Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Improving utilization rate of foliar nitrogen fertilizer by surface roughness engineering of silica sphere

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X-ray diffraction patterns. S-Si, H-Si and SUH-Si were reacted with ammonium chloride at 25 ºC for 24 hours, and then the products were washed with deionized water and anhydrous ethanol by centrifugation. **Figure S2** showed the XRD patterns of S-Si, H-Si, SUH-Si, S-Si with NH_4Cl, H-Si with NH_4Cl and SUH-Si with NH_4Cl. The results showed that, compared with the curves of S-Si, H-Si and SUH-Si, no new peak and peak shift were found in S-Si with NH_4Cl, H-Si with NH_4Cl or SUH-Si with NH_4Cl (The corresponding JCPDS Card of the all four silica sphere are 01-0438), which indirectly indicated that S-Si, H-Si and SUH-Si did not react with ammonium chloride, and the adsorption between them should be attributed to physical adsorption.

It is worth mentioning that ICP was used to detect the concentration of copper ions in SUH-Si and ammonium chloride solution after 72 hours of reaction. No copper ions were detected in the reacted solution, indicating that the SUH-Si does not contain copper and no harm to the environment. Similarly, nickel ions were not detected in the H-Si solution of ammonium chloride, indicating that the H-Si does not contain nickel. Meanwhile, this result was consistent with the XRD test results.

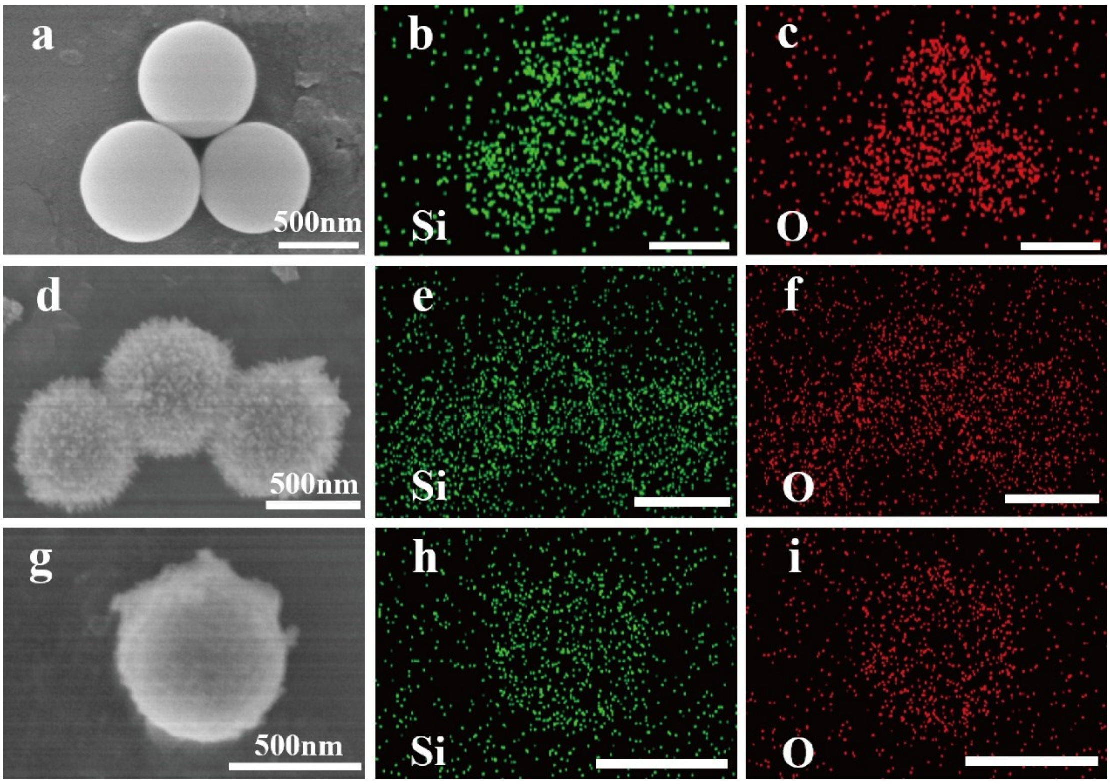

Figure S1. SEM images of S-Si (a), SUH-Si (d), H-Si (g) and (b), (c), (e), (f), (h), (i) corresponding EDX element mappings (Si, O).

