Electronic Supplementary Material (ESI) for Nanoscale Advances.

Tuning the band gap of M-doped titanate nanotubes (M=Fe, Co, Ni, and Cu): An experimental and theoretical study

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Electronic Supplementary Information

Table S1. $H_2Ti_3O_7$ unit cell atomic positions.

Atom symbol	Wyckoff position	x	y	z
H	i	0.4720	0.5	0.4578
H	i	0.5439	0.5	0.1850
Ti	i	0.2333	0.0	0.2236
Ti	i	0.1643	0.0	0.4992
Ti	i	0.1259	0.0	0.8291
O	i	0.1694	0.0	0.0316
O	i	0.1345	0.0	0.3205
O	i	0.0740	0.0	0.5943
O	i	0.0091	0.0	0.8553
O	i	0.3512	0.0	0.1746
O	i	0.2964	0.0	0.4616
O	i	0.2394	0.0	0.7513

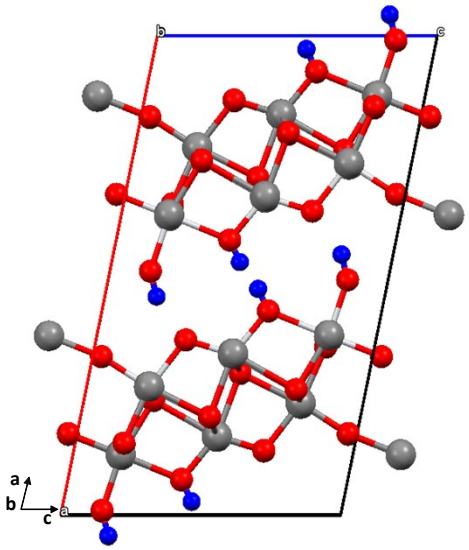

Figure S1. Schematic representation of [010] plane in the crystal unit cell of $H_2Ti_3O_7$

Table S2. Lattice parameters and crystallite size considering (200) plane calculated by Rietveld refinement.

Material	b (Å)	c (Å)	Crystallite size (200) nm
Ti-NT	3.780	9.551	5.13
Cu/Ti-NT	3.756	9.531	2.07
Ni/Ti-NT	3.765	9.555	2.13
Co/Ti-NT	3.783	9.556	2.31
Fe/Ti-NT	3.781	9.554	5.04

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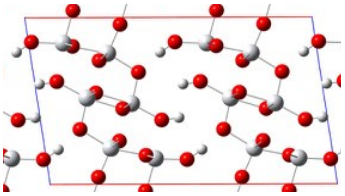
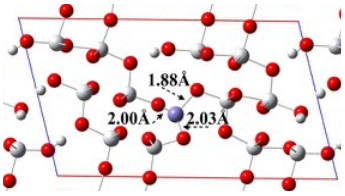
a) Ti-NT



