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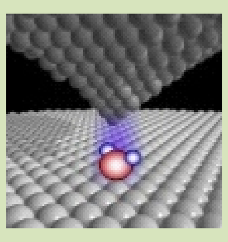
AXA PRIORITARA 2 – COMPETITIVITATE PRIN CDI
Operatiunea 2.1.2: Proiecte CD de înalt nivel stiintific la care vor participa specialisti din strainatate
PROIECT: ***Tehnologii SPFM în reactii ionice ale solutiilor reziduale în sol si realizarea de nanocompozite bazate pe nanotuburi de carbon pentru aplicatii de energie si mediu (SPFM-LA)***

Study of the wetting properties of glycerol on solid substrates at the micro-scale



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Abstract

A non-contact scanning probe technique – Scanning Polarization Force Microscopy (SPFM) – was successfully implemented for the study of the wetting properties of liquids on the surfaces of solid materials, at the micro- and nanoscale. SPFM relies on the measurement and control of the electrostatic force between a conductive AFM cantilever and the investigated surface. Micro- and nanodroplets of glycerol were deposited on solid substrates (mica, graphite, silicon, silicon dioxide) and imaged via SPFM. The technique allowed the direct measurement of the contact angle and the study of its dependence on droplet size.

What is Scanning Polarization Force Microscopy?

SPFM is a **non-contact scanning probe technique** that offers the capability of measuring the **topography of liquid films or droplets** and **soft materials**. It relies on the **measurement of electrostatic interaction (polarization) forces** between a conductive AFM tip and the studied surface. As the electrostatic interaction has a longer range compared to the van der Waals interaction, the tip is able to follow the surface topography at a larger distance than in conventional AFM. SPFM can be used to study the wetting properties of liquids, the topography of biological materials etc.

The SPFM technique

Theory

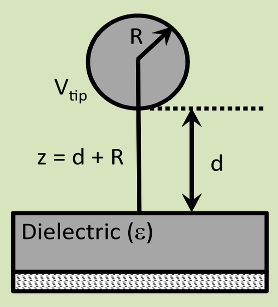
Tip-surface system modeled as a **charged sphere in front of a dielectric surface** => an **image charge** appears inside the dielectric.

Tip charge:

$$Q = 4\pi\varepsilon_0 R V_{tip}$$

Image charge:

$$Q_i = -\frac{\varepsilon-1}{\varepsilon+1}Q = -4\pi\varepsilon_0\frac{\varepsilon-1}{\varepsilon+1}RV_{tip}$$

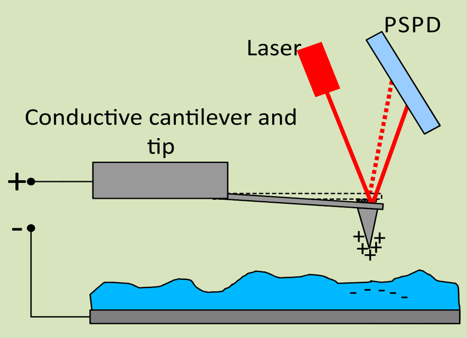


Electrostatic (polarization) force:

$$F = \frac{Q\cdot Q_i}{4\pi\varepsilon_0 z^2} = -4\pi\varepsilon_0\frac{\varepsilon-1}{\varepsilon+1}\frac{R^2}{z^2}V_{tip}^{\ 2}$$

SPFM-DC

- Tip located out of the range of the van der Waals forces => PSPD deflection is zero.
- When applying a **DC bias**, the **electrostatic force** (which will always be **attractive** due to the opposite signs of the charges) causes the cantilever to bend downwards => PSPD deflection becomes negative.
- The magnitude of the deflection also depends on tip-sample separation => by keeping the bending constant during scanning (via the topography feedback loop), one can actually follow the **surface topography in non-contact**.