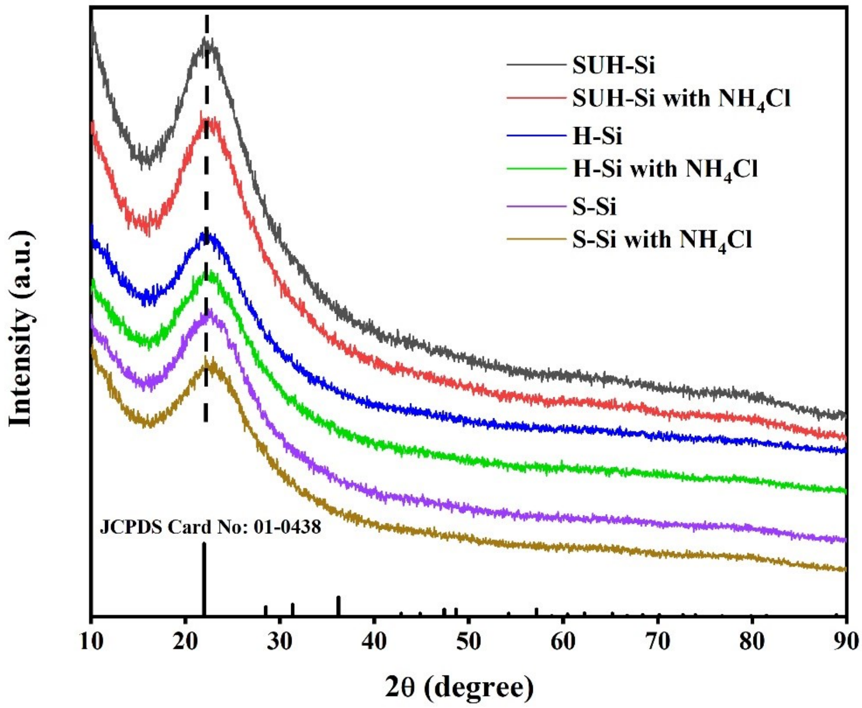

Figure S2. X-ray diffraction patterns of SUH-Si, SUH-Si with NH_4Cl, H-Si, H-Si with NH_4Cl, S-Si, and S-Si with NH_4Cl.

