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Depth Dependent Chemical Information in the Liquid-Solid Interface of Nanoparticles in Solutions by Conventional X-ray Photoelectron Spectroscopy

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***Abstract*—Iron oxides are promising materials for a wide range of applications including photocatalytic water splitting, energy storage, and heterogeneous catalysis. However, understanding the interaction between iron oxide nanoparticles (Fe_2O_3 nps) and liquid water at the molecular level remains challenging due to the limitations of conventional surface analysis techniques. In this study, we present an in-situ X-ray Photoelectron Spectroscopy (XPS) investigation of Fe_2O_3 nps suspended in aqueous solution using a custom-designed environmental cell (e-cell), sealed with ultrathin silicon nitride (SiN) membranes. The attenuation of Fe 2p photoelectrons through 3–5 nm thick membranes was modeled and experimentally verified, enabling successful detection of chemical states within the aqueous suspension. Depth relevant information revealed a layered structure of the nps, with surface hydroxide species, an Fe_2O_3 core, and an intermediate FeOx phase. Spectra close to the valence band region confirmed the liquid nature of the encapsulated solution via the detection of water molecular orbitals, while ionic Na^+ signals further demonstrated the method's capability for detecting dissolved species. This approach provides a powerful platform for real-time chemical analysis of solid-liquid interfaces under ambient-like conditions, with broad implications for catalysis, electrochemistry, and environmental science.**

***Index Terms*—In-situ XPS, Iron oxide nps, Solid-liquid interface, Environmental cell, Aqueous suspension, Redox chemistry, Dissolved ions**

I. Introduction

IRON oxides possess a combination of attractive characteristics—such as low toxicity, robust stability, and low cost—that make them suitable for numerous emerging technologies. For instance, α-Fe_2O_3 has a band gap that is nearly optimal for driving solar-powered water splitting, carried out through the reaction:

$$H_2O \rightarrow 1/2O_2 + H_2$$

enabling the conversion of sunlight into chemical fuel and providing a significant pathway for hydrogen generation.[1] Additionally, α-Fe_2O_3 is being explored for energy-storage applications, particularly as an anode material in lithium-ion batteries, as well as in various heterogeneous catalytic processes.[2]

Understanding how water dissociatively chemisorbs on solids is a central topic in surface science, as surface hydroxyls can strongly modify surface characteristics and strongly influence reactivity. [3] Beyond its relevance to electrochemical and photoelectrochemical water splitting—where external conditions drive the breaking of O–H bonds—the basic mechanisms by which water interacts with clean, well-defined surfaces remain under active investigation. Although debates persist in certain systems regarding whether water adsorbs intact or dissociates upon adsorption, it is widely recognized that surface imperfections, especially on metal-oxide substrates, can promote the spontaneous cleavage of water molecules.

The aforementioned applications make fundamental understanding of Iron (Fe and FexOy) reactivity at the liquid/solid interface, crucial for rational design of materials. A number of experimental approaches for the study of liquids at the molecular level, with the use of surface sensitive techniques, have been proposed during the last two decades. X-Ray Photoelectron Spectroscopy (XPS) has been applied on liquids using different experimental setups like: ambient pressure XPS[4], use of environmental cells, consisting of a few layers thick graphene[5, 6], grapheme oxide[7], or silicon nitride membranes[8] and with the use of liquid-microjets [9].

II. Experimental

In the present study the approach used to study the liquid/solid interface, was proposed by Raimu Endo et al.[8] We created an environmental cell (e-cell) in which a liquid can be sealed inside a cavity, using a 5nm thick SiN membrane as a window, quasi-transparent for X-rays/photoelectrons, that separates the vacuum from the environment (Figure 1). The nanoparticle (np) suspension used, is the alpha-Fe_2O_3 10nm np 15wt% water dispersion (99.9% purity, Orange-Red) from US Research Nanomaterials, Inc. The np suspension was encapsulated in silicon microchips (SiMPore, Inc.), with a 25 x 25 μm window covered by a 5 nm-thick SiN membrane at the center of the 3-mm-long microchip. The microchips were used as received, without any further treatment before the introduction in the Ultra High Vacuum (UHV) chamber.

