Supporting Information

Boosting up photocatalytic H_2 evolution activity of Fe_2O_3 polymorphs (α-, γ- and β-Fe_2O_3) by fullerene [C_{60}] -modification and dye-sensitization under visible light irradiation

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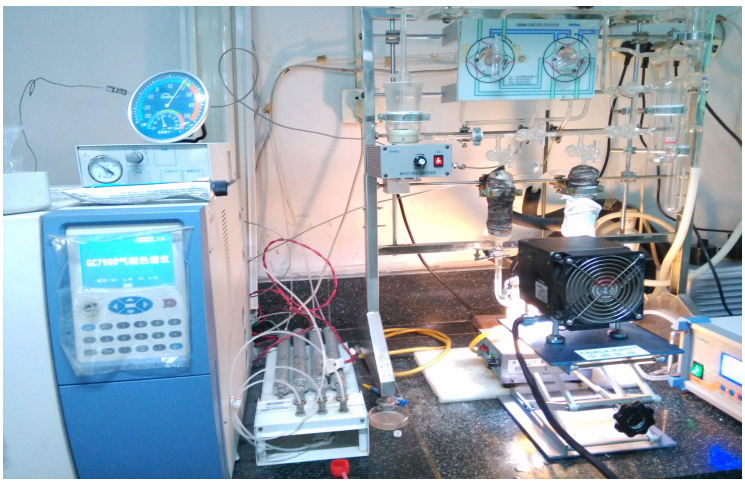

Fig. S1 The photocatalytic H_2 production equipment with the gas chromatography (GC7900, Tian Mei, Shanghai) by nitrogen as a carrier gas.

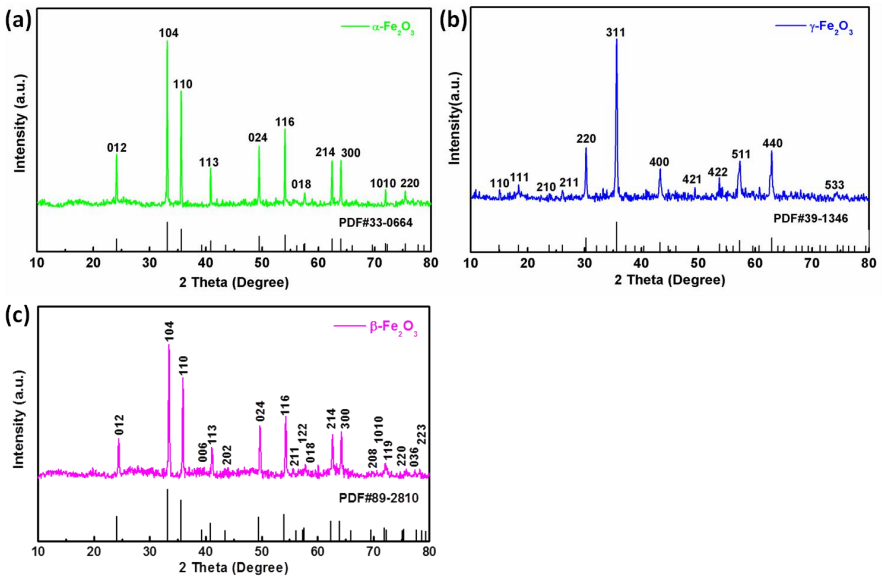

Fig. S2 The X-ray diffraction patterns of α-Fe_2O_3 (a), γ-Fe_2O_3 (b), and β-Fe_2O_3 (c).