SPFM-AC

Applied tip voltage: $V_{tip}\cdot\sin(\omega t)+V_{DC}$

Existing local surface potential: $V_{surf}(x,y)$

Resulting polarization force:

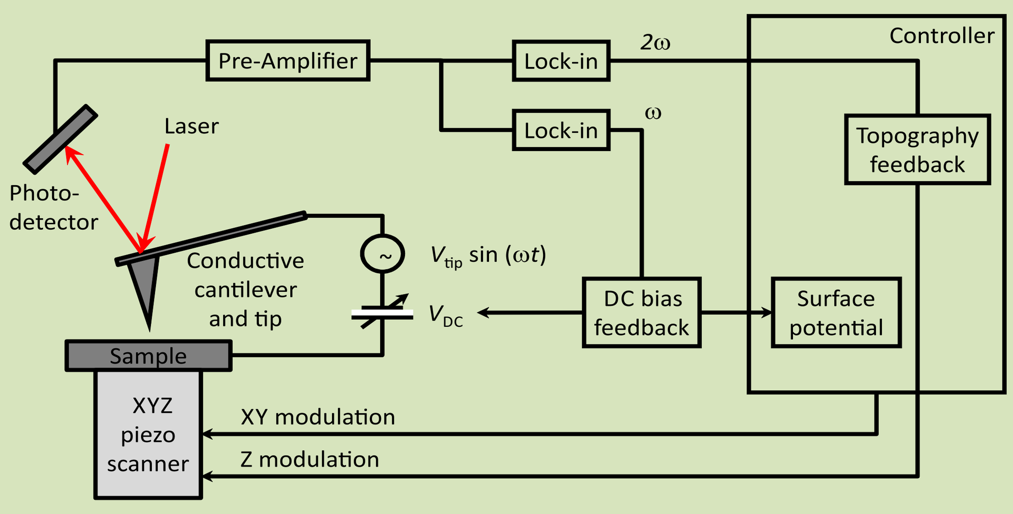
$$F = -4\pi\varepsilon_0\frac{\varepsilon-1}{\varepsilon+1}\frac{R^2}{z^2}\left(V_{tip}\cdot\sin(\omega t)-V_{surf}\right)^2 =$$

$$= -4\pi\varepsilon_0\frac{\varepsilon-1}{\varepsilon+1}\frac{R^2}{z^2}\left[-\frac{1}{2}V_{tip}^{\ 2}\cdot\cos(2\omega t)+2V_{tip}\cdot\left(V_{DC}-V_{surf}\right)\sin(\omega t)+\frac{1}{2}V_{tip}^{\ 2}+\left(V_{DC}-V_{surf}\right)^2\right]$$

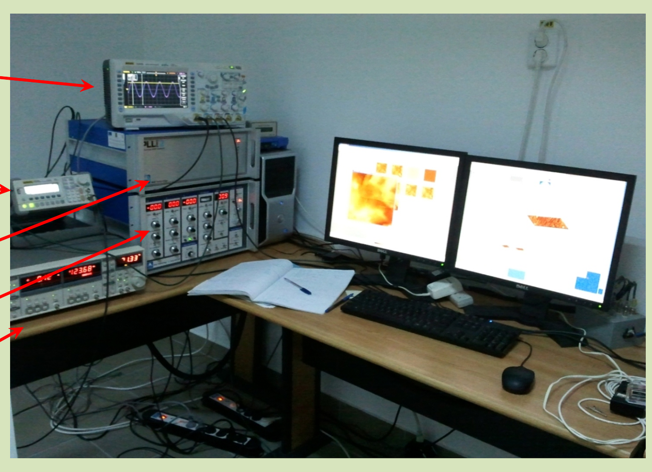
$$= F(2\omega)+F(1\omega)+F(0\omega)$$

The three components of F can be separated using a lock-in technique. $F(2\omega)$ is then used as an input for the topography feedback; while following the surface topography, the nulling of $F(1\omega)$, achieved when $V_{DC} = V_{surf}$, provides an (x,y) map of the local surface potential (Scanning Kelvin Probe Microscopy – SKPM).

