: 200°C
T. Flow: 0.2 ml/min
B. conc: 50% MeOH/50% ACN
Product Name: EV-16
Instrument No: 0200352
Lot No: P130929-XL369359
Column: 4.6*250mm, kromasil C18-5
Solvent A: 0.1%Trifluoroacetic in 100% Acetonirile
Solvent B: 0.1%Trifluoroacetic in 100% Water
Gradient: 
0.01min  30%  70%
25.0min  55%  45%
25.01min 100%  0%
30min     Stop
Flow rate: 1.0ml/min
Wavelength: 220nm
Volume: 10ul

Supplementary Figure S2. HPLC result for G7HV2(TV2)2.
File Name: safari.dts  Dispersant Name: Water
Record Number: 2380  Dispersant RI: 1.330
Material RI: 1.33  Viscosity (cP): 0.8872
Material Absorption: 0.00  Measurement Date and Time: Sunday, December 15, 2013 ...

System
Temperature (°C): 25.0  Duration Used (s): 110
Count Rate (kcps): 74.8  Measurement Position (mm): 4.65
Cell Description: Disposable sizing cuvette  Attenuator: 6

Results

<table>
<thead>
<tr>
<th>Diam. (nm)</th>
<th>% Intensity</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-Average (d.nm): 2710</td>
<td>Peak 1: 880.6</td>
<td>100.0</td>
</tr>
<tr>
<td>PdI: 0.966</td>
<td>Peak 2: 0.000</td>
<td>0.0</td>
</tr>
<tr>
<td>Intercept: 0.500</td>
<td>Peak 3: 0.000</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Result quality: Refer to quality report

Size Distribution by Intensity

<table>
<thead>
<tr>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

Size (d.nm)

[Graph showing size distribution by intensity]
<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Mean</th>
<th>Std Dev</th>
<th>Number %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4000</td>
<td>5.645</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.8033</td>
<td>6.983</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.8285</td>
<td>6.571</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.7195</td>
<td>8.721</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5932</td>
<td>10.10</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.9649</td>
<td>11.70</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.117</td>
<td>13.64</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.294</td>
<td>15.62</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.459</td>
<td>18.17</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.736</td>
<td>20.04</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2.010</td>
<td>22.89</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2.328</td>
<td>25.86</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2.696</td>
<td>28.64</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3.122</td>
<td>31.62</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3.656</td>
<td>34.75</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4.187</td>
<td>37.97</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4.849</td>
<td>40.06</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

![Statistics Graph (1 measurements)](image)

Red: Mean with ±1 Standard Deviation error bar

b
File Name: sefar.cdt
Dispersant Name: Water
Record Number: 2380
Dispersant RI: 1.330
Material RI: 1.33
Viscosity (cP): 0.8872
Material Absorption: 0.00
Measurement Date and Time: Sunday, December 15, 2013 ...

System
Temperature (°C): 25.0
Duration Used (s): 110
Count Rate (kcps): 74.8
Measurement Position (mm): 4.65
Cell Description: Disposable sizing cuvette
Attenuator: 6

Results

\[
\begin{array}{cccc}
\text{Z-Average (d.nm):} & 2710 & \text{Peak 1:} & 690.6 \\
\text{PDI:} & 0.966 & \text{Peak 2:} & 0.000 \\
\text{Intercept:} & 0.500 & \text{Peak 3:} & 0.000 \\
\text{Diam. (nm)} & \% \text{Intensity} & \text{Width (nm)} & \\
\end{array}
\]

Result quality: Refer to quality report

Size Distribution by Number

![Size Distribution Graph](image-url)
Supplementary Figure S3. Details for DLS of $G_7$HV$_2$(TV)$_2$/MnCaO$_3$ (a-d). We don’t use ultrasonic for the DLS experiments.
Supplementary Figure S4. FTIR spectra G$_7$HV$_2$(TV)$_2$/MnCaO$_x$. 
Supplementary Figure S5. UV-Vis spectrum of G$_7$HV$_2$(TV)$_2$/MnCaO$_x$. The arrow shows UV-VIS peak for Mn(III)/(IV).
Supplementary Figure S6. **Water oxidation.** Set-up for electrochemical water oxidation.