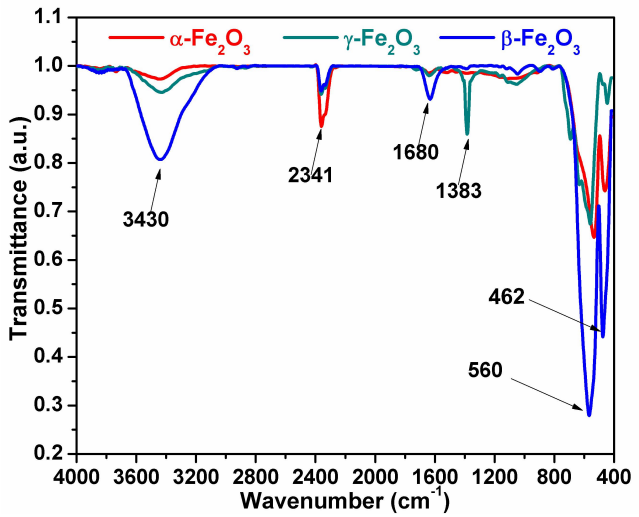

Fig. S3 FTIR spectra of α-Fe_2O_3, γ-Fe_2O_3, and β-Fe_2O_3. The peak at 1383 cm^{-1} can attribute to residual NO_3^- peaks after the heat treatment of γ-Fe_2O_3. The peak at 1680 cm^{-1}, 2341 cm^{-1}, and 3430 cm^{-1} can respectively attribute O-H bending vibration, O=C=O stretching vibration, and O-H stretching.

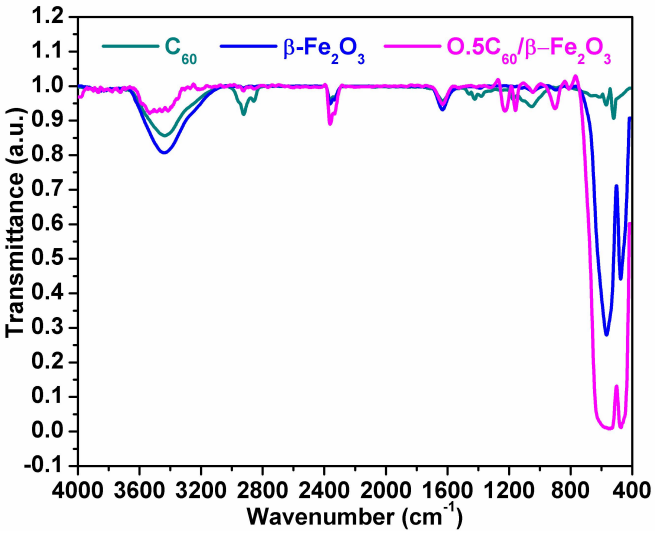

Fig. S4 FTIR spectra of C_{60}, β–Fe_2O_3, and 0.5C_{60}/ β–Fe_2O_3.

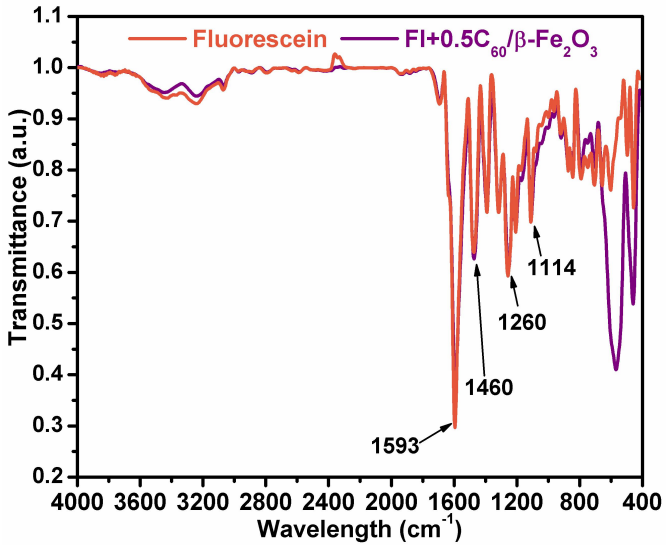

Fig. S5 FTIR spectra of fluorescein and Fl+0.5C_{60}/ β–Fe_2O_3.

