Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Ideal dopant to increase charge separation efficiency in Hematite photoanodes: Germanium

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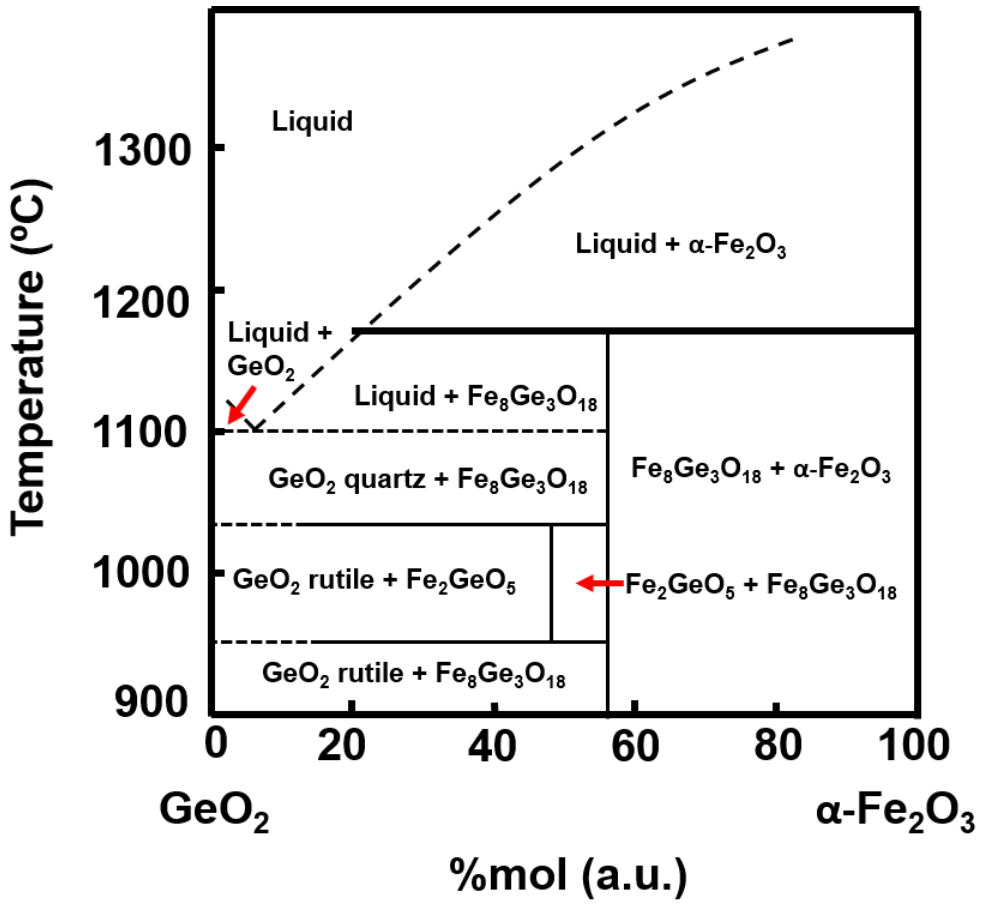

Figure S1- Fe_2O_3 – GeO_2 phase diagram.[1] (Adapted and reproduced with permission. Copyright 1984, Elsevier Ltd.)