a= 15.992 Å
b= 3.791 Å
c= 9.474 Å
α = 89.996°
β = 98.440°
γ = 89.986°

b) Fe/Ti-NT

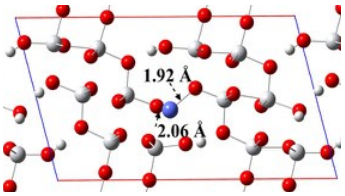
Q_{Fe}=0.59 *e*



a= 16.585 Å
b= 3.805 Å
c= 9.354 Å
α = 90.049°
β = 104.726°
γ = 89.059°

c) Co/Ti-NT

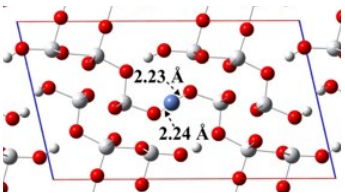
Q_{Co}=0.42 *e*



a= 16.559 Å
b= 3.744 Å
c= 9.375 Å
α = 89.944°
β = 102.932°
γ = 89.887°

d) Ni/Ti-NT

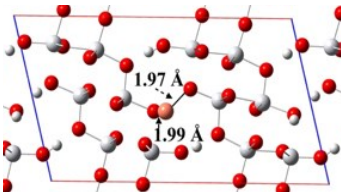
Q_{Ni}= 0.56 *e*



a= 16.595 Å
b= 3.799 Å
c= 9.245 Å
α = 90.125°
β = 104.840°
γ = 98.185°

e) Cu/Ti-NT

Q_{Cu}= 0.62 *e*



a= 16.526 Å
b= 3.812 Å
c= 9.343 Å
α = 90.634°
β = 104.271°
γ = 96.622°

Figure S2. Optimized molecular models with the corresponding relaxed lattice parameters, and atomic charge transfer using the Hirshfeld scheme (Q_M) of the systems under study: a) pristine Ti-NT, b) Fe/Ti-NT, c) Co/Ti-NT, d) Ni/Ti-NT, and e) Cu/Ti-NT. Red, white, gray, purple, blue, indigo and orange spheres indicate O, H, Ti, Fe, Co, Ni and Cu atoms, respectively.

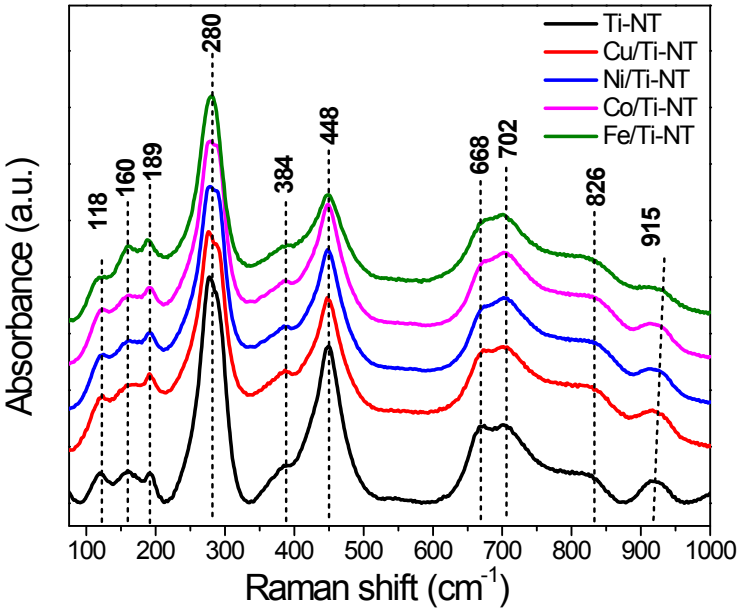


Figure S3. Raman spectra of all as-prepared Ti-NT.

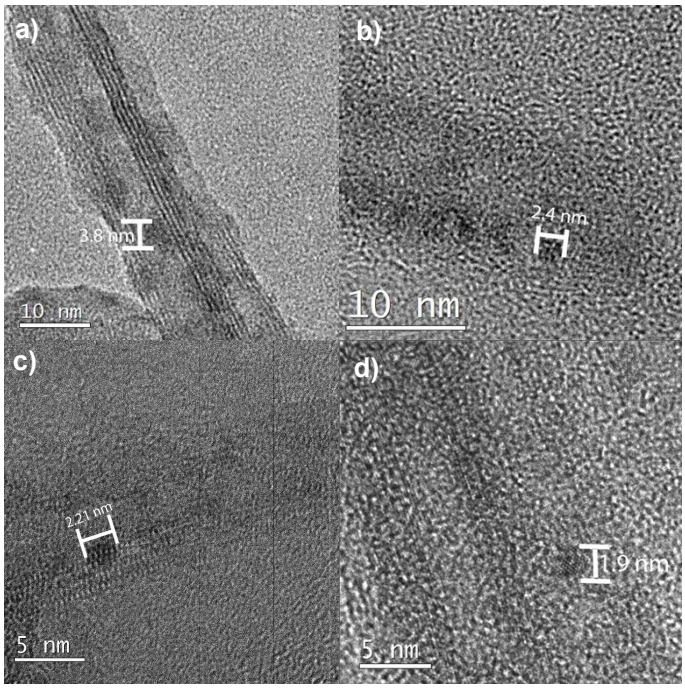


Figure S4. TEM images of a) Cu/Ti-NT, b) Ni/Ti-NT, c) Co/Ti-NT and, d) Fe/Ti-NT.