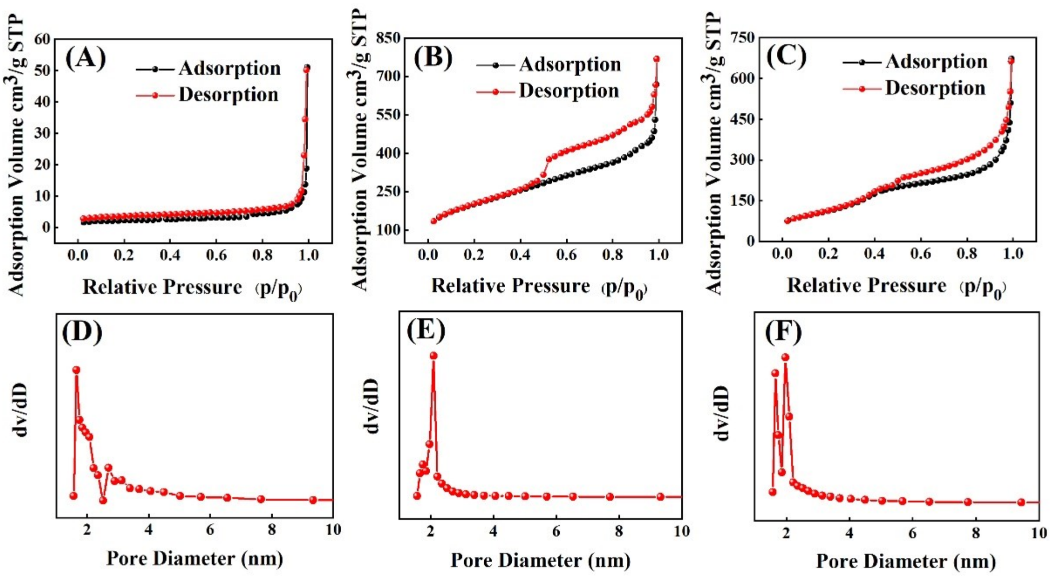

Figure S3. Nitrogen adsorption–desorption isotherm of S-Si (A), H-Si (B) and SUH-Si (C); DFT pore size distributions of S-Si (D), H-Si (E) and SUH-Si (F).

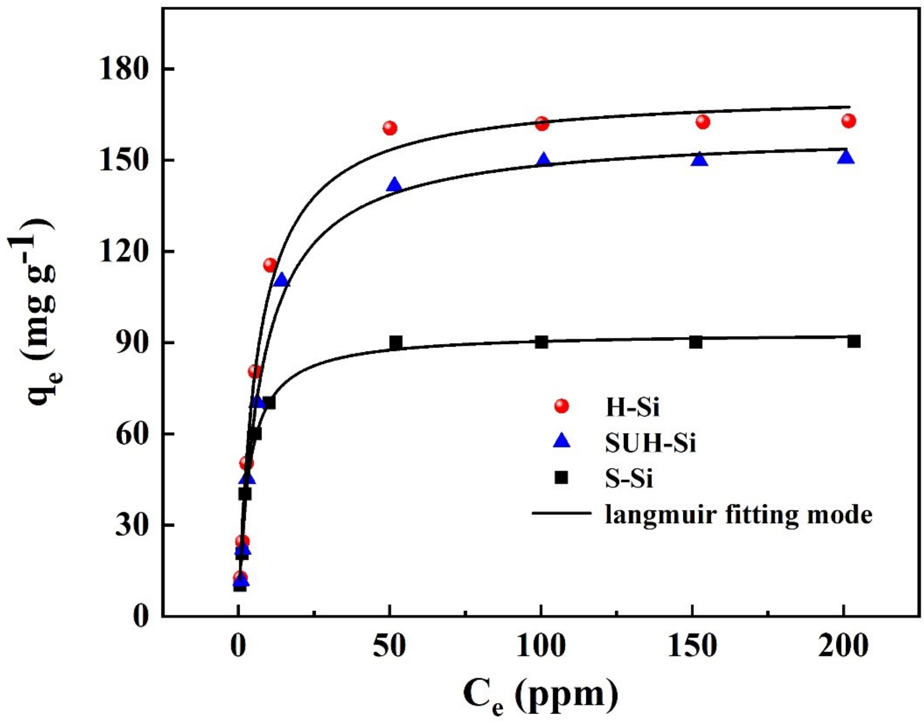

Figure S4. Adsorption isotherm of NH_4Cl on H-Si, SUH-Si and S-Si. C_e (ppm) is the equilibrium concentration of the NH_4Cl solution and q_e (mg g^{-1}) is the amount of NH_4Cl adsorbed at equilibrium.