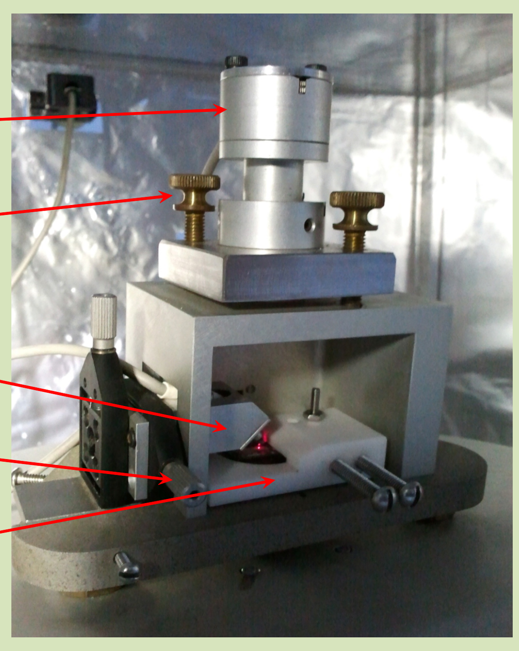
SPFM implementation at CSSNT



Electronics



AFM head

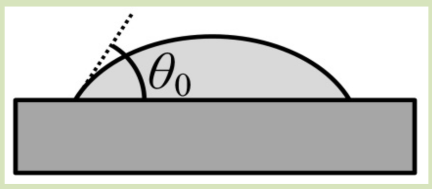


The AFM / SPFM laboratory of our Center was developed around a home-built advanced SPM system, which is currently driven by a state-of-the-art controller and is capable of: "classical" AFM (contact, non-contact, intermittent contact), STM, MFM, I-AFM (current AFM), SPFM and much more.

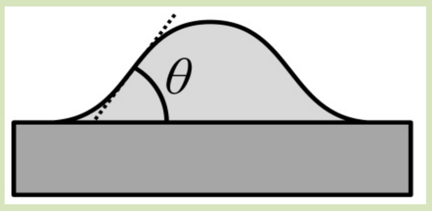
Study of the wetting properties of liquids

Contact angles

For **macroscopic droplets**, the contact angle θ_0 is defined as the angle at which the liquid meniscus meets the substrate, measured through the liquid.



