Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

for

Complex dielectric transformation of UV-*vis* diffused reflectance spectra for estimating optical band-gap energies and materials classification

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Methods

Synthesis of materials

Synthesis of MIL-53(Fe)

MIL-53 (Fe) was synthesized following the recipe of Férey et al. with partial modification using microwave technique. The synthesis temperature and time was optimised at 120°C for 15 minutes. The bulk synthesis of MIL-53(Fe) was carried out in Monowave 300 (Anton Paar) microwave reactor. After synthesis, the resulting orange-yellow suspension was centrifuged and dried in hot air oven at 150°C for 12 hours. The final synthesized product (orange-yellow powder) was stored in an air tight desiccator for post treatment.

All new variants of MIL-53 (Fe) were synthesized by modifying the reaction stoichiometry of Férey et al., using microwave technique [Monowave 300, Anton Parr].

Synthesis of Li-MIL-53(Fe)

The reaction mixture consisting of anhydrous Iron (III) chloride (2.433 g; 15 mmol), Lithium acetate di hydrate (0.2433 g; 2.381 mmol) and Benzene1,4 dicarboxylic acid (2.492 g; 15 mmol) in N, N-dimethyl formamide (150 mL) was poured into a conical flask. The mixture was stirred for approximately 4 hours and then filled into a 30 ml reaction vial and sealed tightly via silicone septa and was loaded into the microwave reactor. The synthesis temperature and duration was set at 120°C for 15 minutes.

After synthesis, the resulting reddish-orange suspension was centrifuged and dried in hot air oven at 150 °C for 12 hours and was stored in an air tight desiccator for post treatment.

Synthesis of Na-MIL-53(Fe)

The reaction mixture consisting of anhydrous Iron (III) chloride (2.433 g; 15 mmol), Sodium acetate (0.2433 g; 2.966 mmol) and Benzene-1, 4 dicarboxylic acid (2.492 g; 15 mmol) in N, N-dimethyl formamide (150 mL) was poured into a conical flask. The mixture was stirred for approximately 4 hours and then filled into a 30 ml reaction vial and sealed tightly via silicone septa and was loaded into the microwave reactor. The synthesis temperature and duration was set at 120°C for 15 minutes.

After synthesis, the resulting dull red suspension was centrifuged and dried in hot air oven at 150 °C for 12 hours and was stored in an air tight desiccator for post treatment.

Synthesis of K-MIL-53(Fe)

The reaction mixture consisting of anhydrous Iron (III) chloride (2.433 g; 15 mmol), Potassium acetate (0.2433 g; 2.479mmol) and benzene-1, 4 dicarboxylic acid (2.492 g; 15 mmol) in N, N-dimethyl formamide (150 mL) was poured into a conical flask. The mixture was stirred for approximately 4 hours and then filled into a 30 ml reaction vial and sealed tightly via silicone septa and was loaded into the microwave reactor. The synthesis temperature and duration was set at 120^{o}C for 15 minutes.

After synthesis, the resulting red suspension was centrifuged and dried in hot air oven at 150 ^{o}C for 12 hours and was stored in an air tight desiccator for post treatment.

Synthesis of S-MIL-53(Fe)

The reaction mixture consisting of anhydrous Iron (III) chloride (2.433 g; 15 mmol), Sodium sulphide (0.2433 g; 2.479mmol) and benzene-1, 4 dicarboxylic acid (2.492 g; 15 mmol) in N, N-dimethyl formamide (150 mL) was poured into a conical flask. The mixture was stirred for approximately 4 hours and then filled into a 30 ml reaction vial and sealed tightly via silicone septa and was loaded into the microwave reactor. The synthesis temperature and duration was set at 120^{o}C for 15 minutes.

After synthesis, the resulting red suspension was centrifuged and dried in hot air oven at 150 ^{o}C for 12 hours and was stored in an air tight desiccator for post treatment.