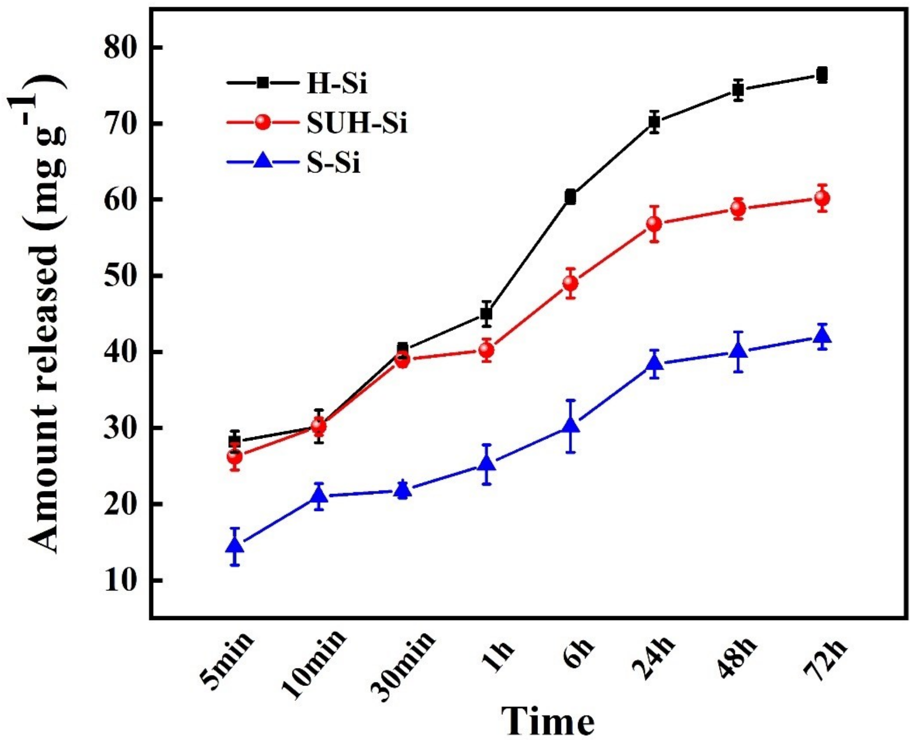

Figure S5. Release behavior of NH_4Cl in H-Si-N, SUH-Si-N and S-Si-N for 72h.

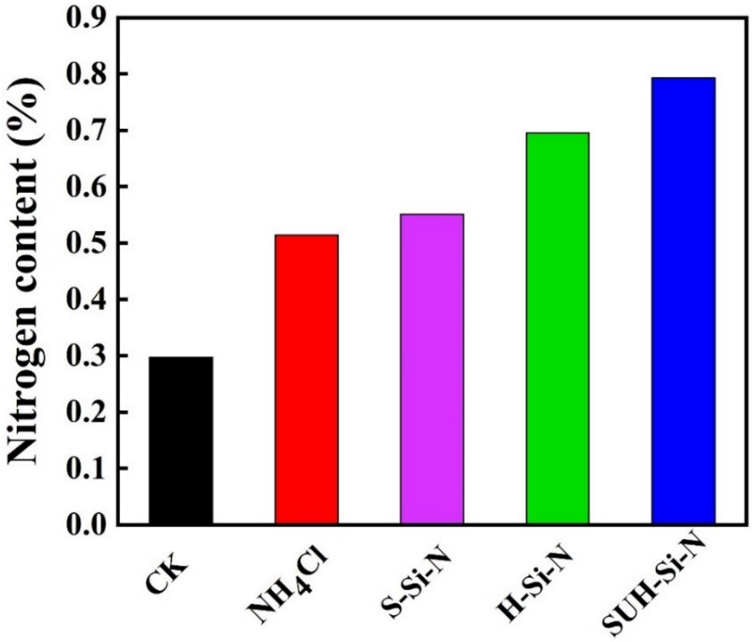

Figure S6. The percentage of total nitrogen in maize seedlings sprayed with deionized water, NH_4Cl solution, S-Si-N, H-Si-N and SUH-Si-N.