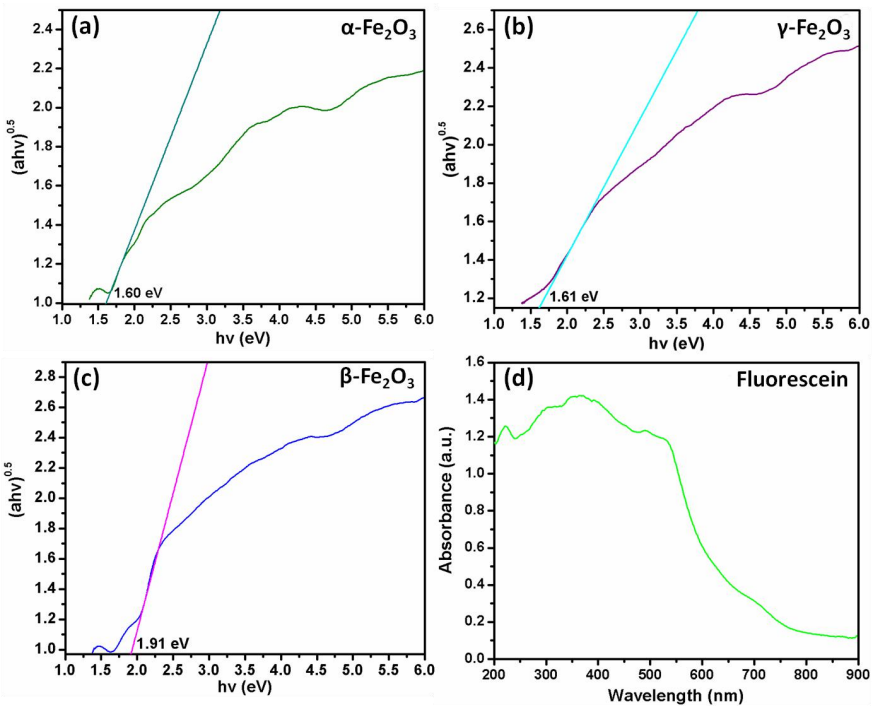

Fig. S6 The $(\alpha hv)^{0.5}$ versus hv curve of the Fe_2O_3 polymorphs ((a) α-Fe_2O_3, (b) γ -Fe_2O_3, and (c) β-Fe_2O_3). The band structure of these samples are calculated by the KubelKa-MunK(KM) method according to the following equation: $\alpha hv=A(hv-Eg)^2$, where α is the absorption coefficient, hv is the photo energy, Eg is the direct band gap, and A is a constant. The UV-vis diffuse reflectance spectra of fluorescein (d).

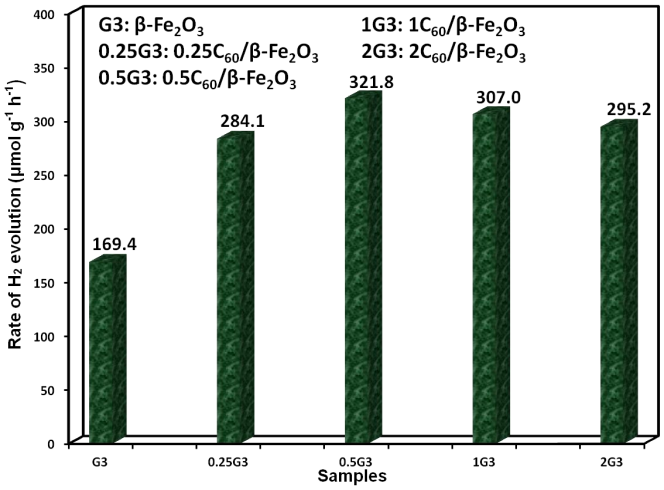

Fig. S7 The H_2 evolution rate of β-Fe_2O_3 composite with different weight amounts of C_{60} cocatalyst.(0.25 wt%, 0.5 wt%, 1 wt%, and 2 wt%)

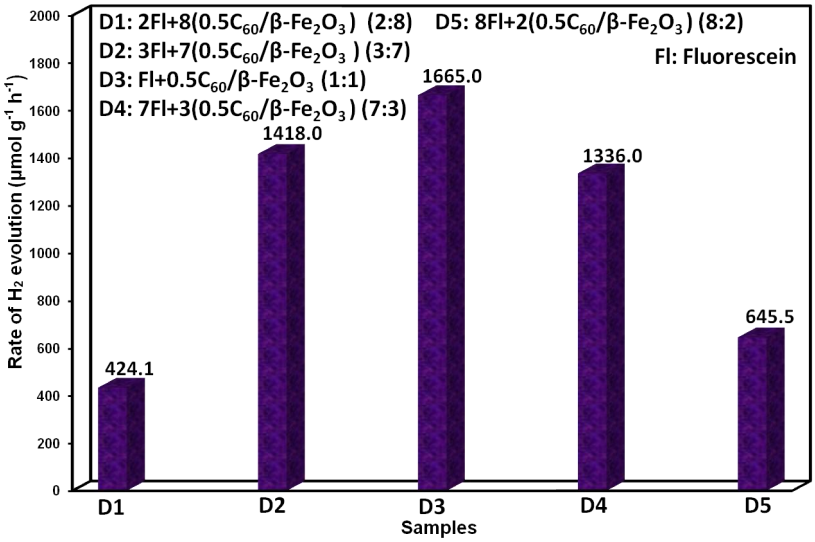

Fig. S8 Fl(Fluorescein)+0.5C_{60}/β-Fe_2O_3 (0.005g) mass ratios of 2:8, 3:7, 1:1, 7:3, 8:2 were respectively tested the rate of photocatalytic H_2 evolution under visible light irradiation.

