

Electron Work Function – An Effective Parameter for *In-situ* Reflection of Electron Activities in Various Processes

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Electron work function (EWF) is the minimum energy required to move electrons at the Fermi level from inside a conducting material to its surface with zero kinetic energy [1,2]. This fundamental parameter largely reflects electron activities and is directly related to chemical, physical, and mechanical properties of materials [2-8]. Recent studies have shown that EWF can be used as a sensitive parameter to characterize many surface properties of biomaterials. As an example [9], the affinity of medical implant materials for bacteria can be characterized by EWF. Figure 1A illustrates the adhesive forces of nanocrystalline stainless steel samples with different grain sizes. As shown, as the grain size decreases, the adhesion decreases due to the fact that the passive film becomes more protective, blocking the interaction between the steel and surrounding media. Such a trend is consistent with the variations in electron work function, as shown in Figure 1B. A higher surface EWF corresponds to a higher degree of reluctance for interacting with the environment. The decrease in the number of bacteria bound to the surfaces with an increase in EWF provides direct evidence.

Another example is the use of EWF in analyzing the photocatalytic activity of TiO₂ nanotubes (TNTs). TNTs have been used for different applications such as DNA biosensor [10], detection of bacteria [11] and toxic compounds [12]. TNTs have also been explored for immobilizing proteins and enzymes in biomaterial and biosensor applications [13,14]. Many of the application are related to the photocatalytic activity of TNTs, which is usually evaluated by variations in photocurrent and absorbance under illumination. However, the photocurrent response or absorbance does not provide sufficient information for full understanding of the photocatalytic behaviour of TNTs.

Recent studies have demonstrated that the electron work function is a very sensitive parameter for in-situ analysis of photocatalytic activity of TNTs [15]. Figure 2 illustrates variations in the work function of TiO₂ nanotubes with different tube lengths (corresponding to the anodization duration; the larger the anodization duration, the longer the nanotubes). Figures 2A, C, E and G illustrate variations in EWF of the TNTs illuminated successively by lights having wavelengths of 670 nm, 650 nm, 550 nm, 450 nm, 420 nm, 400 nm and 390 nm. As shown, EWF of the TNTs was relatively stable when they were illuminated by lights of 670 nm and 620 nm, indicating that the photonic energies of the lights are not sufficient to excite electrons in the TNTs. While when the wavelength of incident light is in the absorption range of TNTs lower than 550 nm, electrons can be excited accompanied with an apparent decrease in EWF. The observed decrease in EWF with a decrease in the wavelength of incident light is an indication of photon-induced electron-hole separation, which requires photons with their energy above a certain level.

The TNTs were also illuminated successively by the lights with different wavelengths in a reversed order. Corresponding variations in EWF are illustrated in Figures 2B, D, F and H. As shown, after illuminated by 390 nm-light, TNTs-2 h did not respond much to lights with longer wavelengths, indicating that almost no $e^- - h^+$ recombination occurred in the TNTs under illumination with lower photon energies. Or in other words, continuous illumination with lower photon energies could sustain the state of electrons that were initially excited by photons

with higher energies, or suppress $e^- - h^+$ recombination. However, for TNTs anodized for 4 h, their EWF raised up under illumination in a range of longer wavelengths (550-670 nm) after 390 nm illumination. This suggests that $e^- - h^+$ recombination occurred, which could not be suppressed by illumination with the lower photon energies in this wavelength range. The recombined $e^- - h^+$ pairs could be re-separated under the illumination with the lower-energy photons, but the electrons could only be excited to relatively lower energy states that correspond to higher EWF. This range of longer wavelengths, which could not suppress $e^- - h^+$ recombination, extended to 420-670 nm for TNTs-12 h and TNTs-16 h. It appears that longer TNTs do not only provide more recombination centers as suggested [16,17], but also have larger driving forces for $e^- - h^+$ recombination.

The above observations demonstrate that EWF is related to the photocatalytic process involving electron-hole separation and

