

X-ray-Induced Changes in Wettability

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We observed that hard X-ray irradiation modifies the wettability of a variety of inorganic materials. The smooth surfaces of all tested inorganic materials (ZnO, p-Si, Al₂O₃, SrTiO₃, TiN, ZnS, CuO, Ag₂O, and Cr₂O₃) change during irradiation to a state of superhydrophilic wettability, and such changes are explained by the accumulation of positive surface charges by photoelectron emission. The initial wettability state is re-established within several minutes of storage in deionized water.

Introduction

The possibility to control the solid surface wettability with a simple approach is quite attractive because of potential industrial applications.^{1,2} We show that exposure to X-rays modifies this parameter in an easy and tunable way—reaching a state of superhydrophilicity. This is interesting because research in this domain focuses on changes to superhydrophobicity (contact angle CA < 10°) or superhydrophobicity (CA > 150°) that can be used in many devices such as biosensors, microfluidic tools, and intelligent membranes.³

Different external factors such as pH,⁴ light irradiation,^{5,6} electric field,⁷ and temperature⁸ were tested to achieve wettability control. Irradiation is especially attractive because of its flexible on and off switching, remote control, and other advantages for practical applications.^{9,10} Furthermore, the photon effects themselves can lead to interesting devices such as smart windows.¹¹

Unfortunately, the smooth surfaces of inorganic materials usually show limited wettability changes during ultraviolet/visible irradiation,¹² with a few exceptions such as ZnO, TiO₂, and WO₃. Nanostructures with rough surfaces enhance the wet-

tability changes, but their fabrication is complicated and affected by reproducibility problems.

We found that irradiation by short-wavelength photons in the hard X-ray range induces wettability changes for the smooth surfaces of a variety of inorganic materials. This phenomenon leads to superhydrophilicity in all of the materials that we tested. The transition is reversible, and the initial state is recovered by discharging after a short storage time in deionized water.

Experimental Section

We tested the surfaces of ZnO, p-Si, Al₂O₃, SrTiO₃, TiN, ZnS, CuO, Ag₂O, and Cr₂O₃. The experimental surfaces were prepared as follows. ZnO was grown on a Si(100) substrate by rf magnetron sputtering to 100 nm thickness. The other materials (p-Si and Al₂O₃ wafers and bulk-type SrTiO₃, TiN, ZnS, CuO, Ag₂O, and Cr₂O₃) were commercially purchased. The surface area of the tested materials was 1.0 × 1.0 cm². Synchrotron hard X-rays (dose rate ~10³ Gy s⁻¹) from the Pohang Light Source (PLS) 7B2 beamline¹³ were used for the irradiation. High-brilliance synchrotron hard X-rays were available from the storage ring at 2.5 GeV and 150 mA. Spatially coherent X-rays in the photon energy range of 10–60 keV were used to irradiate the inorganic materials. We carefully aligned the irradiated area in real time by monitoring the irradiated surface using X-ray microscopy.¹⁴ The wettability was estimated from the contact angle θ of water droplets on each surface. After completing the X-ray irradiation, we measured the water contact angle on the irradiated surface using a water droplet (~4 μ L) and a 1 Gpixel digital camera (Sony Cybershot, DSC-G1). Electrostatic force microscopy (EFM) (XE-100) was used to measure the surface potential.

Results and Discussion

Figure 1 shows the comparison of the water contact angle before and after irradiation on the surfaces of ZnO, p-Si, Al₂O₃, SrTiO₃, TiN, and ZnS: in each case, the irradiation induces a transition to superhydrophilicity. Similar results were also obtained for metal oxides CuO, Cr₂O₃, and Ag₂O and were interesting because ultraviolet-induced transitions are rare for oxide surfaces.¹² The transition time was relatively rapid (e.g., < 10 min for ZnS, ZnO, and SrTiO₃). The X-ray irradiation times