Table S1. The Crystallite size, physicochemical properties, and band gap using the as-prepared samples.

Sample	Crystallite size(nm)[a]	BET surface area ($m^2\ g^{-1}$)[b]	Pore volume ($cm^3\ g^{-1}$)[b]	Average pore size (nm)[b]	Band gap (eV)[c]
α-Fe_2O_3	47.10	1.5418	—	—	1.60
$1C_{60}/\alpha$-Fe_2O_3	—	2.5311	—	—	—
γ-Fe_2O_3	27.87	4.7966	—	—	1.61
$1C_{60}/\gamma$-Fe_2O_3	—	5.4423	—	—	—
β-Fe_2O_3	42.48	13.6316	0.03114	9.1375	1.91
$0.5C_{60}/\beta$-Fe_2O_3	—	10.7991	0.02273	8.4207	—
$1C_{60}/\beta$-Fe_2O_3	—	9.0692	0.01763	7.7768	—

[a] Average crystallite size was determined from the Scherrer's formula, $D= 0.9\lambda/\beta \cos\theta$.
[b] Specific surface area was calculated from the linear part of BET plot. [C] The band gaps for the composites are estimated by plotting $(\alpha h\nu)^{0.5}$ versus $h\nu$, in which α being the absorption coefficient.

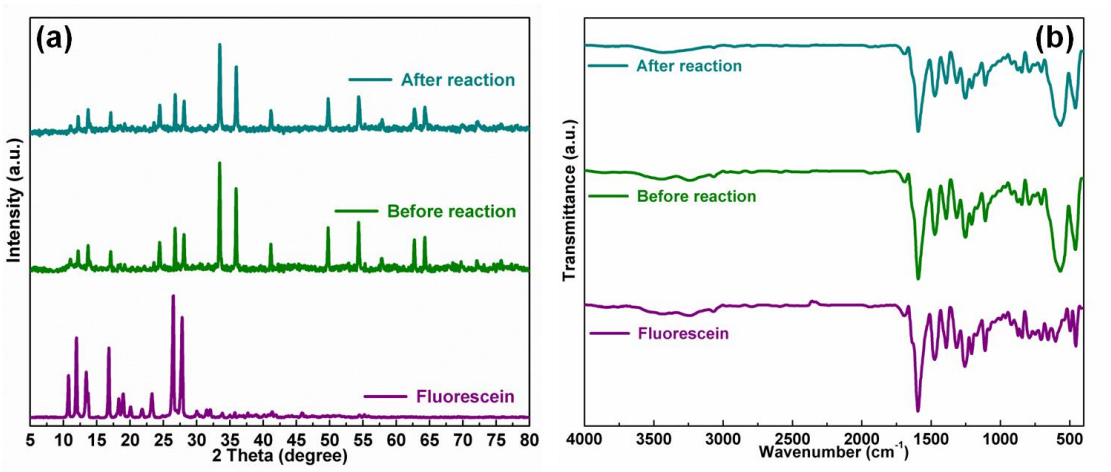

Fig. S9 Powder XRD patterns (a) and FTIR spectra (b) of fluorescein, Fl+0.5C_{60}/β-Fe_2O_3 sample of before, and after reactions.

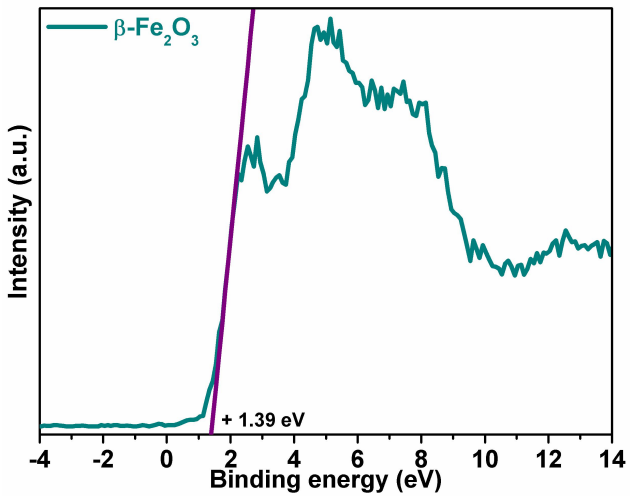

Fig. S10 The VB XPS of β-Fe_2O_3.