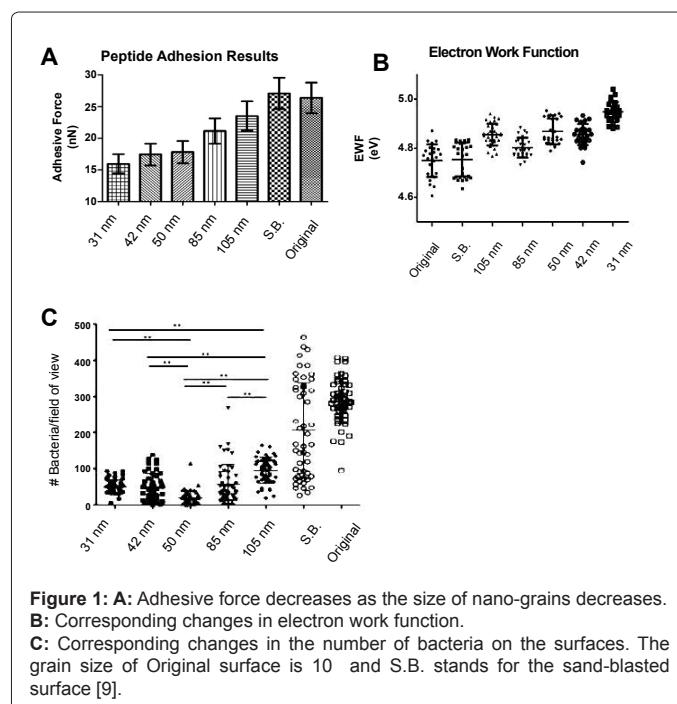


Figure 1: A: Adhesive force decreases as the size of nano-grains decreases. B: Corresponding changes in electron work function. C: Corresponding changes in the number of bacteria on the surfaces. The grain size of Original surface is 10 and S.B. stands for the sand-blasted surface [9].

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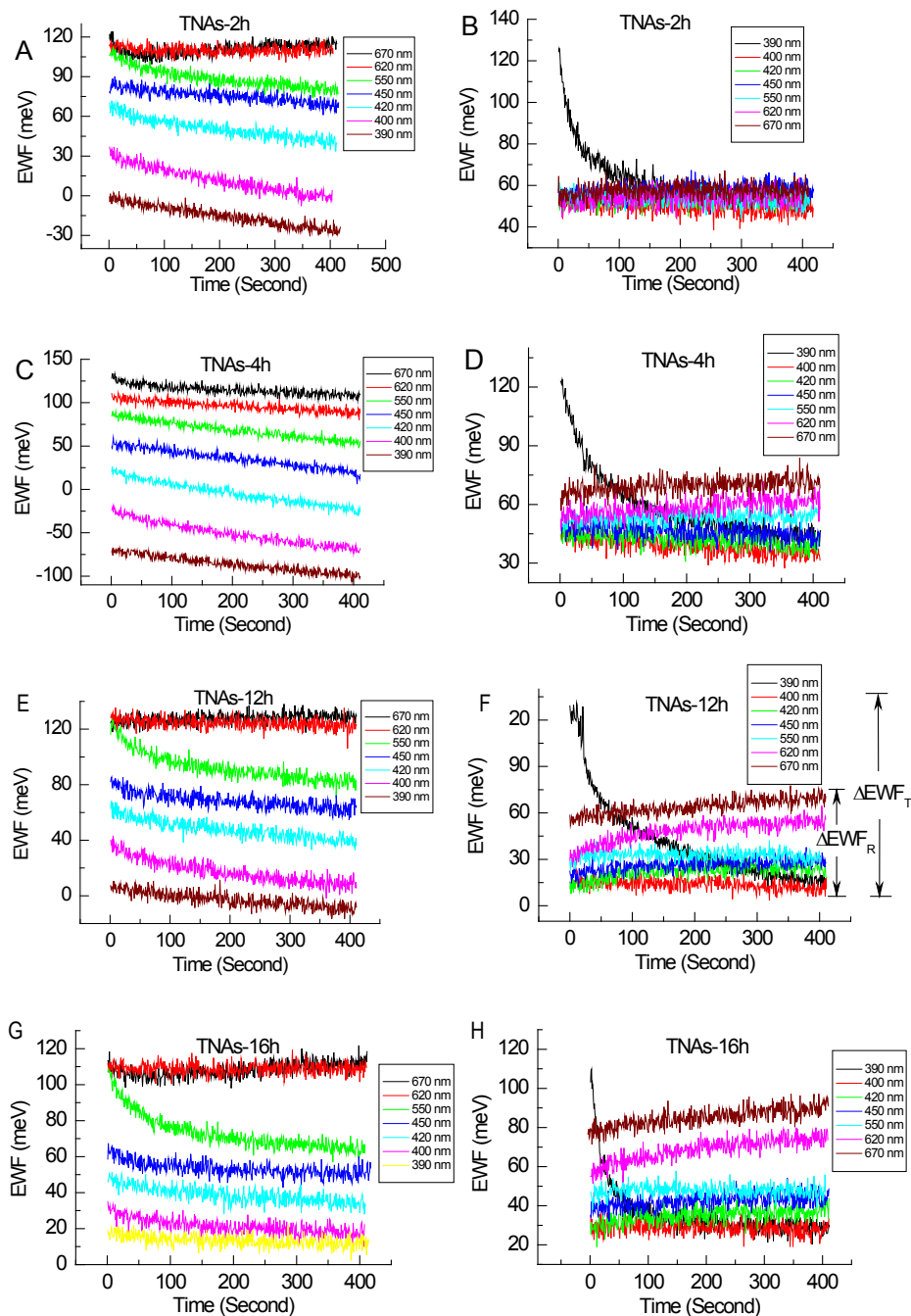


