Theory for Potential of Zero Charge and Capacitance on Metal with Nanocorrugated Steps

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Supporting Information

Electronic Spillover Corrected Local Mean and Gaussian Curvatures

Geometric local curvatures are also influenced by the delocalization of electronic density outside the metallic surface. The finite spillover of electrons up to the distance δ outside the metallic surface in normal direction accounted through differential geometry formula for the curvature of parallel surfaces. This electronic spillover causes opposite influence on the effective curvature at the concave and the convex sites. This effect is accounted through the corrected mean ($H'_s(x,y)$) and Gaussian ($K'_s(x,y)$) curvatures with δ obtained through the Steiner's formulas, given as[1]

$$H'_s(x,y) = \frac{H_s(x,y) - K_s(x,y)\delta}{1 - 2H_s(x,y)\delta + K_s(x,y)\delta^2} \quad , \quad K'_s(x,y) = \frac{K_s(x,y)}{1 - 2H_s(x,y)\delta + K_s(x,y)\delta^2} \quad \text{(S1)}$$

The outward electronic spillover distance δ has different sign convention. It is taken to be positive from the vaccum side approach to the solid metal electrode, whereas it has negative sign convention from the material side approach. This spillover correction causes asymmetric contribution to the curvature along the step geometry. The step curvature anisotropy induces the distribution of electronic charges over the surface which can be analyzed in terms of the local electronic capacitance. The overall variation in the electronic and electrochemical properties can be obtained by formulation the average curvatures of randomly nanocorrugated metal step surface, discussed in the following segment.

Average Mean Curvature

The principal curvatures along the metal steps (x-direction) and the step-edge (y-direction) are represented in terms of first and the second derivatives of surface profile, given as

$$H_s(x,y) = \frac{\zeta_{xx}(x,y) + \zeta_{yy}(x,y)}{2} \tag{S2}$$

where, $\zeta_{yy}(x,y) = \zeta_{xx}(x,y)\,\tilde{\zeta}_y(y)^2 + \zeta_x(x,y)\,\tilde{\zeta}_{yy}(y)$ using surface profile expression (eq 5) given in the main article. Equation S2 can be written as

$$H_s(x,y) = \frac{\zeta_{xx}(x,y)(1+\tilde{\zeta}_y(y)^2) + \zeta_x(x,y)\,\tilde{\zeta}_{yy}(y)}{2} \tag{S3}$$

The ensemble averaged mean curvature over all the possible random configuration of nanocorrugation along y-axis is given by

$$\langle H_s(x,y)\rangle \approx \frac{\langle\zeta_{xx}(x,y)\rangle(1+\langle\tilde{\zeta}_y(y)^2\rangle)}{2} \tag{S4}$$

Since the random nannocorrugation along the step-edge (y-direction) is taken as centered random process therefore, $\langle\tilde{\zeta}_{yy}(y)\rangle = 0$ in the above equation. Therefore, the first and second derivatives of surface profile is given as

$$\begin{aligned}
\zeta_x(x,y) &= \frac{1}{2\sqrt{3}}\left(1-\tanh^2\left[\frac{x}{a}+\frac{\tilde{\zeta}(y)}{a}\right]\right),\\
\zeta_{xx}(x,y) &= -\frac{1}{\sqrt{3}\,a}\tanh\left[\frac{x}{a}+\frac{\tilde{\zeta}(y)}{a}\right]\left(1-\tanh^2\left[\frac{x}{a}+\frac{\tilde{\zeta}(y)}{a}\right]\right)
\end{aligned} \tag{S5}$$

The average curvature distribution of the random nanocorrugation along the step-edge is considered as a centered Gaussian process having Gaussian correlation function as $W(y) = e^{-y^2/a^2}$. The several ensemble averaged morphological properties for the given statistics as: $\langle\tilde{\zeta}(y)\rangle = 0$, $\langle\tilde{\zeta}^2(y)\rangle = h^2$, $\langle\tilde{\zeta}_y^2(y)\rangle = 2h^2/a^2$. For a given randomly nanocorrugated step edge, the roughness is characterized by mainly two parameters, i.e., root mean square nanocorru-

gation width ($2h$) and the transverse correlation length (a as a lattice parameter) along the step-edge. Further, putting eq S5 in the eq S4 and taking the ensemble average over all the random configuration of nanocorrugated step-edge, we obtained the ensemble averaged step mean curvature as

$$\langle H_s(x,y)\rangle = -\frac{1}{2\sqrt{3}\,a}\tanh\left[\frac{x}{a}-\frac{h^2}{a^2}\right]\left(1-\tanh^2\left[\frac{x}{a}-\frac{h^2}{a^2}\right]\right)\left(1+\frac{2\,h^2}{a^2}\right) \tag{S6}$$

The average mean curvature along the metal step profile is obtained considering the two neighboring step given by

$$\overline{\langle H_s\rangle} = \frac{1}{2l_T}\int_{-l_T}^{l_T}\int_{-\infty}^{\infty} H_s(x,y)\,dy\,dx \approx \frac{1}{2l_T}\int_{-l_T}^{l_T}\langle H_s(x)\rangle\,dx \tag{S7}$$

The statistical averaging fix the random nanocorrugation along y-direction with mean square nanocorrugation width fluctuation as $h^2 = \langle\tilde{\zeta}(y)^2\rangle$ for a centered random Gaussian process. Such transformation is achieved by the cumulant expansion of surface profile along the step-edge with resultant relation as $\langle\tanh(\frac{x}{a}+\frac{\tilde{\zeta}(y)}{a})\rangle = \tanh(\frac{x}{a}-\frac{h^2}{a^2})$. Details of this transformation are provided in the main article from eqs 6 to 8.