Synthesis of MIL-125(Ti)

A stoichiometric mixture of anhydrous Titanium iso propoxide (0.6 ml), 1, 4 benzene dicarboxylic acid (0.3323 gm) and 20 ml of DMF/Methanol was taken in a glass vial. Microwave was irradiation for 40 min and temperature of 120 ^{o}C. Resulting gel like precipitate was re suspended in DMF and was centrifuged at 3000 rpm. The supernatant was discarded, the crystals obtained was dried in hot air oven at 175 ^{o}C to remove excess solvent.

Synthesis of NH_2-MIL-125(Ti)

A stoichiometric mixture of anhydrous Titanium iso propoxide (0.6 ml), 2-amino-benzene dicarboxylic acid (0.3323 gm) and 20 ml of DMF/Methanol was taken in a glass vial. Microwave was irradiation for 40 min and temperature of 120 ^{o}C. Resulting gel like precipitate was re suspended in DMF and was centrifuged at 3000 rpm. The supernatant was discarded, the crystals obtained was dried in hot air oven at 100^{o}C to remove excess solvent.

Synthesis of α-Fe_2O_3 powder

α-Fe_2O_3 was synthesized following the reaction stoichiometry of Chaudhari et al. Solutions of Iron (III) chloride (1 M) and Urea (1 M) were mixed thoroughly and heated at 90 ºC for 120 minutes. The resulting product contained basic iron oxide and ammonium chloride. This product was centrifuged and dried in hot air oven. Ammonium chloride was a sublimate and hence the resulting product on dying was found to be basic iron oxide. The product was sintered at 240 ºC for 150 minutes to obtain α-Fe_2O_3. The reddish-brown powder (α-Fe_2O_3) was stored in vacuum desiccator.

Analytical methods

Dielectrics Model (Mathematical workout)

Followed by conversion of extinction coefficient $k(\upsilon)$of the material and refractive index $n(\upsilon)$ spectra into complex dielectric functions of frequency/wavelength ($\varepsilon_{complex}$).

$$\varepsilon_{complex} = \varepsilon_{real} - i\varepsilon_{imaginary}$$

$$\varepsilon_{real} = n(\upsilon)^2 - k(\upsilon)^2$$

$$\varepsilon_{imaginary} = 2n(\upsilon)k(\upsilon)$$

The complex transformation of dielectric functions was transformed into polar coordination system thereby enabling spatial independence. Thus reducing Penn model into a two parameter model with spatial independence (hence an infinite inhomogeneous medium).

$$\phi = \tan^{-1}\frac{\varepsilon_{imaginary}}{\varepsilon_{real}} = \tan^{-1}\frac{2n(\upsilon)k(\upsilon)}{n(\upsilon)^2 - k(\upsilon)^2}$$

On plotting the dispersion –dissipation plot of dielectric materials was treated with the energy of the photon incident on the material reflects the optical characteristics of the sample.

$$\phi = \tan^{-1}\frac{\varepsilon_{imaginary}}{\varepsilon_{real}} = \tan^{-1}\frac{2n(\upsilon)k(\upsilon)}{(n(\upsilon) - k(\upsilon))(n(\upsilon) + k(\upsilon))}$$

And at

$$\phi \to -\frac{\pi}{2}, n(\upsilon) - k(\upsilon) \to 0$$

The following absorption coefficient (α) is directly proportional to the extinction coefficient $k(\upsilon)$ is then modelled with the Tauc equation as:

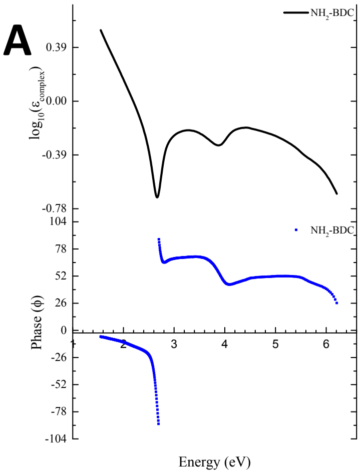
$$n(\upsilon) = A_o\sqrt{1 - \frac{E_g}{E}}$$