For **microscopic droplets**, the liquid meniscus does not meet the substrate at a precise angle and the profile of the droplets has two inflexion points. The slope at these inflexion points gives the effective (microscopic) contact angle θ.



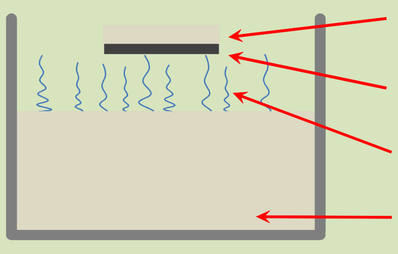
For microscopic droplets, the relation between the effective (microscopic) contact angle, the macroscopic contact angle, the height of the droplets (e), the potential energy between the interfaces (P) and the surface tension of the liquid (γ) is given by

$$\theta^2 = \theta_0^2+\frac{2}{\gamma}[P(e)+eP'(e)] \Longrightarrow P(e)-eP'(e) = (\theta^2-\theta_0^2)\frac{\gamma}{2}$$

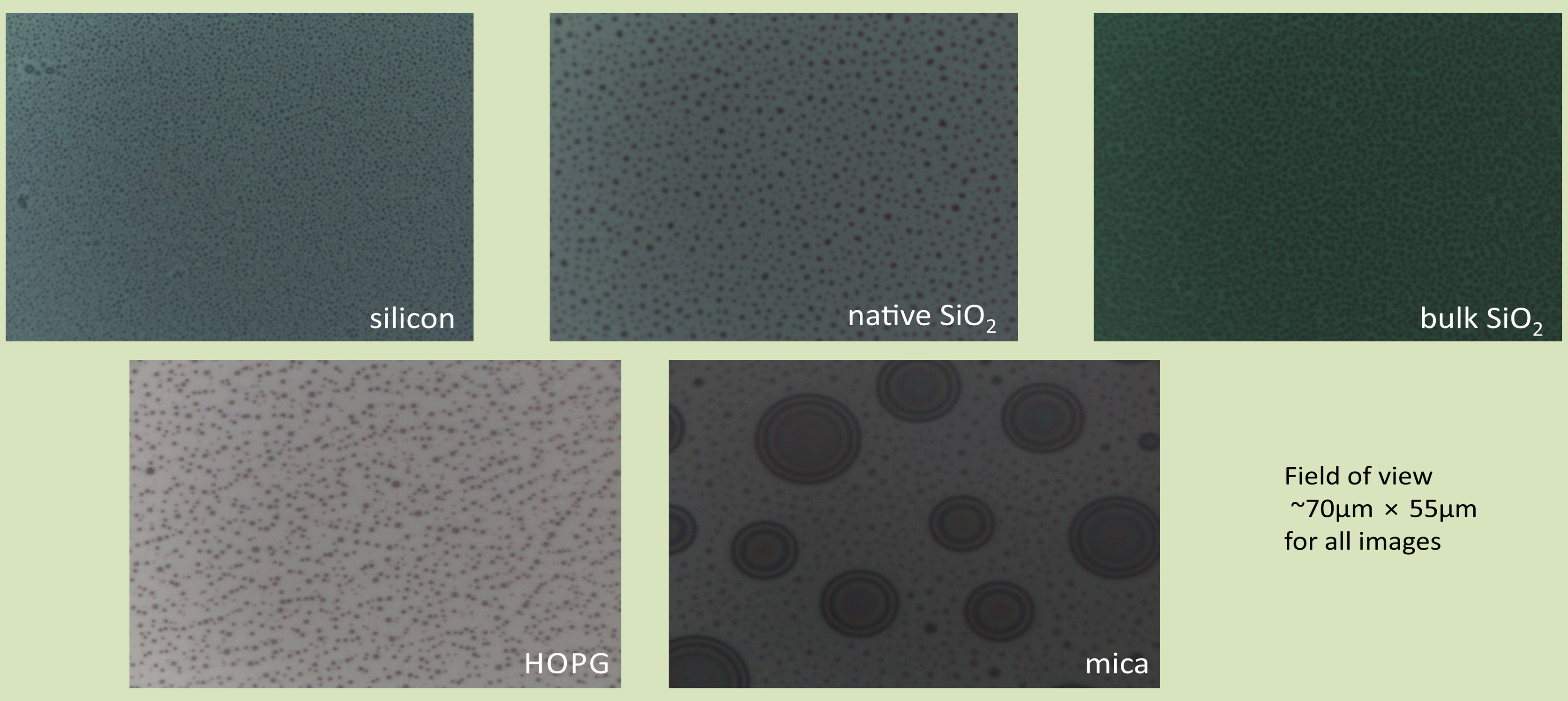
Hence, the dependence of surface potential energy with height, $P(e)$, can be calculated after determining from experimental measurements the dependence of contact angle on droplet height, θ(e).

