Shape optimization of a meniscus-adhered nanotip

Shihao Tian, [a,b] Xudong Chen [a,b] and Quanzi Yuan *[a,b]

[a]State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China
[b]School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China
*Corresponding Author: Quanzi Yuan. Email: yuanquanzi@lnm.imech.ac.cn

1. The profile equation of the meniscus

In Fig. S1a and S1b, a tip is submerged in liquid, and liquid climbs along the tip, forming a meniscus because of the balance of capillary force and gravity. Here we invoke the following pressure argument: Immediately underneath the surface, Laplace's pressure is equal to the hydrostatic pressure[1]:

$$P_0 + \frac{\gamma}{R(y)} = P_0 - \rho g y \tag{S1}$$

where P_0 is the outer pressure, y is the height of the surface above the horizontal plane, $R^{-1}(y)$ is the curvature at a particular point, ρ and γ are respectively the density and surface tension of the liquid. Equation (1) can simplify to:

$$-Ry = \kappa^{-2} \tag{S2}$$

where κ^{-1} is the capillary length. And the curvature $1/R$ can be expressed as:

$$\frac{1}{R} = -\frac{\frac{d^2y}{dx^2}}{\left[1+\left(\frac{dy}{dx}\right)^2\right]^{3/2}} \tag{S3}$$

After further integration, we can obtain the profile equation of the meniscus:

$$x = \frac{w}{2} + \kappa^{-1}\text{arccosh}\left(\frac{2\kappa^{-1}}{y}\right) - 2\kappa^{-1}\left(1-\frac{y^2}{4\kappa^{-2}}\right)^{1/2} \tag{S4}$$

In MD simulations, we regulate the initial shape of the meniscus based on this equation. After relaxation, the shape remains stable.
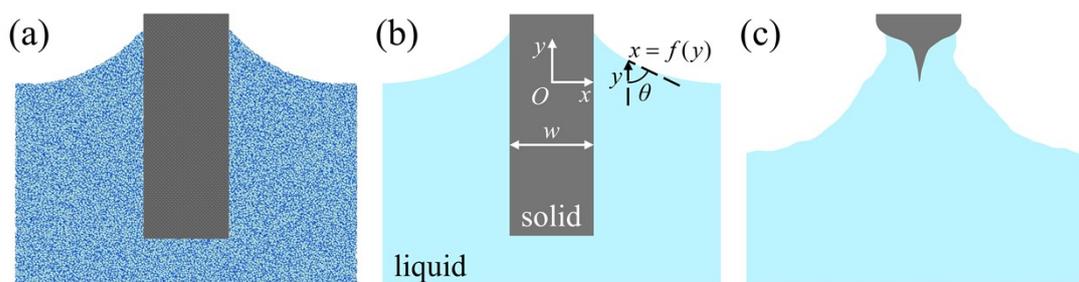

Fig. S1 (a) Atom view of the simulation domain. Blue balls (hydrogen atoms) and cyan balls (oxygen atoms) depict water molecules. Charcoal grey balls are solid atoms. (b) Surface view of the simulation domain. (c) Surface view of the optimized tip with a meniscus when $\varepsilon = 0.48$ and $w = 99.96$

Å.

2. The criterion for the dissolution of an atom

When one atom dissolves in liquid, leaving the solid surface, its central symmetry parameter (CSP)[2] becomes higher. The definition follows:

$$CSP = \sum_{i=1}^{N/2} \left| \boldsymbol{R}_i + \boldsymbol{R}_{i+N/2} \right|^2 \tag{S5}$$

where N represents the coordination number (N = 12 for face-centered cubic, N = 8 for body-centered cubic lattices), $\boldsymbol{R}_i$ and $\boldsymbol{R}_{i+N/2}$ are vectors from the central atom to a particular pair of nearest neighbors. $N/(N\text{-}1)/2$ possible neighbor pairs could contribute to eqn (S5). The quantity in the sum is computed for every pair, and the $N/2$ smallest are used, which are the pairs of atoms in symmetrically opposite positions versus the central atom[3]. For lattice sites in an ideal centrosymmetric crystal, the contributions of all neighbor pairs will counteract, and the resulting CSP will be 0. If one atom dissolves in liquid, the symmetry is broken, and CSP increases.