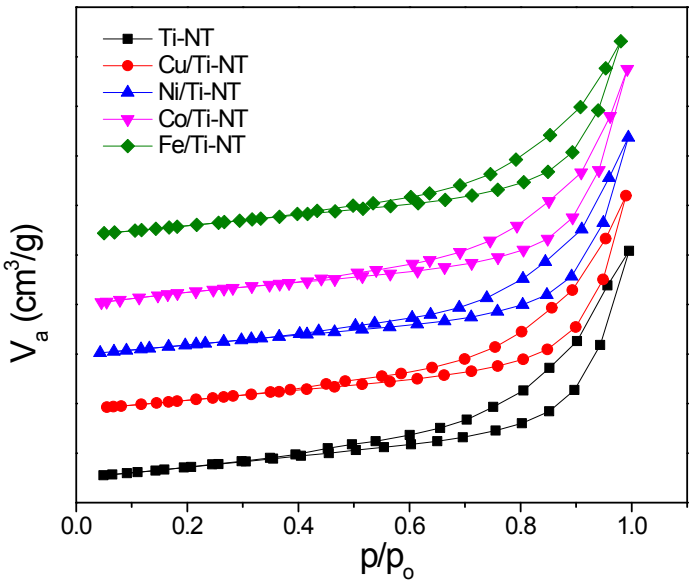


Figure S5. N_2 adsorption-desorption isotherms of all as-prepared Ti-NT.

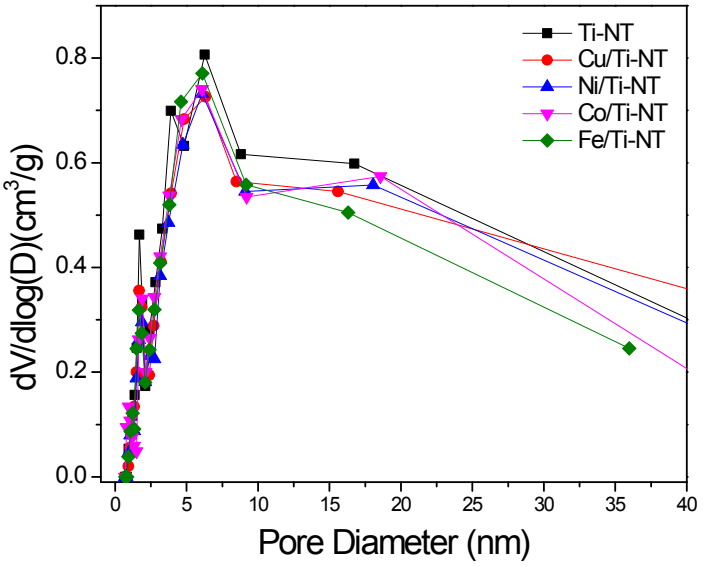


Figure S6. BJH pore size distribution of all as-prepared Ti-NT.

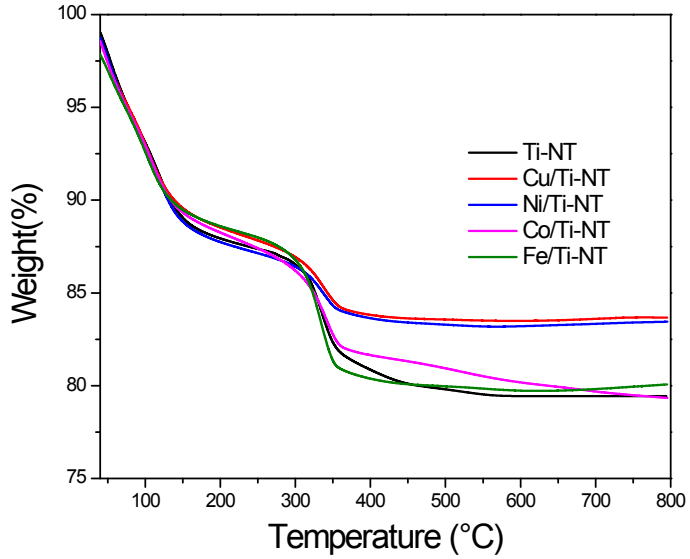


Figure S7. Thermogravimetric decomposition curves of all as-prepared Ti-NT.