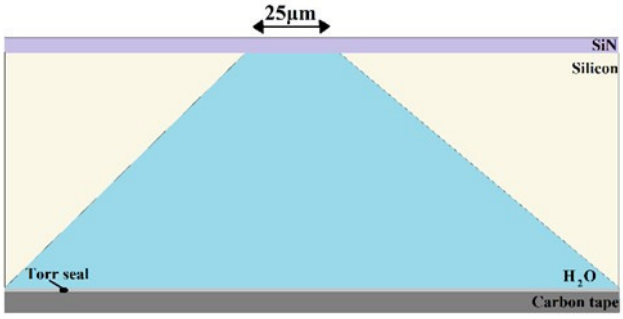


Figure 1. Cross-sectional schematic representation of the Si chip filled with H_2O, sealed on the top side by a SiN membrane and with Torr seal glue on the bottom side.

The XPS measurements were performed using a Kratos AXIS Ultra DLD XPS system with a hemispherical energy analyzer and a conventional lab-based monochromatic Al Kα source, operated at 15 keV and 150 W. The X-rays were incident at an angle of 45° with respect to the surface normal. Analysis was performed at a pressure ~$3x10^{-9}$ mbar. High resolution core level spectra were measured with a Pass Energy (PE) of 40 eV, except Fe 2p regions that were recorded with 80 ev PE. The XPS experiments on the e-cell were performed without the use of an electron gun (e-gun), although for the dried samples on HOPG an e-gun was used and directed electrons on the sample for charge neutralization. Ion sputtering was performed by accelerating Ar^+ ions (4 kV, 15 mA emission) towards the e-cell's surface for 40 sec. The estimated thickness of the removed layer under the sputtering conditions used in this study, is 2nm for each 40 sec cycle.

The 25 μm wide SiN window of 5 nm thickness, can hold 2.25 atm of pressure according to the manufacturer's standards, which is more than twice the ambient pressure inside the e-cell. It is expected that SiN thickness of ~2.5 nm could still hold more than 1 atm of pressure. The attenuation ratio, I_{exp} / I_0, of photoelectrons for the Fe 2p peak can be calculated by the equation:

$$I_{exp} / I_0 = \exp (d / \lambda_{IMFP} \cdot \cos \theta) \quad (1)$$

where d, λ_{IMFP}, and θ are the thickness of the membrane, the inelastic mean free path of Fe 2p and the take-off angle of photoelectrons, respectively. The λ_{IMFP} for photoelectrons with kinetic energy of ~776.0 eV ($E_{kin} = hv - E_{binding}$, hv = 1486.6 eV) below a layer of inorganic compound, is 2.7 nm. Angle θ in the experimental setup used in these measurements is 0° (cos θ = 1), because the electron analyzer was placed parallel to the surface normal of the e-cell surface.

Figure 2 shows that the experimental setup used for these studies is expected to permit 15.7% of the inelastic emitted Fe 2p photoelectrons from the solution to pass a 5 nm thick SiN membrane. When the SiN is thinner, around 3 nm thick, the 33.0% of the inelastic emitted Fe 2p photoelectrons from the solution are expected to pass through the membrane. These theoretical calculations clearly demonstrate that recording of the Fe 2p peak through a thin SiN membrane is possible when using conventional X-Rays. In order to improve the signal to noise ratio, long recorded times might be needed.

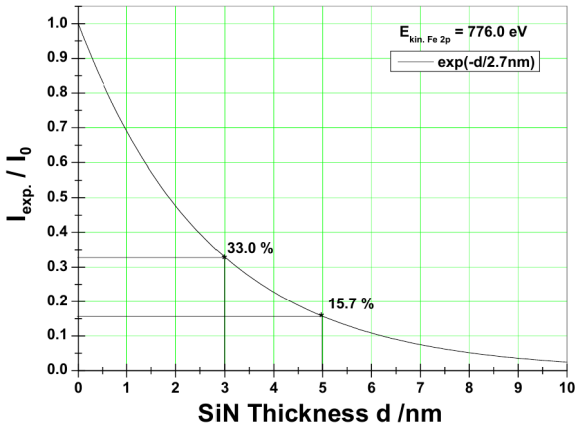


Figure 2. Attenuation ratio of the Fe 2p photoelectron intensity (I_{exp} / I_0) passing through the SiN membrane as a function of the membrane thickness.