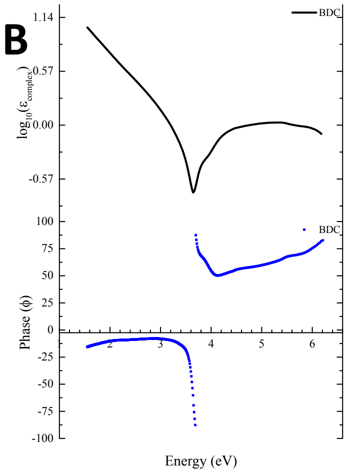
$$\frac{1}{E} = -\frac{1}{A_o^2 E_g} n(\upsilon)^2 + \frac{1}{E_g}$$

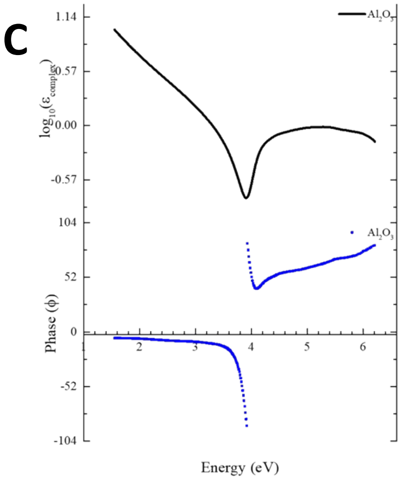
$$\frac{1}{E} = -\mu_0 n(\upsilon)^2 + \frac{1}{E_g}$$

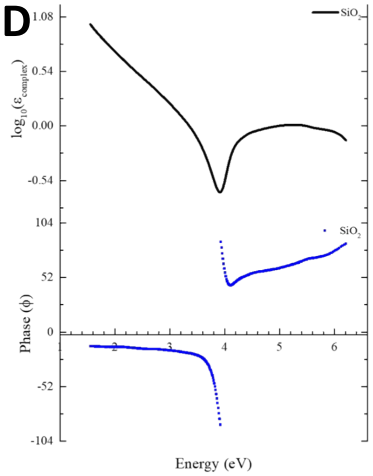
Results and Discussion

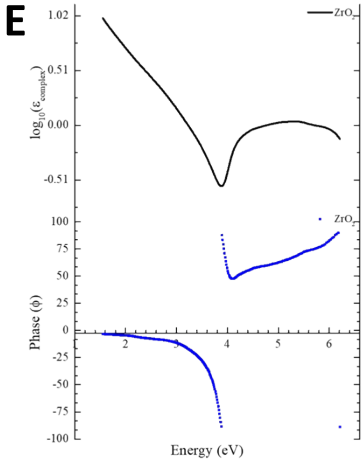
1. Dielectrics Model (dispersion –dissipation Vs energy plot)