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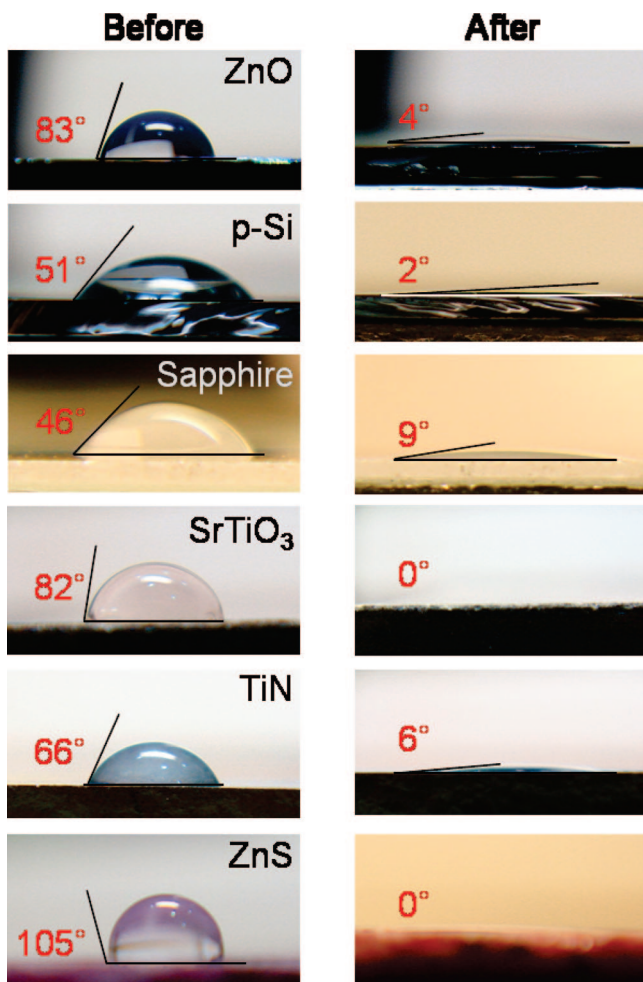


Figure 1. X-ray irradiation induces superhydrophilic transitions of the wettability for the smooth surfaces of a variety of inorganic materials.

Table 1. X-ray Irradiation Times Required for Superhydrophilic Transitions

materials	irradiation times (min)
ZnO	10
p-Si	20
Al ₂ O ₃	54
SrTiO ₃	8
TiN	36
ZnS	10

required for superhydrophilic transitions are summarized in Table 1.

What is the cause of these phenomena? A simple analysis shows that surface charging is the likely explanation. Photoelectron emission can indeed cause surface charging during ultraviolet or X-ray irradiation, corresponding to a change in the surface potential with time, $V(t)$, with respect to irradiation time^{14,15}

$$V(t) = V(\infty)[1 - \exp(-t/\tau)] \quad (1)$$

where $V(\infty)$ is the infinite potential and τ is the time constant. In the meanwhile, the contact angle change before (θ_0) and after (θ) charging is expressed by the electrowetting Young–Lippmann equation¹⁶

$$\cos \theta - \cos \theta_0 = CV^2 \quad (2)$$

where C is a constant that is inversely proportional to the water surface tension. Equations 1 and (2) give

$$(\cos \theta - \cos \theta_0)^{1/2} = A[1 - \exp(-t/\tau)] \quad (3)$$

where $A = C^{1/2}V(\infty)$. This relation is experimentally confirmed: Figure 2a shows its best fit to the experimental data with $A = 0.91$ and $\tau = 0.84$ min (~ 50 s). The validity of eq 3 was positively tested for all of the materials that we investigated, confirming that the wettability transition by X-ray irradiation is always due to surface charging.

The recovery in air is relatively slow, as shown in Figure 2b for ZnO: it takes about 80 min to reach the initial water contact angle. Note, however, that this is much faster than for the ultraviolet-induced wettability changes of smooth surfaces.¹⁷

The recovery of the initial wettability is simply explained by discharging. This conclusion is corroborated by the fact that the recovery is much faster when the ZnO sample is stored in deionized water, occurring in less than 1 min. For the other samples, the corresponding time is a few minutes (Table 2).

The hypothesis of surface charging and discharging is further confirmed by surface potential measurements with the dc EFM. Figure 3a,b shows the surface potential images for ZnO in air before and after 40 min of irradiation (the surface potential was measured 30 min after irradiation). The results demonstrate that the surface potential is strongly increased by irradiation. Then, it gradually decreases with time after irradiation, again reaching the initial value in ~ 80 min as seen in Figure 3c, consistent with Figure 2b.