III. Results & Discussion

he Fe 2p peaks that were recorded through the SiN window are shown in Figure 3 in comparison to the Fe 2p spectrum acquired from the dried Fe_2O_3 np aqueous suspension on HOPG. The as-received window was contaminated mainly by SiO_2 and Carbon preventing the recording of the XPS signal from the suspension inside the e-cell. After removing surface atomic layers with Ar^+ sputtering, the Fe 2p peaks were recorded, for the 5nm and 3nm thick windows. Peak deconvolution of the data, showed in both cases the existence of three chemical states of iron in the suspension. It is obvious that Fe_2O_3 np were able to dissociate water inside the solution, creating iron hydroxide species on the np surface. Signal for the Fe_2O_3 state is detected in the Fe 2p region and also a lower BE contribution at ~708.0 eV attributed to FeO_x with $x < 1$. It is known that water interaction with Fe_2O_3 reduces iron from Fe^{3+} to Fe^{2+} due to the creation of oxygen vacancies,[10] but in the present study we recorded that inside the aqueous solution, iron oxide is reduced even to lower oxidation state than Fe (II). The same solution that was dried in the ambient on HOPG, shows that the reduction caused from water is from Fe (III) to Fe(II) as reported in the literature.

The lower than Fe (II) oxidation state of Fe2O3 suspension in water, indicates stronger water-np interaction that was not previously observed. XPS studies on dried samples were not able to capture the real oxidation state of Iron inside the solution making the current experimental approach invaluable for in-situ measurements. The presence of hydroxides on the dried sample is expected in the literature [11], as hydroxides are stable enough to be detected on metals under Ultra High Vacuum conditions.

By removing ~2 nm of SiN layer on top of the np suspension, we are able to record Fe 2p photoelectrons from ~2nm

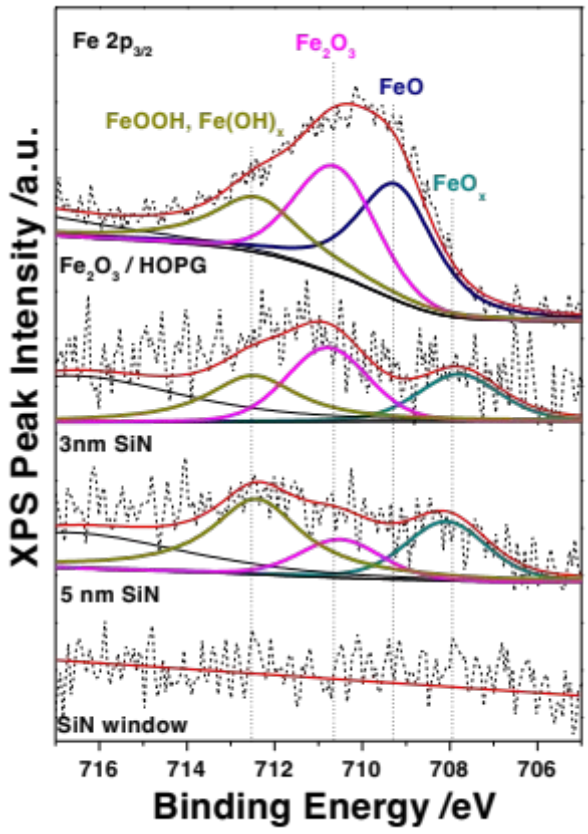
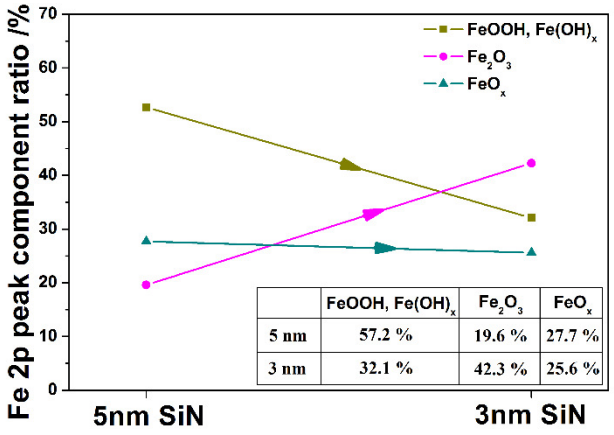


Figure 3. Fe 2p photoelectron spectra acquired from the e-cell filled with Fe2O3 np aqueous suspension without charge neutralization in comparison to the Fe 2p spectrum acquired from the dried Fe2O3 np aqueous suspension on HOPG.