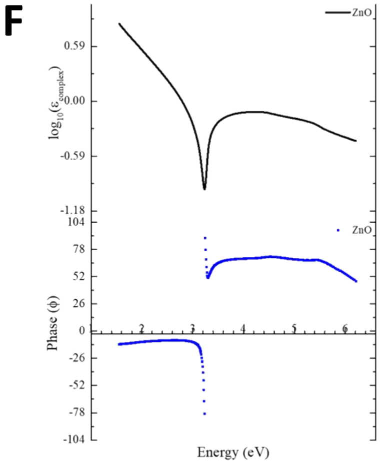


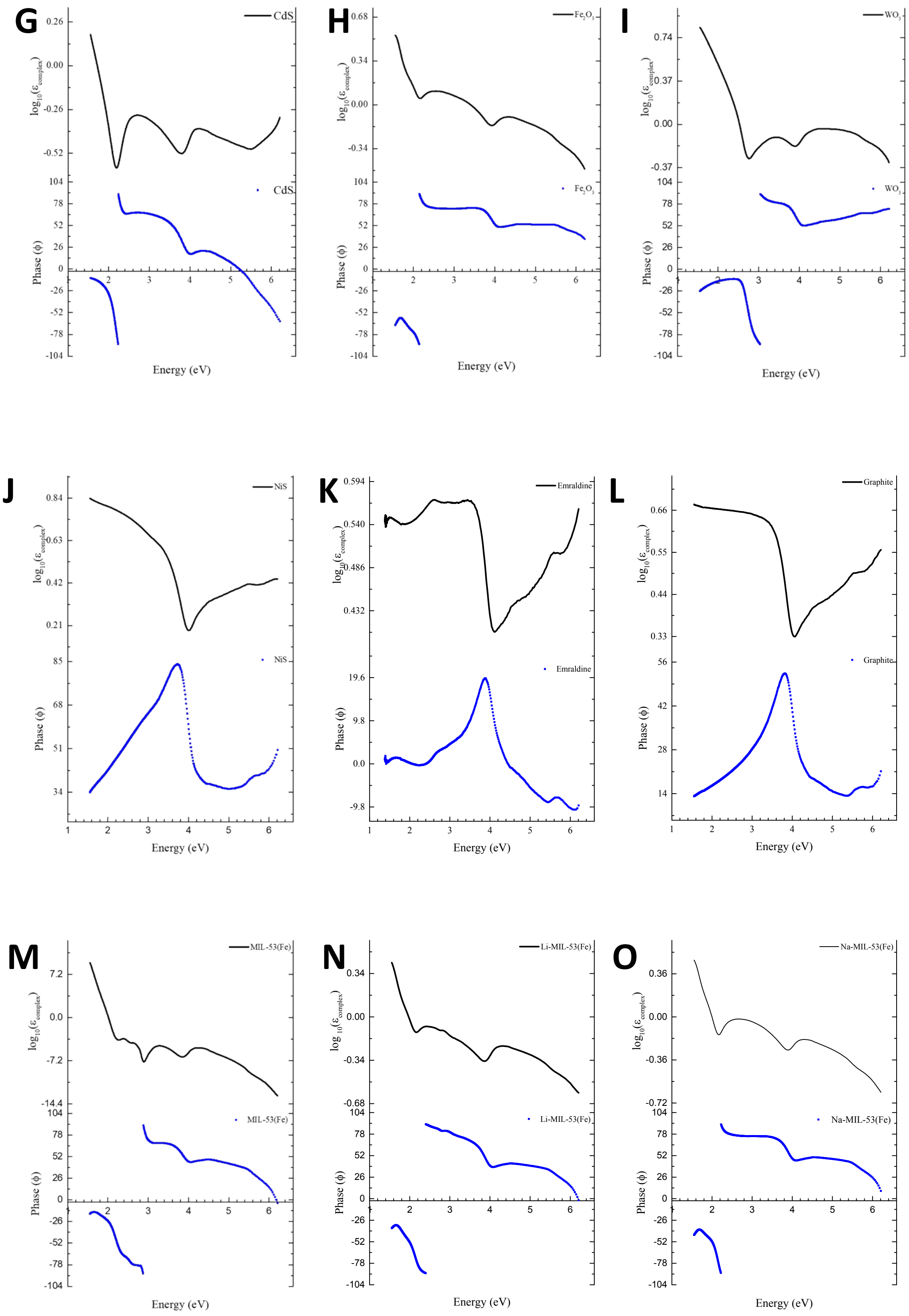




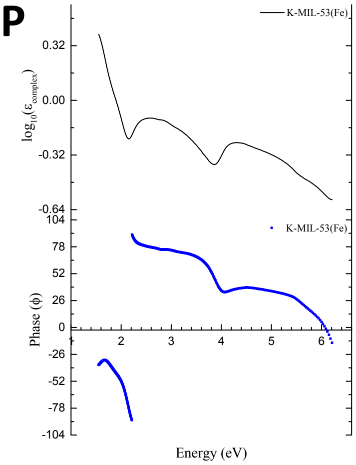




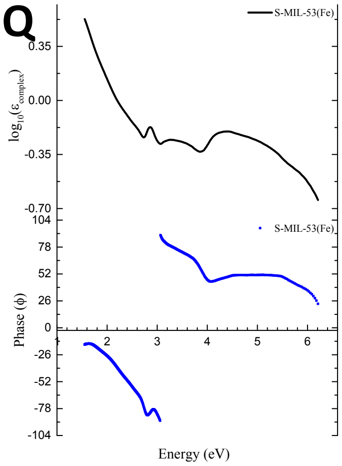



G
CdS
log10(εcomplex)
0.26
0.00
-0.26
-0.52
Phase (ϕ)
104
78
52
26
0
-26
-52
-78
-104
Energy (eV)
H
Fe2O3
0.68
0.34
0.00
-0.34
I
WO3
0.74
0.37
0.00
-0.37
J
NiS
0.84
0.63
0.42
0.21
85
68
51
34
K
Emraldine
0.594
0.540
0.486
0.432
19.6
9.8
0.0
-9.8
L
Graphite
0.66
0.55
0.44
0.33
56
42
28
14
M
MIL-53(Fe)
7.2
0.0