Figure 2: The effect of illumination with different wavelengths from 390 nm to 670 nm (A, C, E, G) and from 670 nm to 390 nm (B, D, F, H), on changes in EWF of TNAs-2 h, TNAs-12 h, and TNAs-16 h.

Anodization potential=20 V; Annealing temperature=45°C [15].

recombination. The study clearly shows that EWF is an effective parameter reflecting the photocatalytic behavior of TiO₂ nanotubes, and helps to get an insight into the semiconductors' photo-activities with different views that may not be achieved using traditional techniques, such as diffuse reflection spectrum and photo-electrochemical measurement.

In conclusion, EWF has been demonstrated to be a sensitive parameter with great potential for a variety of sensor applications.

References

1. Marder MP (2000) Condensed matter physics. John Wiley and Sons Inc. New York, USA.
2. Subrahmanyam A, Kumar CS (2010) Kelvin probe for surface engineering: Fundamentals and design. CRC, London, UK.
3. Kabra D, Song MH, Wenger B, Friend RH, Snaith HJ (2008) High efficiency composite metal oxide-polymer electroluminescent devices: A morphological and material based investigation. Adv Mater 20: 3447-3452.

4. Yang L, Luo S, Li Y, Xiao Y, Kang O, et al. (2010) High Efficient photocatalytic degradation of p-nitrophenol on a unique Cu₂O/TiO₂ p-n heterojunction network catalyst. Environ Sci Technol 44: 7641-7646.
5. Grover R, Carthy BM, Zhao Y, Jabbour GE, Sarid D, et al. (2004) Kelvin probe force microscopy as a tool for characterizing chemical sensors. Appl Phys Lett 85: 3926-3928.
6. Moutinho HR, Dhere RG, Jiang CS, Yan YF, Albin DS, et al. (2010) Investigation of potential and electric field profiles in cross sections of CdTe/CdS solar cells using scanning Kelvin probe microscopy. J Appl Phys 108: 074503.
7. Hua GM, Li DY (2011) Generic relation between the electron work function and Young's modulus of metals. Appl Phys Lett 99: 041907.
8. Li DY (2002) Kelvin probing technique: A promising method for the determination of the yield strain of a solid under different types of stress. Physica Status Solidi A 191: 427-434.
9. Yu B, Lesiuk A, Davis E, Irvin RT, Li DY (2010) Surface nanocrystallization for Bacterial control. Langmuir 26: 10930-10934.
10. Song M, Zhang R, Wang X (2006) Nano-titanium dioxide enhanced biosensing of the interaction of dacarbazine with DNA and DNA bases. Mater Lett 60: 2143-2147.
11. He F, Liu S (2004) Detection of *P. aeruginosa* using nano-structured electrode-separated piezoelectric DNA biosensor. Talanta 62: 271- 277.
12. Khan R, Dhayal M (2008) Nanocrystalline bioactive TiO₂-chitosan impedimetric immuosensor for ochratoxin-A. Electrochem Commun 10: 492-495.
13. Macak JM, Tsuchiya H, Taveira L, Ghicov A, Schmuki P (2005) Self-organized nanotubular oxide layers on Ti-6Al-7Nb and Ti-6Al-4V formed by anodization in NH₄F solution. J Biomed Mater Res A 75: 928-933.
14. Xiao P, Garcia BB, Guo Q, Liu DW, Cao GZ (2007) TiO₂ nanotubes arrays fabricated in different electrolytes for biosensing. Electrochem Commun 9: 2441-2447.
15. Fu N, Tang X, Li D (2012) Application of *in situ* measurement of photo-induced variations in electron work function for in-depth understanding of the photocatalytic activity of TiO₂ nanotubes. Nanotechnology 23: 275704.
16. Beranek R, Macak JM, Gärtner M, Meyer K, Schmuki P (2009) Enhanced visible light photocurrent generation at surface-modified TiO₂ nanotubes. Electrochim Acta 54: 2640-2646.
17. Paulose M, Shankar K, Varghese OK, Mor GK, Grimes CA (2006) Application of highly-ordered TiO₂ nanotube-arrays in heterojunction dye-sensitized solar cells. J Phys D: Appl Phys 39: 2498-2503.