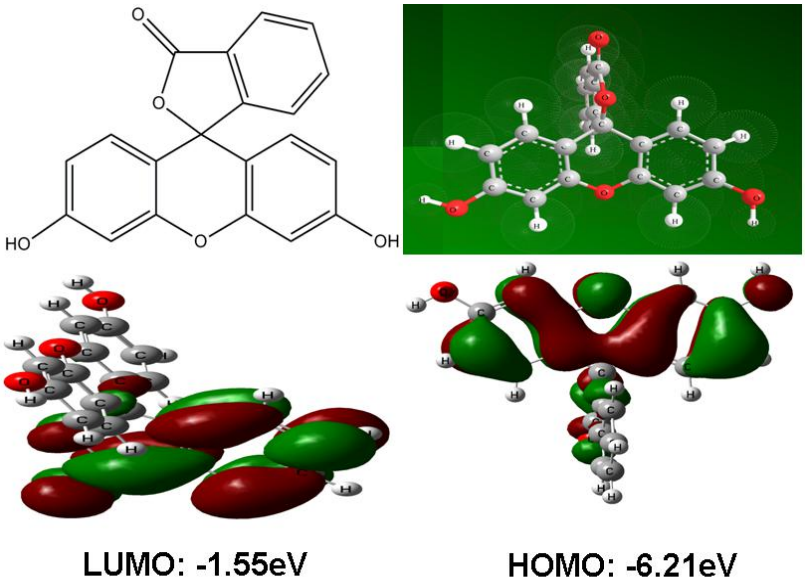

Fig. S11 B3LYP/6-31G calculated molecular orbital amplitude plots and energy levels of HOMO and LUMO of fluorescein.

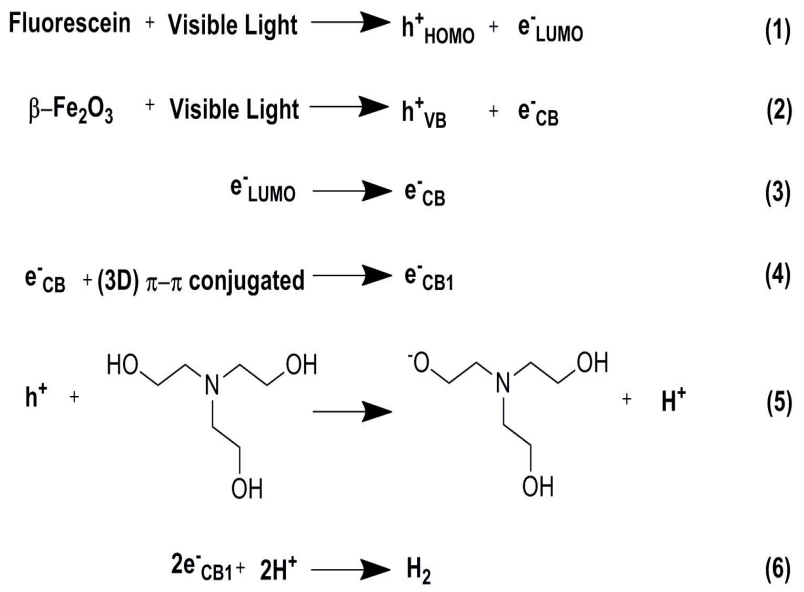

Fig. S12 The specific process of photocatalytic H_2 evolution.

Both fluorescein and β-Fe_2O_3 can be excited by visible light(equation (1), (2)), and then, the electrons injected from fluorescein into the CB of β-Fe_2O_3 (equation (3)). Subsequently, the excited electrons on β-Fe_2O_3 were migrate to the surface of C_{60} by the formation of stronger interaction and interface contact through C_{60} modified

β-Fe_2O_3 with conjugative three-dimensional π system (equation (4)). Most of the holes are consumed by TEOA (equation (5)), promoting the separation of photogenerated electrons and producing more H^+ to participate in the following reaction. Sequentially, two H^+ obtain electrons on the surface of C_{60} to form H_2 (equation (6)).