Electronic Supplementary Information

Defect Engineering in 1D Ti-W Alloys Nanotube Arrays and Their Correlated Photoelectrochemical Performance

Ali A. Abdelhafiz[a], Mohamed A. Ganzoury[b], Ahmad W. Amer[b], Azza A. Faiad[b]‡, Ahmed M. Khalifa[b]‡, Siham Y. AlQaradawi[c], Mostafa A. El-Sayed[d], Faisal M. Alamgir[a], Nageh K. Allam[b]*

[a] School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, Georgia 30332, United States

[b] Energy Materials Laboratory (EML), School of Sciences and Engineering, The American University in Cairo, New Cairo 11835, Egypt

[c] Department of Chemistry and Earth Sciences, College of Arts and Sciences, Qatar University, Doha 2713, Qatar

[d] Laser Dynamics Laboratory, School of Chemistry and Biochemistry, 901 Atlantic Drive, Atlanta, Georgia 30332, United States

Figure. S1 shows inefficient anodization for NH$_4$F concentration of 0.15g for 4 hours, and onset of efficient nanotube anodization at NH$_4$F concentration of 0.25 g for 1hour.
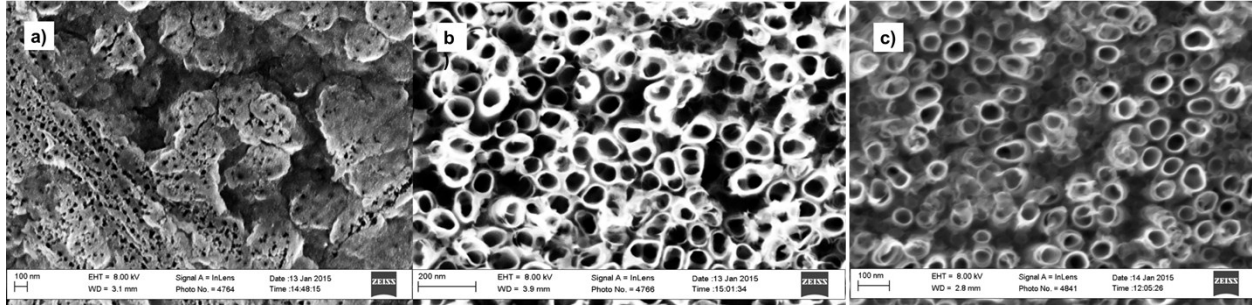

Figure S1. SEM of nanotubes arrays synthesized by electrochemical anodization: a.) at 0.15 g of NH$_4$F for 4 hours b.) at 0.25 g of NH$_4$F for 1 hour and c.) at 0.35 g of NH$_4$F for 1 hour.

Figure.S2 shows the Mott-Shottcky plots for all studied samples under illumination. All samples showed positive slopes, which are characteristic of n-type semiconductors. The donor densities (N$_D$) were calculated from the slope of the curves, at frequencies where the capacitance is non-dependent on the frequency, using the following relation:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{e\varepsilon\varepsilon_r A N_D}\right)\left(V_{Applied} - V_{FB} - \frac{KT}{e}\right) \qquad (s1)$$

Where A, e, ε, ε_r, V_{FB} and C_{sc} are the electrode surface area (taken as the apparent surface area of the cell,) the electron charge, the dielectric constant, the vacuum permittivity, the flat band potential and the space charge capacitance, respectively.

It is important to note here that It is widely-accepted that Mott-Schottky analysis can give high degrees of error in defining the flat-band potentials for nanostructured samples for a number of well-known reasons, such as ignoring Helmholtz capacitance[1], very high surface state capacitance[2], nonuniform charge distribution[3], the presence of the dielectric barrier layer underneath the nanotubes[2], or the inaccuracy of measuring the surface area included in the relation due to surface roughness[4]. For these reasons, and others, flat-band potentials were not extracted from the presented plots. Donor densities, on the other hand, were presented for comparative purposes only.
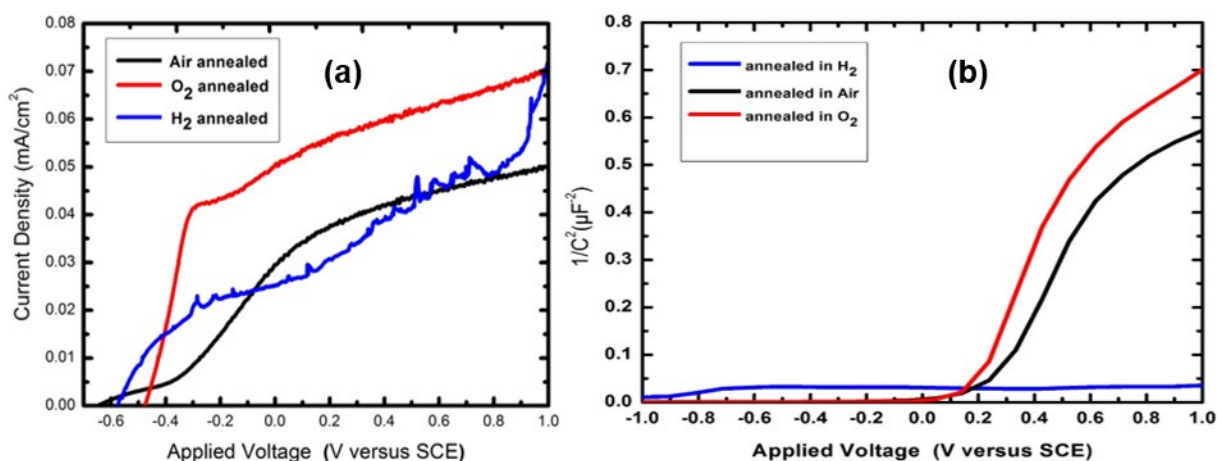
Figure s2. (a) I-V characteristics and (b) Mott-Schottky plot plots for all studied samples under illumination

Electron lifetime was calculated using the J-t transients from the following relation:

$$-\frac{t}{\tau} = ln\left[\frac{I - I_f}{I_i - I_f}\right] \qquad (s2)$$

where I is the photoanodic current, I_i , I_f are the current at the initial and final steady state, respectively. τ is the electron lifetime constant , which is calculated at (I, t) that makes the right hand side of equation (s2) equal (-1) [5].

References:

1. F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, P. Bogdanoff and A. Zaban, *J. Electrochem. Soc.*, 2003, **150**, E293-E298.
2. H. Ge, H. Tian, Y. Zhou, S. Wu, D. Liu, X. Fu, X.-M. Song, X. Shi, X Wang and N. Li, *ACS Appl. Mater. Interfaces*, 2014, **6**, 2401–2406.
3. A. G. Sanchez, M. Katunar, W. Schreiner, G. Duffo, S. Cere and D. J. Schriffin, *Acta Chim. Slov.*, 2014, **61**, 316–327.
4. I. Cesar, K. Sivula, A. Kay, R. Zboril and M. Grätzel, *J. Phys. Chem. C*, 2009, **113**, 772–782.

5. M. Radecka, M. Wierzbicka, S. Komornicki and M. Rekas, Phys. B, 2004, 348, 160–168.