Deposition of glycerol micro- and nanodroplets

Glycerol droplets were created on the substrates by condensation: the substrates were held upside down inside a Berzelius glass containing heated glycerol, at a height of ~5 mm above the liquid surface. After a few seconds the surface of the substrates achieved a "foggy" appearance, which proved the presence of microscopic droplets.

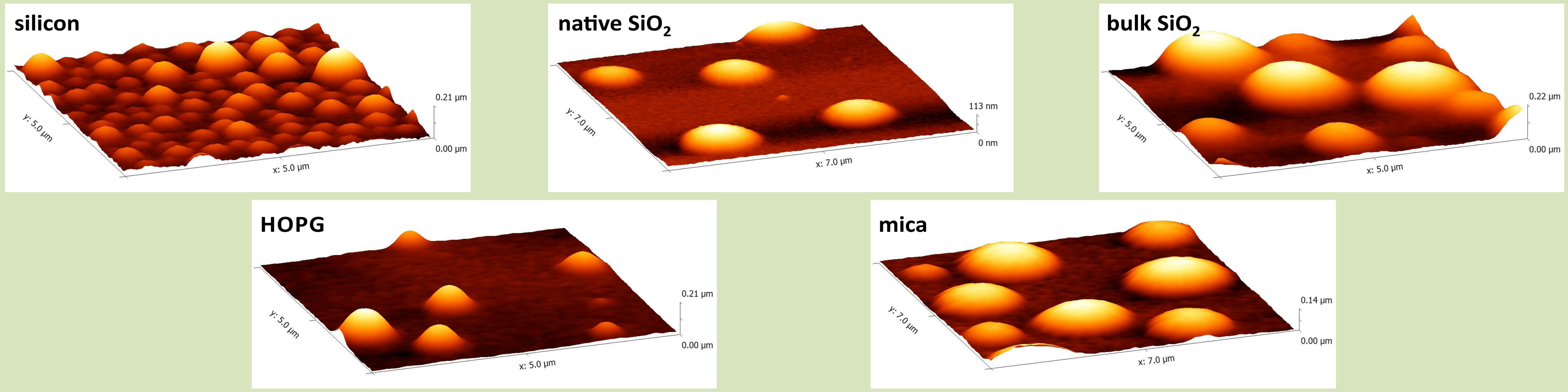


Optical analysis of deposited glycerol droplets



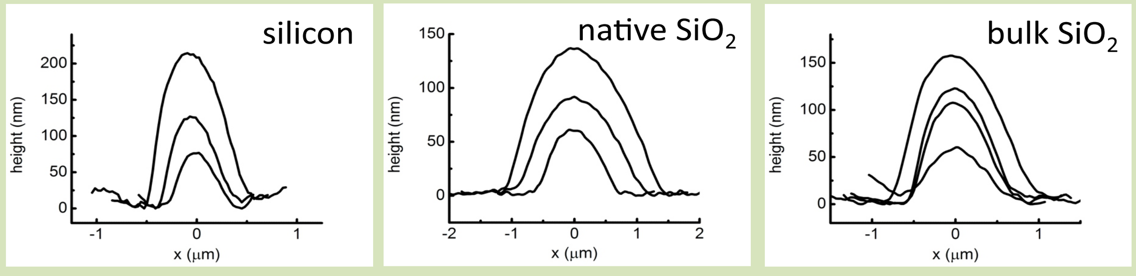
Field of view ~70μm × 55μm for all images

Visualising glycerol micro- and nanodroplets by SPFM

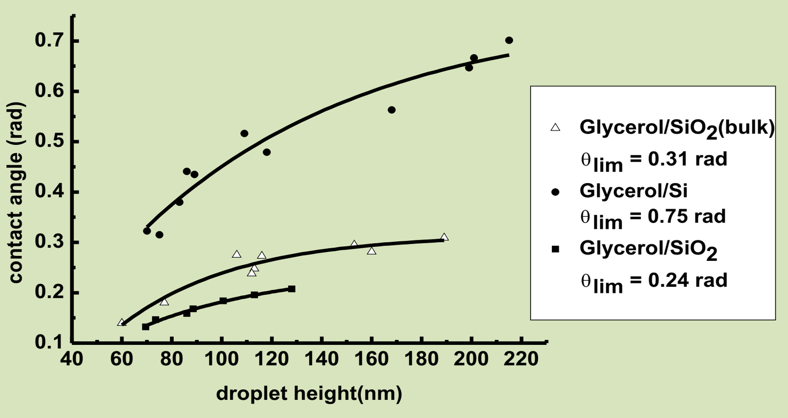


Line-cut profiles of the droplets

Extracted from the SPFM topography images for Si, native SiO_2 and bulk SiO_2

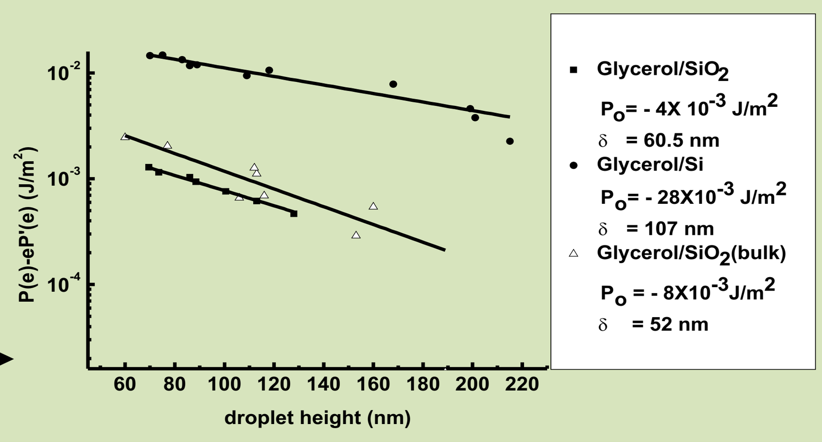


Direct calculation of the microscopic contact angle θ and determination of its dependence on droplet height



Contact angle dependence on droplet height allowed the determination of the **potential energy** dependence on droplet height using

$$\theta^2 = \theta_0^2+\frac{2}{\gamma}[P(e)+eP'(e)] \Longrightarrow P(e)-eP'(e) = (\theta^2-\theta_0^2)\frac{\gamma}{2}$$



$P(e) = -28\cdot 10^{-3}\exp(-e/107\ \mathrm{nm})\ \mathrm{J/m^2}$
for glycerol on Silica

$P(e) = -4\cdot 10^{-3}\exp(-e/60.5\ \mathrm{nm})\ \mathrm{J/m^2}$
for glycerol on native SiO_2

$P(e) = -8\cdot 10^{-3}\exp(-e/52\ \mathrm{nm})\ \mathrm{J/m^2}$
for glycerol on bulk SiO_2

ACKNOWLEDGMENTS

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