To accelerate the simulation, we consider the simulation system as an open system,[4] where the atoms with CSP over 10.37 are regarded to dissolve. These dissolving particles have little influence on the following dissolution process and move away from the simulation system. We applied MD simulations to justify the reasonableness. One solid atom was put in a water droplet with 2200 water molecules, and CSP of the solid atom was recorded every 1 ps within 2.43 ns. The frequency distribution of CSP is shown in Fig. S2a. CSP is greater than 10.37 in 67% moments, where 10.37 has the max count. Hence 10.37 is the CSP value where one atom dissolves into the water. What's more, we performed MD simulations of no-acceleration dissolution and obtained the correlation of d (the distance between a dissolving atom and the solid boundary) and CSP, which is shown in Fig. S2b. CSP increases rapidly and then increases slowly when CSP is over about 10 and d is over about 11 Å, which indicates that the dissolving atoms with d over 11 have similar periphery environment. In other words, the atoms with CSP greater than 10 are far away from the solid part and have the characteristic of dissolution. Therefore, we define 10.37 as the critical CSP value to distinguish the atom to dissolve or not dissolve. In the MD simulations of tip dissolution, we calculated the CSP of solid atoms every 20 ps, and identified the dissolving atoms.
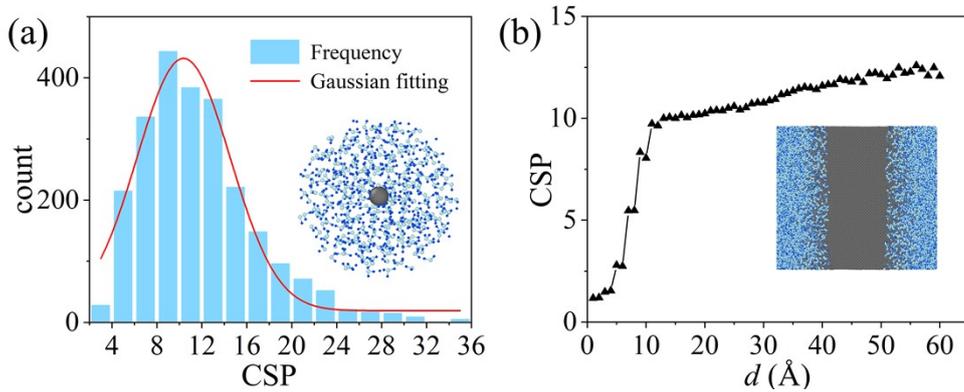

Fig. S2 (a) Frequency distribution of CSP with one solid atom surrounded by liquid molecules. (b) The distance distribution with CSP. The *x*-coordinate d represents the distance between dissolving atoms and the solid boundary. Inset images give MD simulation models.

3. Experimental configuration and details

As shown in Fig. S3, the tungsten filament with a diameter of 300 μm is vertically dipped into the aqueous solution bath of sodium hydroxide. The tungsten filament fixed on the lifting platform has a purity of 99.99%. The aqueous

solution with a molar concentration of 3 mol/L is prepared by deionized water and analytically pure reagents of sodium hydroxide, which is placed into a 130 × 60 × 60 mm bath. The external electric field supplied by a direct current (DC) power source is applied to control the dissolution with the filament as the positive pole and the liquid bath as the negative pole. The potential difference between the positive and negative electrodes is set to 9.0 V. At this electric field, the ambient temperature is 22 °C, and the contact angle hysteresis is measured as 75°. More details can be found in our former work.[5]
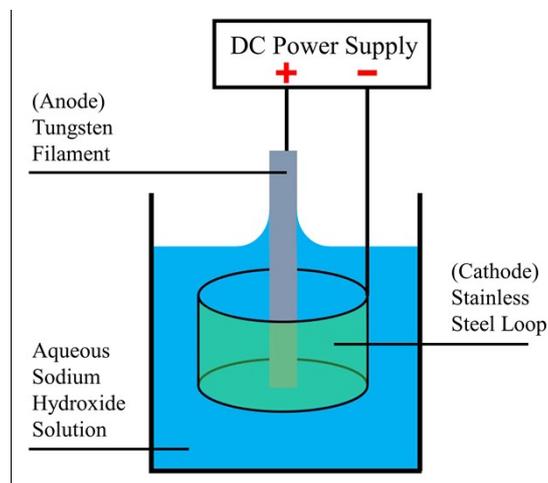

Fig. S3 Schematic diagram of the dissolution experiment where a cylindrical tungsten filament vertically immersed into an electrolyte bath is dissolved under external electric fields. The electrolyte is aqueous sodium hydroxide solution. The positive and negative electrodes are the tungsten filament and the liquid bath, respectively.

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