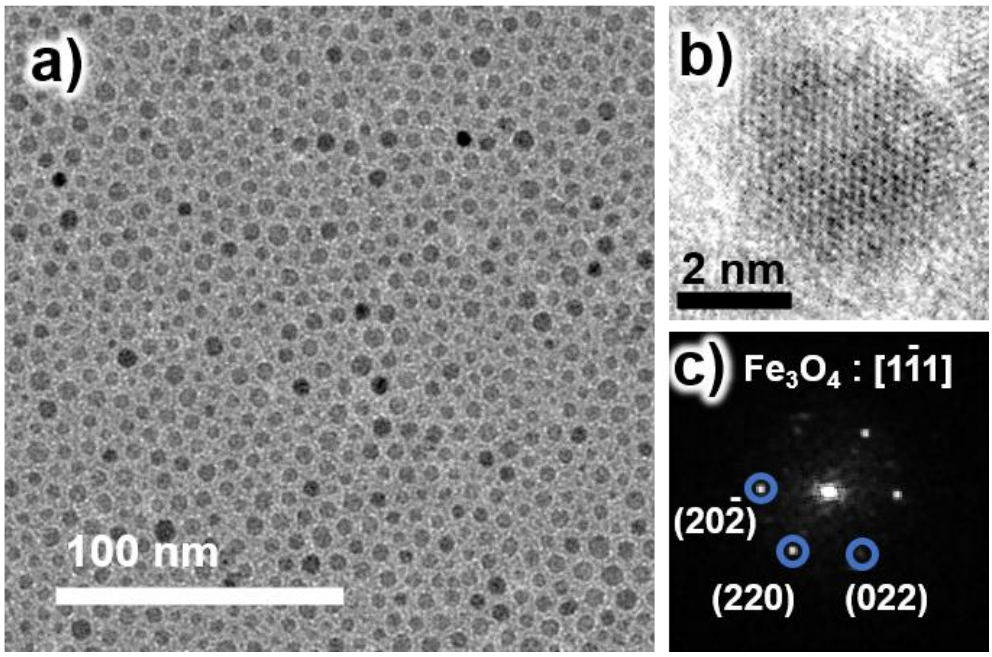

Figure S2– TEM characterization of the pure Fe_3O_4 nanoparticles. a) Low TEM image of the Fe_3O_4 nanoparticles; b) high resolution TEM image of Fe_3O_4 nanoparticle oriented along the [111] zone axis; c) FFT of the Figure S2b.

Table S1 – Experimental results of photocurrent density of different Ge concentrations incorporated in magnetite synthesis.

[Ge] (%)	J_{photo} *(mA cm^{-2})*
3.2	1.8
1.7	2.4
0.8	1.8
0.4	1.3

Table S2 - Experimental results of photocurrent density of different deposited layers by spin coating method.

Layers	J_{photo} *(mA cm^{-2})*
1 Layer	2.4
2 Layers	3.2
3 Layers	3.2
4 Layers	2.7

Table S3 - Experimental results of photocurrent density of different sintering times of FeGe1 films at 850 ºC.

Sintering time (minutes)	J_{photo} *(mA cm^{-2})*
1	0.1
2	1.3
3	1.8
4	3.2
5	2.8
10	2.0
15	2.2
20	1.7