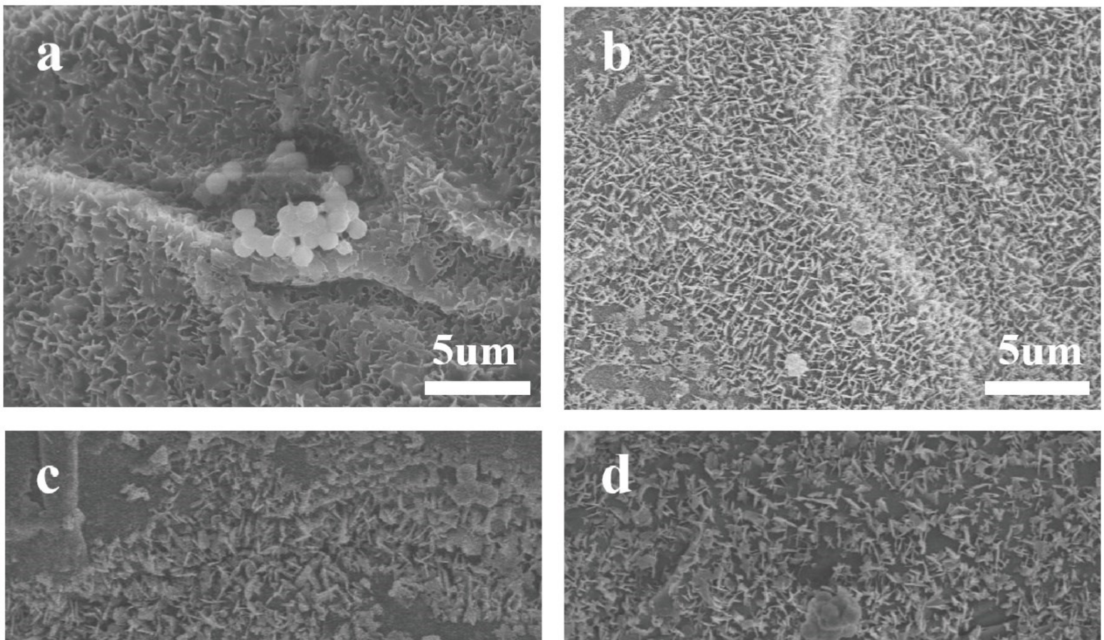

Figure S7. SEM images of S-Si-N adhered on peanut leaf surface (a) and maize leaf surface (b); H-Si-N adhered on peanut leaf surface (c) and maize leaf surface (d).

The calculation for action forces of silica sphere on the plan leaf surface

As shown in **Figure S8**, the silica spheres were subjected to van der Waals force (F_{vdw}), gravity (G), supporting force (F_s), friction force (F_f) and capillary force (F_c) on the plan leaf surface and impulsive force (F_i) of the water drop.

The van der Waals force (F_{vdw}) of SUH-Si on the plan leaf surface was attributed to the radially distributed of nanotubes on the surface of SHU-Si, which can be calculated by following equation:

$$F_{vdw} = \frac{HR}{6D^2} \tag{1}$$

where R is the diameter of protruded nanotubes (3 nm); D represents the contact width between leaf structure and protruded nanotubes of SHU-Si (10-100 nm); H denotes Hamaker constant (8×10^{-14} J). Thus, the maximum F_{vdw} of SUH-Si on the plan leaf surface was calculated to be 4×10^{-7} N, when the D is 10 nm, while the minimum F_{vdw} was 4×10^{-9} N as 100 nm of D parameter.

Since one singe SUH-Si has a mass of nanotubes, the overall F_{vdw} of SUH-Si on the plan leaf surface should be $N \times F_{vdw}$ (N is the contact number of nanotubes on the plan leaf surface).

N can be calculated by the following equation:

$$N = \frac{S_1}{S_2} \tag{2}$$

where S_1 indicates the contact area between SUH-Si and irregular grooves of peanut leaves, which was estimated to be 10000 nm^2; S_2 represents the surface area between the center of the nanotube on the surface of SUH-Si, which can be calculated as the equation $S_2=\pi\times r^2=3.14\times6^2=113.04$ nm^2. According to the equation (2), the N was estimated to be approximately 88. Thus, the overall F_{vdw} of SUH-Si on the plan leaf surface was calculated to be 3.52×10^{-7} N.

The van der Waals force (F_{vdw}) of H-Si on the plan leaf surface should be calculated by the following equation:

$$F_{vdw} = \frac{A}{6}\left[\frac{rR}{Z_0(r+R)} + \frac{R}{(Z_0+r)^2}\right] \tag{3}$$

where A indicates Hamaker constant (1×10^{-20} J); r represents the radius of overhang on the plan leaf surface (1×10^{-7} m); R denotes the spherical radius of H-Si (2.5×10^{-7} m); Z_0 is the distance from the silica sphere to plan leaf surface (3×10^{-10} m). Thus, the both F_{vdw} of H-Si were calculated to be 1.32×10^{-9} N.