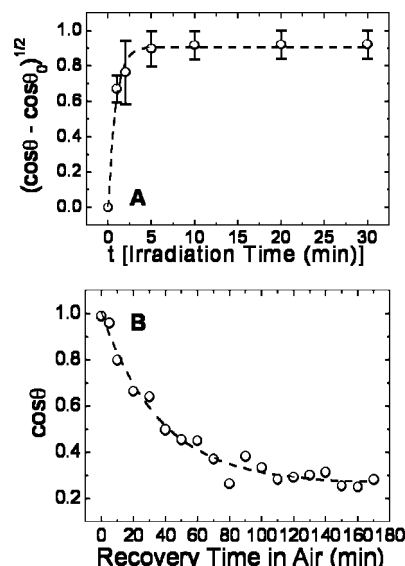


Figure 2. (A) Wettability transition dynamics for the ZnO surface during X-ray irradiation. The plot of $(\cos \theta - \cos \theta_0)^{1/2}$ vs t is consistent with eq 3. (B) Recovery in air of the initial water contact angle after irradiation.

Table 2. Recovery Times Required for the Initial Wettability in Deionized Water

materials	recovery times (min)
ZnO	1
p-Si	8
Al ₂ O ₃	3
SrTiO ₃	6
TiN	5
ZnS	7

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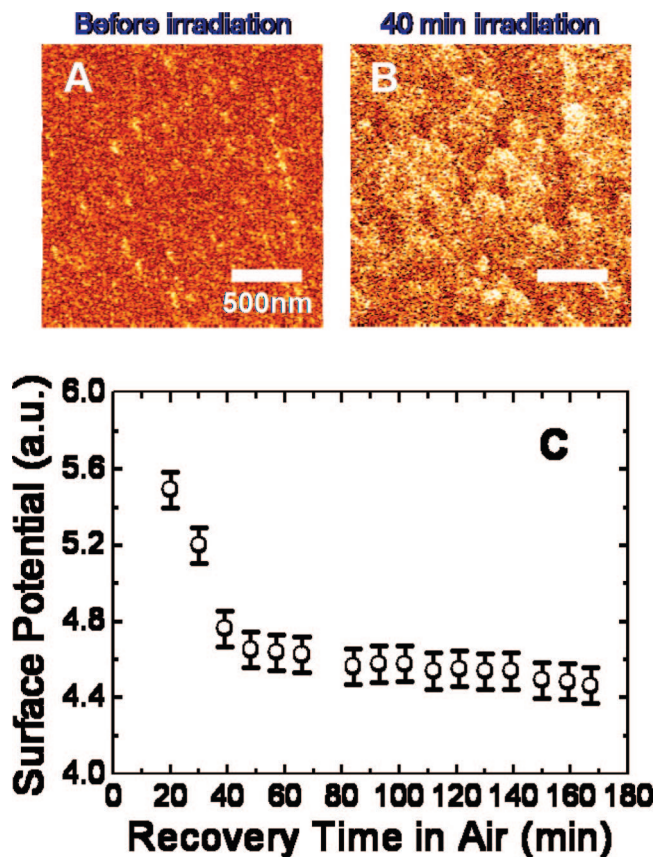


Figure 3. dc EFM surface images of a ZnO surface (A) before irradiation and (B) 30 min after a 40 min irradiation. (C) Gradual decrease in time for the surface potential in air.

To test the reversible character of the wettability transition, we went through several 20 min irradiation cycles, followed by storage/discharge. As shown in Figure 4a for ZnO (and also found for the other materials), the transition continues to be reversible both in air and in deionized water.

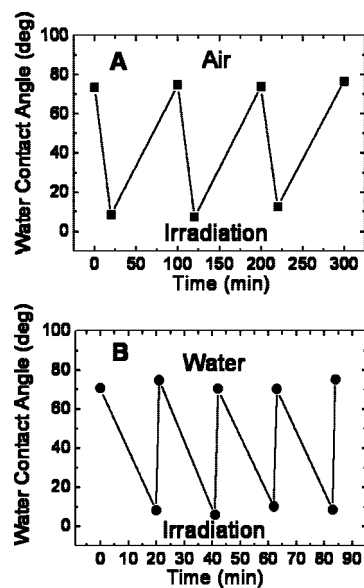


Figure 4. Reversible wettability transition of a ZnO surface verified over several irradiation–storage cycles in (A) air and (B) deionized water.

In summary, we first report X-ray-irradiation-induced superhydrophilic transitions in wettability for several different smooth surfaces of inorganic materials. The superhydrophilic transition is due to surface charging by photoelectron emission during X-ray irradiation. This wettability change is reversible both in air and in deionized water. This phenomenon could be exploited for applications such as microfluidic devices or smart windows.

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