-7.2
-14.4
N
Li-MIL-53(Fe)
0.34
0.00
-0.34
-0.68
O
Na-MIL-53(Fe)
0.36
0.00
-0.36
-0.72
1
2
3
4
5
6

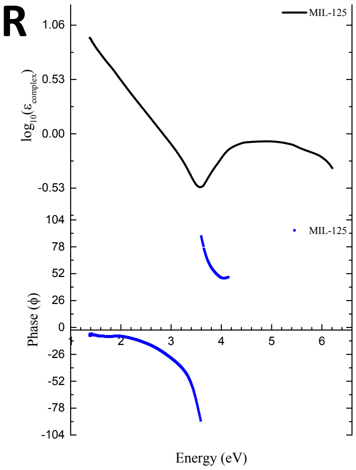
P


K-MIL-53(Fe)
0.32
0.00
-0.32
-0.64
$\log_{10}(\varepsilon_{complex})$
K-MIL-53(Fe)
104
78
52
26
0
-26
-52
-78
-104
Phase (ϕ)
1
2
3
4
5
6
Energy (eV)

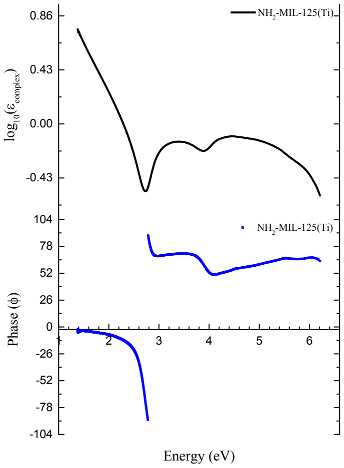
Q


S-MIL-53(Fe)
0.35
0.00
-0.35
-0.70
$\log_{10}(\varepsilon_{complex})$
S-MIL-53(Fe)
104
78
52
26
0
-26
-52
-78
-104
Phase (ϕ)
1
2
3
4
5
6
Energy (eV)