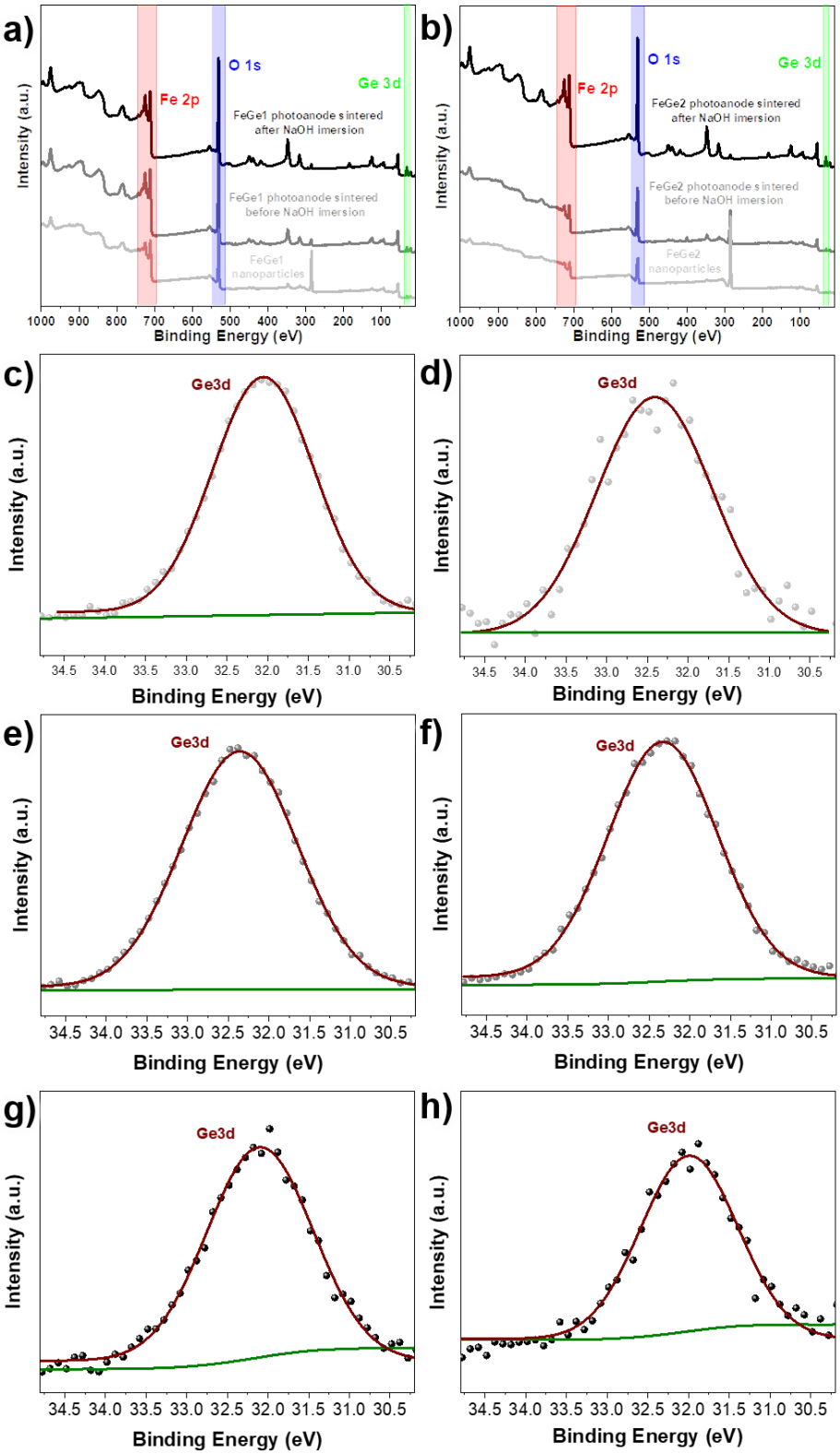

Figure S3– XPS spectra of the Ge–hematite: (a) survey spectrum of FeGe1 nanoparticles, FeGe1 photoanode sintered before and after the contact to NaOH solution; (b) survey spectrum of FeGe2 nanoparticles, FeGe2 photoanode sintered before and after the contact to NaOH solution; High-resolution XPS spectrum of the Ge 3d region: (c) FeGe1 nanoparticles, (d) FeGe2 nanoparticles, (e) FeGe1 photoanode before leaching with NaOH, (f) FeGe2 photoanode before leaching with NaOH, (g) FeGe1 photoanode after leaching with NaOH, and (h) FeGe2 photoanode after leaching with NaOH.

According to the high-resolution XPS spectrum of the Ge 3d, for two films containing germanium, a shift of the spectra after the contact of NaOH solution has been observed. This shift can be related to the environmental chemistry of germanium, as seen in Figure S1, for lower concentrations of GeO_2 in lower temperatures occurs the presence of two phases, GeO_2 rutile, and $Fe_8Ge_3O_{18}$ and according to equation S1, the GeO_2 in the presence of OH^-, it reacts and forms a soluble complex, leaving only the germanium atoms that are inside the crystal lattice of hematite[2].

