Electronic Supplementary Information (ESI)

Density functional theory (DFT) investigation on the structure and photocatalysis properties of double-perovskite Gd$_{1-x}$Ca$_x$BaCo$_2$O$_{5+\delta}$ ($0 \leq x \leq 0.4$)

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Table S1. Lattice parameters of Gd$_{1-x}$Ca$_x$BaCo$_2$O$_{5+\delta}$ ($0 \leq x \leq 0.5$)

| $x$ | a (Å) | b (Å) | c (Å) | Cell volume (Å$^3$) |
|-----|-------|-------|-------|---------------------|
| 0   | 3.91  | 3.87  | 7.54  | 114.12              |
| 0.1 | 3.92  | 3.87  | 7.55  | 114.43              |
| 0.2 | 3.91  | 3.88  | 7.54  | 114.48              |
| 0.3 | 3.92  | 3.86  | 7.55  | 114.50              |
| 0.4 | 3.92  | 3.88  | 7.55  | 114.72              |

Fig. S1. Chemical structural molecular formula of congo red.
**Fig. S2.** Electronic density of states of the simulated GdBaCo$_2$O$_{5+\delta}$. (a) the total density of states, (b) Sum of Co and O density of states, (c) the partial DOS (PDOS) for Co, (d) the partial DOS (PDOS) for O. $(U_{Co}^{3d}, J_{Co}^{3d}) = (5.0)$ eV in all cases. The Fermi energy is set at 0 eV.

**Fig. S3.** XPS spectra for the Gd$_{1-x}$Ca$_x$BaCo$_2$O$_{5+\delta}$ $(0 \leq x \leq 0.4)$ specimens: wide-survey spectrum (the binding energy is from 0 to 1000 eV)
Fig. S4. XPS spectra for Gd$_{0.8}$Ca$_{0.2}$BaCo$_2$O$_{5+δ}$: O-1s core-level
(the binding energy is from 522 to 542 eV).

Fig. S5. Statistical curve of convergence test results: a) cutoff energy; b) $k$ points.