The gravity (G) of silica sphere on the plan leaf surface can be calculated according to the following equation:

$$G = \rho V g \tag{4}$$

which ρ is material density (2.32×10^3 kg m^{-3}), V denotes the material volume, which can be calculated by the equation $V=4/3\pi r^3\approx6.54\times10^{-20}$ m^3. Thus, the G of silica sphere was calculated to be 1.4×10^{-15} N.

According to the equations of Laplace and Kelvin, the total capillary force (F_c) between planes can be calculated by the following approximation formula:

$$F_c = 2\pi R r_{Iv}(cos\theta_1 + cos\theta_2) \tag{5}$$

where R indicates the radius of silica sphere (250 nm); r_{Iv} represents surface tension of water in air (7.2×10^{-2} N m^{-1}); θ_1 expresses the contact angel between the liquid and the solid upper surface; θ_2 denotes the contact angel between the water liquid and the solid lower surface.

According the contact angle of H-Si and SUH-Si in **Figure 5**, the θ_1 and θ_2 of H-Si were 0° and 150°; while the θ_1 and θ_2 of SUH-Si were 150° and 150°. Thus, the F_c of H-Si could be estimated to 1.52×10^{-8} N, and the F_c of SUH-Si was -1.17×10^{-7} N.

Finally, the friction force (F_f) on the plan leaf surface can be calculated according to the following equation:

$$F_f = \left(F_{vdw} + F_c + F_i cos30^o + Gcos30^o\right)\mu \tag{6}$$

where μ represents the frictional coefficient (0.1-0.3).

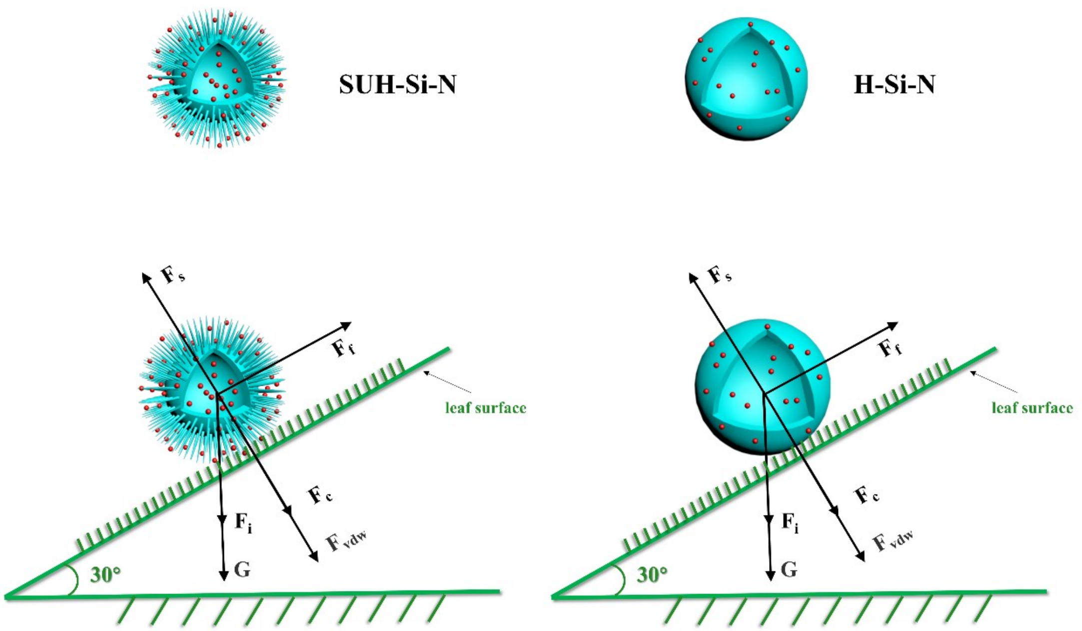

Figure S8. Schematic diagram of force analysis of SUH-Si and H-Si on the leaf surface.