| 1  | <b>Electronic supplementary information (ESI)</b>  |
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| 2  |  |
| 3  | Single-crystalline Bi <sub>2</sub> Fe <sub>4</sub> O <sub>9</sub> synthesized by low-temperature co-precipitation: |
| 4  | Performance as photo- and Fenton catalysts   |
| 5  |  |
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| 17 |  |
| 18 | As shown in Fig. S1, the as-prepared samples exhibit different XRD intensities. The                                |

19 XRD intensity for Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (36 h) is higher than that of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> (6 h), which possibly

20 contributes to the increase in the crystal size or its crystallinity of the former.



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22 Fig. S1. XRD patterns of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> samples synthesized at reaction times of 6 and 36 h.

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Fig. S2 shows the TEM image of  $Bi_2Fe_4O_9$  (6 h) and its electron diffraction ring-pattern,

26 indicating that it is a poly-crystalline material when the reaction time is 6 h.



**Fig. S2.** (a) TEM image of  $Bi_2Fe_4O_9$  (6 h) and (b) the corresponding SAED pattern.

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Fig. S3 shows that the sample synthesized at 6 h has a higher specific surface area of  $142.5 \text{ m}^2 \text{ g}^{-1}$  than that of the sample prepared at 36 h (5.8 m<sup>2</sup> g<sup>-1</sup>).



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Fig. S3. Nitrogen adsorption/desorption isotherm of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> samples synthesized at reaction
times of 6 and 36 h.

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Fig. S4 shows that the sample prepared by 36 h has a higher degradation efficiency of BPA than that of the sample for 6 h. It indicates that the surface area is not the dominant influence in this case, while the exposed facet (001) is possible for the initial condition.



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40 **Fig. S4.** Photocatalytic performance of  $Bi_2Fe_4O_9$  (6 h) and  $Bi_2Fe_4O_9$  (36 h).

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Photo-Fenton oxidation has been reported that it can be excited under UV radiation, 42 visible light irradiation or solar light illumination,<sup>1-3</sup> which depends on the kind of Fe<sup>3+</sup>/ligand 43 complexes with the different ligands.<sup>2, 4-7</sup> The ligand-to-metal charge transfer (LMCT) as a 44 theoretical basis is widely used to explain the process of photo-Fenton oxidation. Without 45 organic ligands in the pure photo-Fenton system, the mainly existing Fe<sup>3+</sup> complexes are 46 FeOH<sup>2+</sup> and Fe( $O_2H$ )<sup>2+</sup>. Herein, assuming under ideal conditions (e.g., pH 2.8), the discussion 47 shown below focuses on the possibility of an overall reaction of photo-Fenton oxidations. 48 Surely, all of derivative processes are based on the previously accepted reports. 49

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51 When the wavelength locates at a range of 280-420 nm, the photo-Fenton oxidation can be 52 induced by aquocomplexes (FeOH<sup>2+</sup>).<sup>5, 8</sup> An overall reaction of the photo-Fenton oxidation can be expressed as Eq.(S1) in the presence of  $H_2O_2$ ,  $Fe^{3+}/Fe^{2+}$ , and light irradiation. It is derived from Eqs. (S2), (S3) and (S4). The pathways of formula derivations are shown below. The derivation is deduced progressively based on the known conditions, such as the initial scheme of Fenton reaction, the hydrolysis reaction of  $Fe^{3+}$ , and the original scheme of photo-Fenton oxidation.

$$58 Fe^{3+} + H_2O_2 + H_2O_+ hv \rightarrow Fe^{2+} + 30H \bullet + H^+$$
(S1)

59 Initial scheme of Fenton reaction<sup>9</sup>:

$$60 \quad Fe^{2+} + H_2O_2 \quad \to \quad Fe^{3+} + OH \bullet + OH^- \tag{S2}$$

61 Hydrolysis reaction<sup>5</sup>:

$$62 \quad Fe^{3+} + H_2^0 \quad \rightarrow \quad Fe^{0}H^{2+} + H^+ \tag{S3}$$

63 Original scheme of photo-Fenton oxidation of aquocomplexes<sup>1, 5, 8</sup>:

$$64 \quad FeOH^{2+} + hv \quad \rightarrow \quad Fe^{2+} + OH \bullet \tag{S4}$$

65

- 66 Formula derivation:
- 67 Combining Eqs. (S3) and (S4) give

$$68 F e^{3+} + H_2 O_+ h v \rightarrow F e^{2+} + O H \bullet + H^+$$
(S5)

69 Eq. (S5) can be rewritten as

$$70 \quad 2Fe^{3+} + \frac{2H_2O}{2} + 2hv \quad \to \quad 2Fe^{2+} + 2OH \bullet + 2H^+ \tag{S6}$$

71 Combining Eqs. (S2) and (S6) give

$$72 Fe^{3+} + H_2O_2 + 2H_2O + 2h\nu \rightarrow Fe^{2+} + 30H \bullet + 2H^+ + 0H^-$$
(S7)

- Where  $H^+ + 0H^- = H_2 0$ , thus giving the overall reaction of photo-Fenton oxidation as Eq. (S1).
- 75

When the Fe(O<sub>2</sub>H)<sup>2+</sup> complexes absorb visible light ( $\lambda \le 650$  nm), the  $HO_2 \bullet$  will be formed through another photo-Fenton oxidation (Eq. (S8)) followed by partial conversion to  $OH \bullet$  *via* the Eq. (S9).<sup>2, 10</sup> Through combining and re-arranging Eqs. (S8), (S9) and (S10), an initial overall reaction of photo-Fenton oxidation in the presence of H<sub>2</sub>O<sub>2</sub>, Fe<sup>3+</sup>/Fe<sup>2+</sup> and visiblelight irradiation also can be expressed by Eq. (S11),

81 Original scheme of photo-Fenton oxidation of  $Fe^{3+}/hydrogen$  peroxide complexes<sup>2</sup>:

83 Conversation between  $OH \bullet$  and  $HO_2 \bullet_{10}$ .

$$^{84} HO_2 \bullet_+ H_2O_2 \rightarrow OH \bullet_+ H_2O_+ O_2 \tag{S9}$$

85 Formation of Fe<sup>3+</sup>/hydrogen peroxide complexes<sup>11</sup>:

$$86 Fe^{3+} + H_2O_2 \to Fe(O_2H)^{2+} + H^+$$
(S10)

87 Overall reaction of photo-Fenton oxidation under visible-light irradiation

$$Fe^{3+} + 2H_2O_2 + hv \rightarrow Fe^{2+} + OH \bullet + H_2O_+O_2 + H^+$$
(S11)

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