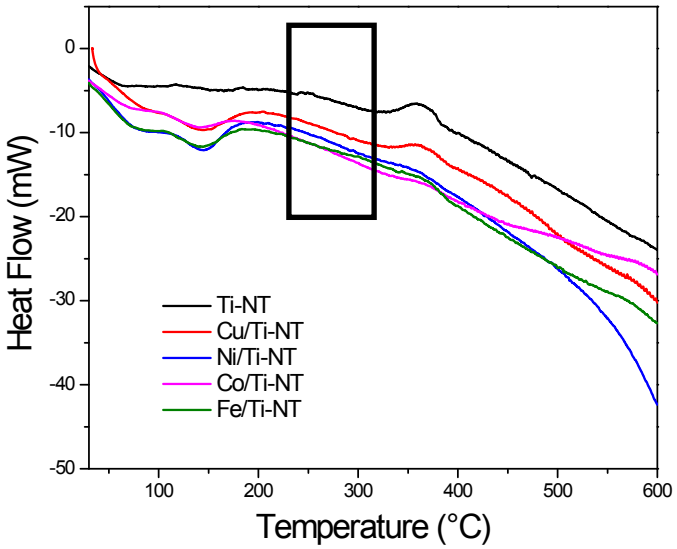


Figure S8. Differential Scanning Calorimetry of all as-prepared Ti-NT.

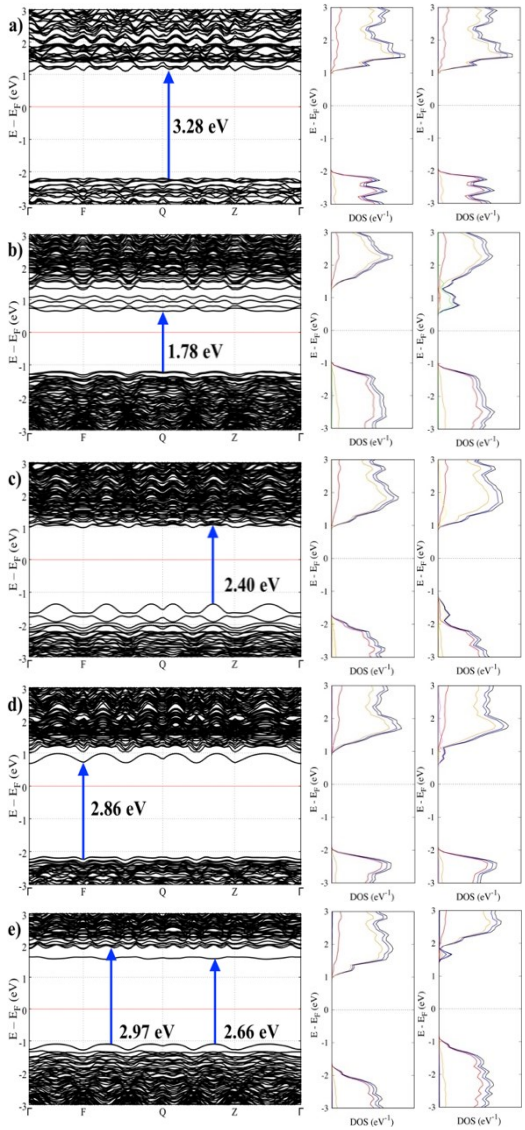


Figure S9. Band structures and partial density states (first column correspond to spin up and first column correspond to spin down) calculated using DFT+U for all complexes under study: (a) Pristine system (Ti-NT), (b) doped with Fe atom, (c) doped with Co atom, (d) doped with Ni atom and (e) doped with Cu atom.