Further, using eq S6 in eq S7, the integration gives the average mean curvature of a randomly nanocorrugated step, given as

$$\overline{\langle H_s\rangle} = \frac{n_a}{8\sqrt{3}\,l_T}\left(\tanh^2\left[\frac{l_T}{a}+\frac{h^2}{a^2}\right]-\tanh^2\left[\frac{l_T}{a}-\frac{h^2}{a^2}\right]\right)\left(1+\frac{2h^2}{a^2}\right) \tag{S8}$$

Similarly, the average of square of principal curvature is obtained by using the simplification as $\mathrm{Arc}(\tanh(x)) \approx \tanh(x)$, given by

$$\begin{aligned}\overline{\langle H_s^2\rangle} = &-\frac{3(36+n_a^2)\,\mathrm{sech}[\frac{l_T}{a}-\frac{h^2}{a^2}]\,\mathrm{sech}[\frac{l_T}{a}+\frac{h^2}{a^2}]\sinh(\frac{2\,l_T}{a})}{16\,a l_T(12+n_a^2)^2}\\ &+\frac{3n_a^2}{16\,a l_T}\left(\psi_1\left[\frac{l_T}{a}-\frac{h^2}{a^2}\right]-\psi_2\left[\frac{l_T}{a}-\frac{h^2}{a^2}\right]+\psi_1\left[\frac{l_T}{a}+\frac{h^2}{a^2}\right]-\psi_2\left[\frac{l_T}{a}+\frac{h^2}{a^2}\right]\right)\end{aligned} \tag{S9}$$

where $\psi_1(u)$ and $\psi_2(u)$ are the function of step morphological parameters and defined as

$$\begin{aligned}\psi_1(u) &= \frac{(72+12n_a^2+(72+8n_a^2)\cosh(2u))\sinh(2u)}{n_a^2(12+n_a^2)(9+2n_a^2+3\cosh(4u)+12\cosh(2u))},\\ \psi_2(u) &= \frac{8(\sinh(4u)+16\sinh(2u))}{(9+2n_a^2+3\cosh(4u)+12\cosh(2u))^2}\end{aligned} \tag{S10}$$

The nanocorrugation along the step-edge is random in nature resulting random curvature distribution. To account for the atomic scale fractal morphological influence, the function $\tilde{\zeta}(y)$ can be defined through the modified 1D Weierstrass-Mandelbrot function.[2–4]

Electronic Spillover Corrected Average Mean and Gaussian Curvatures

From eq S1, the electronic spillover corrected local mean and Gaussian curvatures are written as

$$\begin{aligned}H_s'(x,y) &= (H_s(x,y)-K_s(x,y)\delta)(1-2H_s(x,y)\delta+K_s(x,y)\delta^2)^{-1},\\ K_s'(x,y) &= (K_s(x,y))(1-2H_s(x,y)\delta+K_s(x,y)\delta^2)^{-1}\end{aligned} \tag{S11}$$

Since $2H_s(x,y)\delta + K_s(x,y)\delta^2 \ll 1$, therefore applying the Binomial expansion, we have

$$\begin{aligned}H_s'(x,y) &= (H_s(x,y)-K_s(x,y)\delta)(1+2H_s(x,y)\delta-K_s(x,y)\delta^2),\\ K_s'(x,y) &= (K_s(x,y))(1+2H_s(x,y)\delta-K_s(x,y)\delta^2)\end{aligned} \tag{S12}$$

Further, simplifying the above equation by taking $\overline{\langle K_s\rangle} = 0$, we have electronic spillover corrected average mean and the Gaussian curvatures as

$$\overline{\langle H_s'\rangle} = \overline{\langle H_s\rangle} + 2\delta\overline{\langle H_s^2\rangle}, \quad \overline{\langle K_s'\rangle} = 0 \tag{S13}$$

We have also observed in Figure 2 of main article that the physical term $\overline{\langle H_s^2\rangle}$ is much smaller compared to $\overline{\langle H_s\rangle}$ and contributes less than 1% to the overall curvature therefore, it

is a good approximation to take $\overline{\langle H_s' \rangle} \approx \overline{\langle H_s \rangle}$ while calculating the average WF and PZC.

Acknowledgments

G.K.M. thanks UGC-India for providing Senior Research Fellowship and R.K. acknowledges the University of Delhi, grant no. IOE/FRP/PCMS/2020/27, for financial support.

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