$$GeO_{2(s)} + OH^- \rightarrow HGeO_3^- \quad \text{(S1)}$$

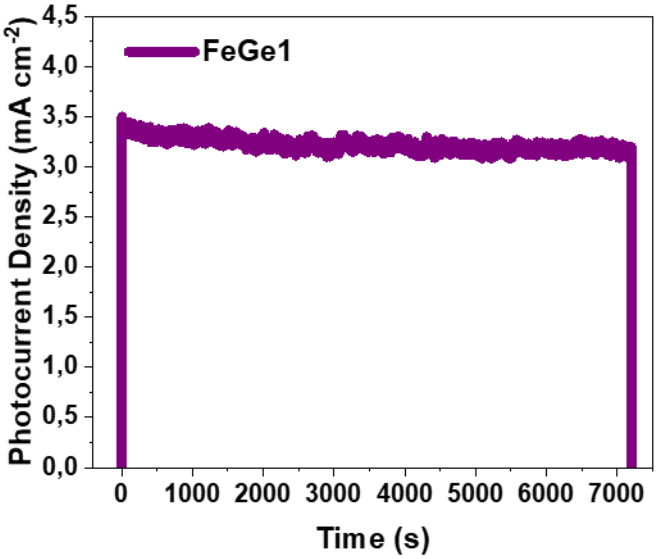

Figure S4 – Chronoamperometry at an applied potential of 1.23 V_{RHE} under illumination (AM 1.5 – 100 mW cm^{-2}) for FeGe1 photoanodes in 1M NaOH electrolyte.

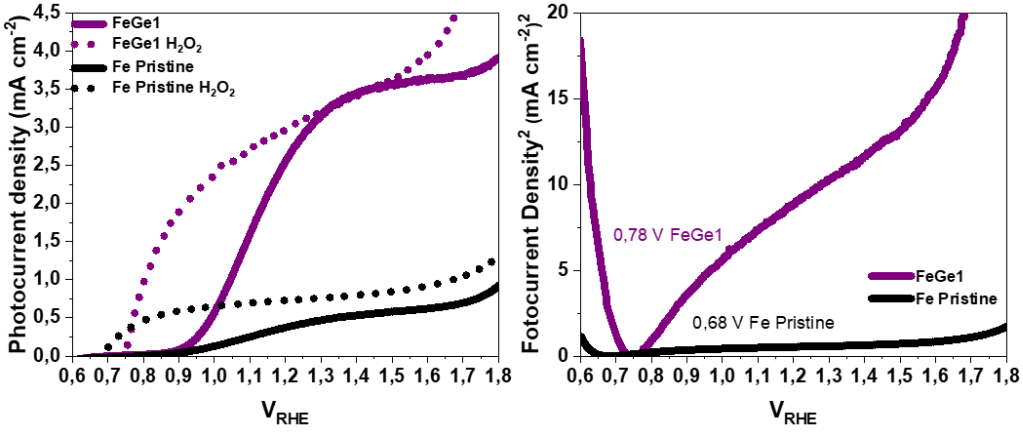

Figure S5 – Photocurrent density x V curves under illumination for the Fe Pristine and FeGe1 films in 1M NaOH electrolyte with and without 0.5M H_2O_2.