Redox potential

The band edges characteristics of a semiconductor were calculated establishing a reference vacuum potential (length direction z = 15 Å) which simulates an electrostatic potential on the surface. Therefore, valence band maximum (E_{VBM}) and conduction band minimum (E_{CBM}) were also estimated to assess potential photocatalysis reactions. These parameters were calculated following the next equations:

$$E_{VBM} = -\Phi + 0.5\ E_{gap} \quad (1)$$

$$E_{CBM} = -\Phi - 0.5\ E_{gap} \quad (2)$$

$$E_{CBM/VBM}^{'} = -E_{CBM/VBM} - (pH=7) - 4.5 \quad (3)$$

Where E_{gap} is the band gap, and $E_{CBM/VBM}^{'}$ is the potential versus the normal hydrogen electrode (pH=7). All calculations were carried out in SIESTA code.[1]

[1] M.J. Ford, SIESTA: Properties and Applications, Computational Methods for Large Systems. (2011) 367–395

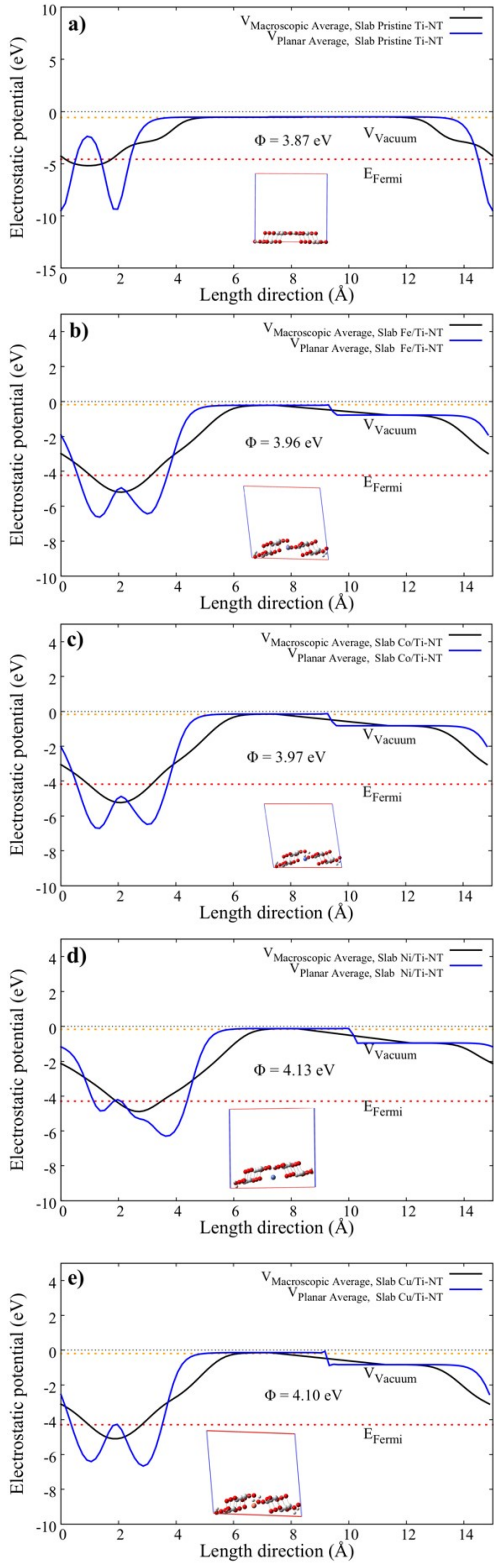


Figure S10. Interactions of a simulated electrostatic potential with the surfaces: (a) Ti-NT, (b)Fe/Ti-NT, (c) Co/Ti-NT, (d) Ni/Ti-TN and (e) Cu/Ti-TN. In order to obtain the work function (Φ), we make in the cell switch axes ("**b**"↔"**c**"), to simulate electrostatic potential in vacuum region (V_{VAC}).