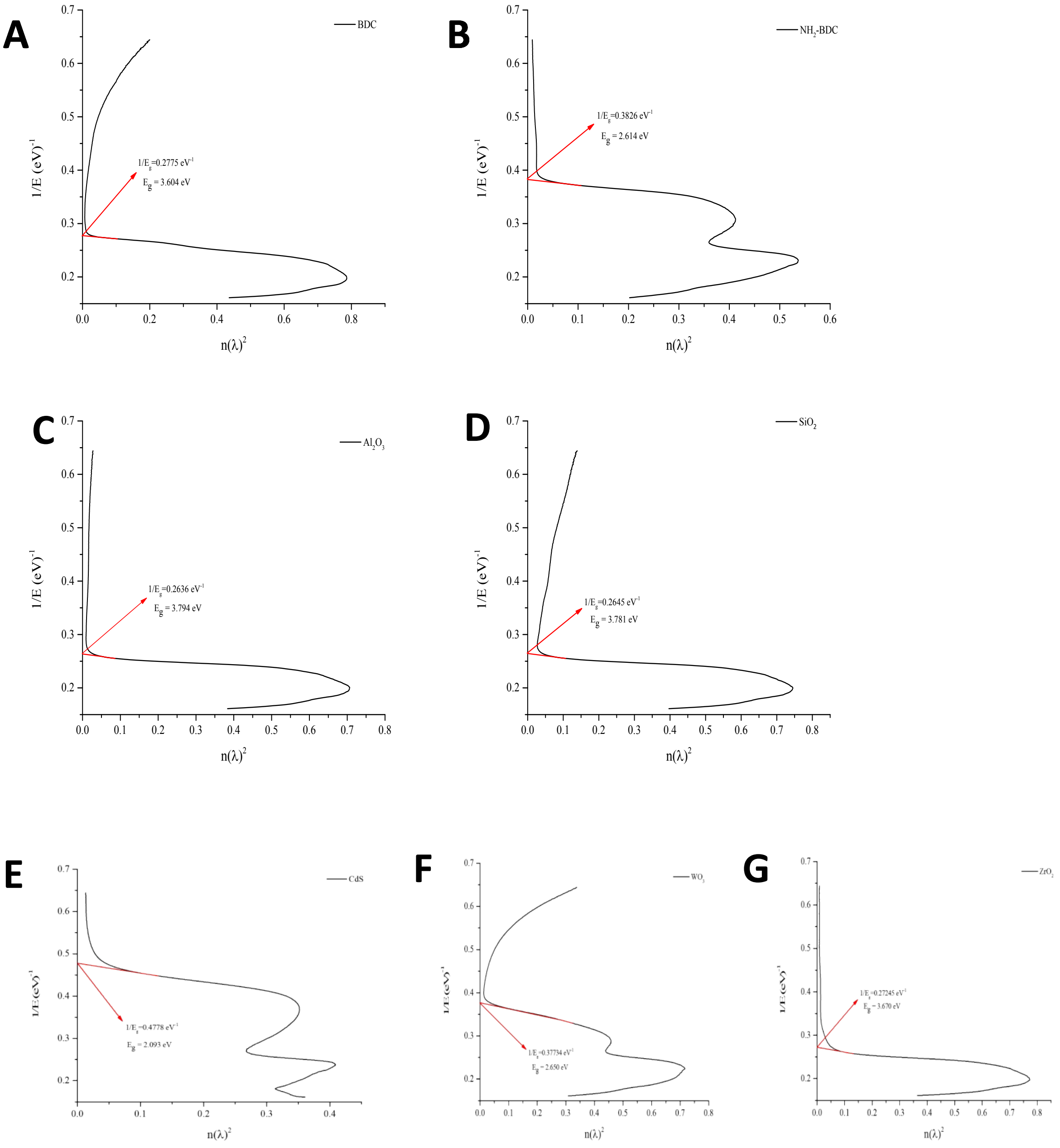
R


MIL-125
1.06
0.53
0.00
-0.53
$\log_{10}(\varepsilon_{complex})$
MIL-125
104
78
52
26
0
-26
-52
-78
-104
Phase (ϕ)
1
2
3
4
5
6
Energy (eV)

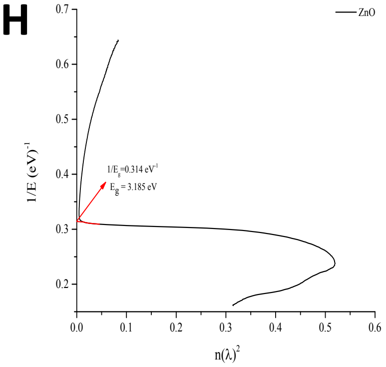
S


NH_2-MIL-125(Ti)
0.86
0.43
0.00
-0.43
$\log_{10}(\varepsilon_{complex})$
NH_2-MIL-125(Ti)
104
78
52
26
0
-26
-52
-78
-104
Phase (ϕ)
1
2
3
4
5
6
Energy (eV)

