Supplemental materials for:

**Photoelectrochemical Response and Electronic Structure Analysis of Mono-Dispersed Cuboid-Shaped Bi$_2$Fe$_4$O$_9$ with Strong Near-Infrared Absorption**

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Figure S1: The \( k \)-points sampling in Brillouin zone of the \( \text{Bi}_2\text{Fe}_4\text{O}_9 \) (BFO) conventional unit cell.
<table>
<thead>
<tr>
<th>Elements</th>
<th>wt. %</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>21.44</td>
<td>65.40</td>
</tr>
<tr>
<td>Fe K</td>
<td>25.38</td>
<td>22.18</td>
</tr>
<tr>
<td>Bi M</td>
<td>53.18</td>
<td>12.42</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Figure S2: EDS data of the fragments around the BFO cuboids. The C and Pt peaks that originate from the conductive tape and the Pt coating, correspondingly, for
enhancing conductivity are not shown. The ratio of Fe: Bi in the fragments is 1.78:1 which is similar to that in BFO cuboids.

Figure S3: The light brown transparent solution of Fe(OH)$_3$ (a) and its Tyndall effect (b).
Figure S4: EDS data of the dried sol. The C peak is originated from the conductive tape. The brown sol is dried at 60 °C for 12h to remove all solvent. The content of Fe...
in the dried sol is 4 times to that of Bi implying the brown sol is primarily composed by iron hydroxide.

\[
d = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}
\]

Lattice parameters of Bi$_2$Fe$_4$O$_9$: a=0.794 nm, b=0.844 nm, c=0.601 nm

\[d_{(141)} = 0.1931 \text{ nm}
\]
\[d_{(330)} = 0.1928 \text{ nm}
\]

Fig S5: Calculation of the interplanar spacing of (141) plane and (330) plane. In many papers, the peak at ~47° is usually indexed as (141). Based on the calculation above, the diffraction peak of (330) will as well appear at ~47°, that’s why this peak is also strengthened in the XRD pattern of DB-BFO.
Figure S6: The XRD pattern of the light yellow precipitate dried at 60 °C, the standard XRD pattern of Bi$_2$O$_3$ with a space group of P21/c is listed below. The light yellow precipitate is obtained as follows. 0.3 mmol Bi(NO$_3$)$_3$·5H$_2$O was added into 40 ml DI water under constant stirring for 1 h and a homogeneous milky suspension was formed as described in the manuscript. The milk-white suspension turned into a light yellow suspension promptly upon the addition of 0.75 mol NaOH, as shown in the inset.
Figure S7: FE-SEM images of Bi$_2$Fe$_4$O$_9$ crystals synthesized at 180 °C with various concentrations of NaOH: (a) 18.75 M NaOH, (b) 12.5 M NaOH, and (c) 6.25 M NaOH for 24 h.
Figure S8: XRD patterns of the products synthesized in various concentrations of NaOH: (a) 18.75 M, (b) 12.5 M, (c) 6.25 M, (d) 2.5 M, (e) 1 M, (f) 0.5 M and (g) 0.25 M at 180 °C for 24 h.
Fig S9: Schematic electronic DOS of Fe$^{3+}$ in octahedral O$_h$ and tetrahedral T$_d$ coordination.