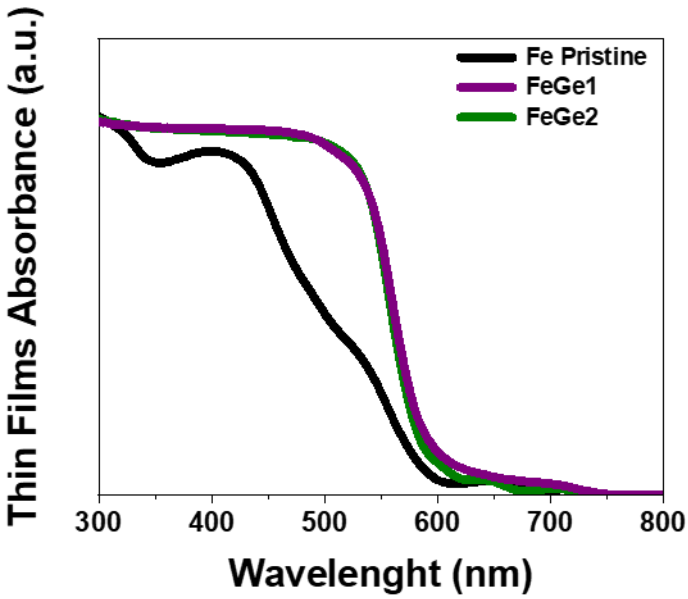

Figure S6 – UV-Vis spectra of Fe Pristine, FeGe1, and FeGe2 films.

The width of depletion layer (W) can be calculated according the following equation:

$$W = \sqrt{\frac{2\varepsilon\varepsilon_0(V-V_{fb})}{qN_d}} \quad \text{(S2)}$$

where ε is the dielectric constant of hematite (80), V is the potential in RHE, V_{fb} is the flat-band potential, q is the elementary charge, and N_d is the donor density.

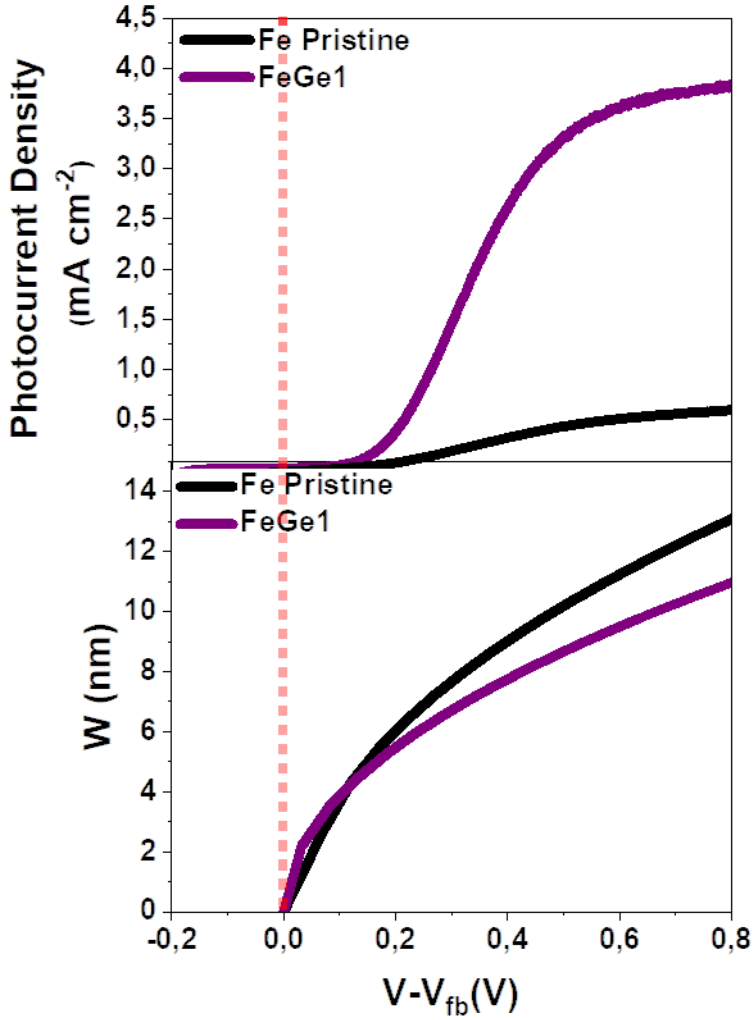

Figure S7 – a) Photocurrent Density, and b) Depletion layer (*W*) as function of (V- V_{fb}).

[1] V. Agafonov, D. Michel, M. Perez, Jorba, M. Fedoroff, *Materials Research Bulletin* **1984**, 19, 233.
[2] O. H. Johnson, *Chemical Reviews* **1952**, 51, 431.