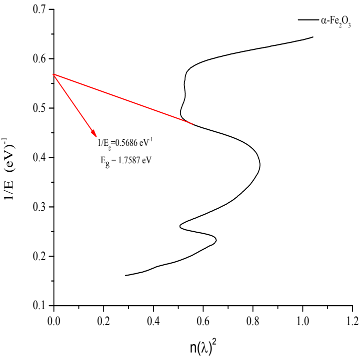
2. n(υ)² Vs 1/E plot for various materials



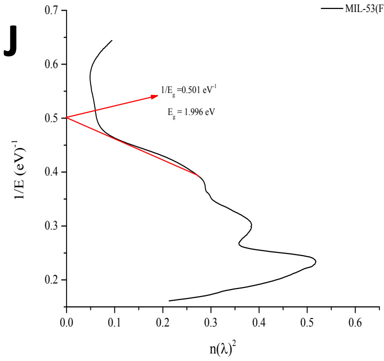
H


ZnO
1/E_g=0.314 eV^-1
E_g = 3.185 eV
1/E (eV)^-1
n(λ)^2
0.7
0.6
0.5
0.4
0.3
0.2
0.0
0.1
0.2
0.3
0.4
0.5
0.6

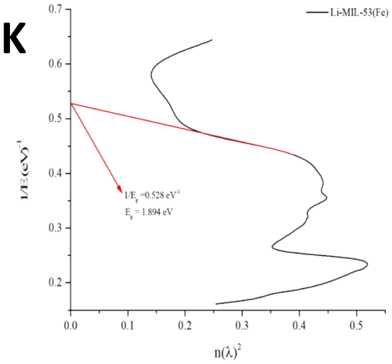
I


α-Fe2O3
1/E_g=0.5686 eV^-1
E_g = 1.7587 eV
1/E (eV)^-1
n(λ)^2
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.2
0.4
0.6
0.8
1.0
1.2

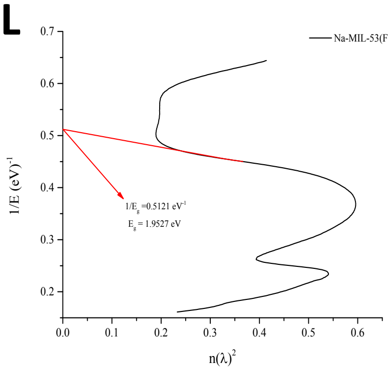
J


MIL-53(Fe)
1/E_g=0.501 eV^-1
E_g = 1.996 eV
1/E (eV)^-1
n(λ)^2
0.7
0.6
0.5
0.4
0.3
0.2
0.0
0.1
0.2
0.3
0.4
0.5
0.6

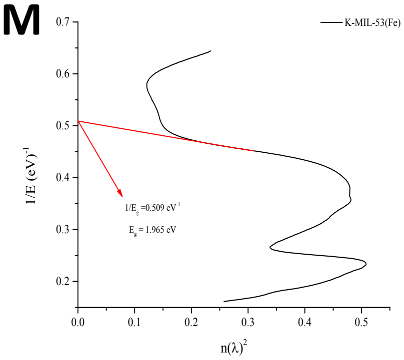
K

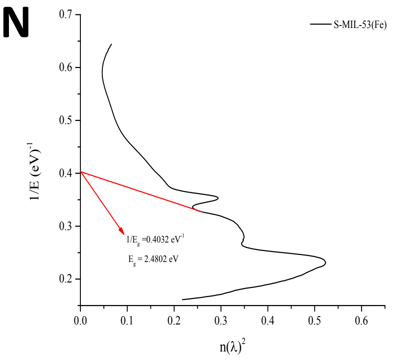

Li-MIL-53(Fe)
1/E_g=0.528 eV^-1
E_g = 1.894 eV
1/E (eV)^-1
n(λ)^2
0.7
0.6
0.5
0.4
0.3
0.2
0.0
0.1
0.2
0.3
0.4
0.5

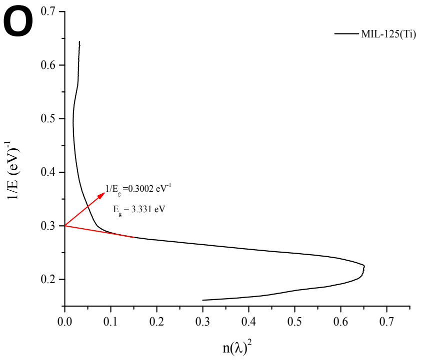
L


Na-MIL-53(Fe)
1/E_g=0.5121 eV^-1
E_g = 1.9527 eV
1/E (eV)^-1
n(λ)^2
0.7
0.6
0.5
0.4
0.3
0.2
0.0
0.1
0.2
0.3
0.4
0.5
0.6

M


K-MIL-53(Fe)
1/E_g=0.509 eV^-1
E_g = 1.965 eV
1/E (eV)^-1
n(λ)^2
0.7
0.6
0.5
0.4
0.3
0.2
0.0
0.1
0.2
0.3
0.4
0.5





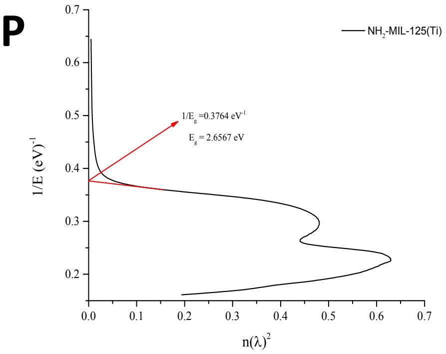


Table S1: Comparison of different electrochemical and theoretical (computational) methods with UV-vis DRS implementing K-M method and Dielectrics model

Materials	**Band Gap (Experimental Methods) (eV)**			**Theoretical Calc. (eV)**
	UV-Vis (KM method)	**UV-Vis (Dielectric method)**	**USP/CV/EIS /XPS/HR-ED**	**DFT/Semi/Empirical methods**
	(The present work)			
Alumina (α-Al_2O_3)	***3.74***	***3.79***	**3.2-4.3**[1–3]	**4.0*-6.3# (GGA)**[1]
Magnesia (MgO)	***3.87***	***3.83***		**4.5(LDA)** [4]
Silica (SiO_2)	***3.77***	***3.78***	**3.55**[5]	**4.5-5.8 (LDA)**[6,7]
Terephthalic acid (BDC)	***3.57***	***3.6***		**4.357 (B3LYP)**[8]
2-amino-terephthalic acid (NH_2-BDC)	***2.56***	***2.61***		**3.273 (B3LYP)**[9]
Titanium dioxide (TiO_2)	***3.1***	***3.26***	**3.1-3.6**[10–14]	**3.12-3.46 (DFT+U)**[11,15]
Zirconia (ZrO_2)	***3.73***	***3.67***	**3.56**[16–18]	**3.5-4.0 (DFT)**[16,17,19]
Haematite (Fe_2O_3)	***1.7***	***1.76***	**1.8-2.2**[20,21]	**2.05-2.1 (LDA)**[22,23]
Tungsten oxide (WO_3)	***2.47***	***2.65***	**2.6-3.2**[24–27]	**2.73-3.78(HF-DFT)**[24,25,27]
Zinc oxide (ZnO)	***3.18***	***3.19***	**3.26-3.35**[28,29]	**3.41(DFT)**[15,30–32]
Cadmium sulphide (CdS)	***1.95***	***2.09***	**2.4-2.96**[33–35]	**2.0(DFT)**[4,31,32]

(USP, XPS ultraviolet/X-ray electron spectroscopy; Cyclic voltammetry (CV); Electrochemical Impendence Spectroscopy (EIS); High Resolution Electron Energy diffraction (HR-ED)

(GGA: Generalized Gradient approximation; LDA: Linear Density Approximation)

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