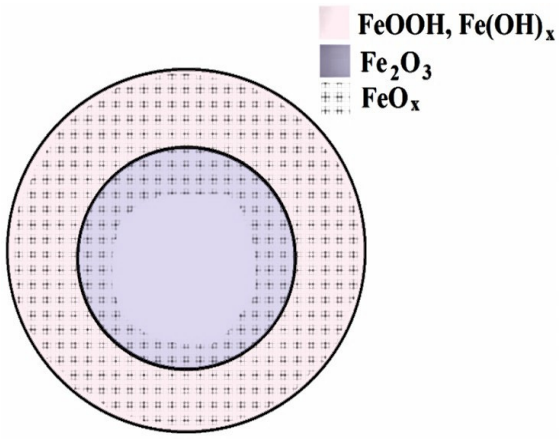
deeper. This depth dependent information (Figure 4) showed that the intensity ratio of the Fe 2p peak contributions changes as a function of the depth of analysis. The hydroxide contribution to the overall Fe 2p signal reduces as we get information from deeper inside the np, the Fe2O3 contribution increases and the FeOx is almost stable (Figure 4).



	FeOOH, Fe(OH)x	Fe2O3	FeOx
5 nm	57.2 %	19.6 %	27.7 %
3 nm	32.1 %	42.3 %	25.6 %

Figure 4. Depth-dependence of the Fe 2p intensity of the different iron chemical states.

The information provided by these changes in the peak intensity ratio, indicate a layered structure of the np due to the interaction with liquid water (Scheme 1). The nps consist of a surface layer of iron hydroxide and a Fe_2O_3 core. The FeOx state of iron, extends within the other two iron states, almost homogeneously from the outer surface layers close to the Fe_2O_3 core.



Scheme 1. Chemical characterization of layered structure of Fe2O3 np in water.

Finally, the strength and the relevance of the current experimental approach is demonstrated by recording the region at low Binding Energies close to the valence band (Figure 5). The electronic structure of liquid water has been the focus of extensive theoretical and experimental investigation, yielding a well-established description of its five filled and three lowest empty molecular orbitals: $(1a_1)^2$ $(2a_1)^2$ $(1b_2)^2$ $(3a_1)^2$ $(1b_1)^2$ $(4a_1)^0$ $(2b_2)^0$ $(3b_2)^0$. The two orbitals at the lowest energies—$1a_1$ (non-bonding) and $2a_1$ (bonding)—originate primarily from the oxygen atom's 1s (entirely) and 2s (predominantly) atomic orbitals. These features are characteristic signatures of liquid-phase water, and detecting them serves as evidence that the sample indeed exhibits liquid-like behavior.

We have to note here that photoelectrons with low Binding Energy have the highest Kinetic Energy possible for the excitation energy of the X-Rays used for conventional XPS. For that reason, the percentage of the inelastic photoelectrons that are expected to pass through the SiN membrane and reach the analyzer, is much higher than the Fe 2p photoelectrons. For that reason, the peak Intensity in the recorded region close the Valence band is much higher than the peak intensity of the region of the Fe 2p peak.

In Figure 5 we can clearly see that the 2α1 molecular orbital of liquid water was recorded for both SiN thicknesses presented in these studies, indicating that the liquid solution was present inside the cell during the measurements.[12, 13] An additional bonus feature is that we were able to record dissolved ions into the liquid. The Na^+ (2p) peak was recorded indicating the presence of Na ions in the solution. [14, 15] The capability of recording the presence of elements in their ionic state in liquids can have tremendous impact to environmental studies making the current experimen-

tal approach valuable to studies form other fields than catalysis.

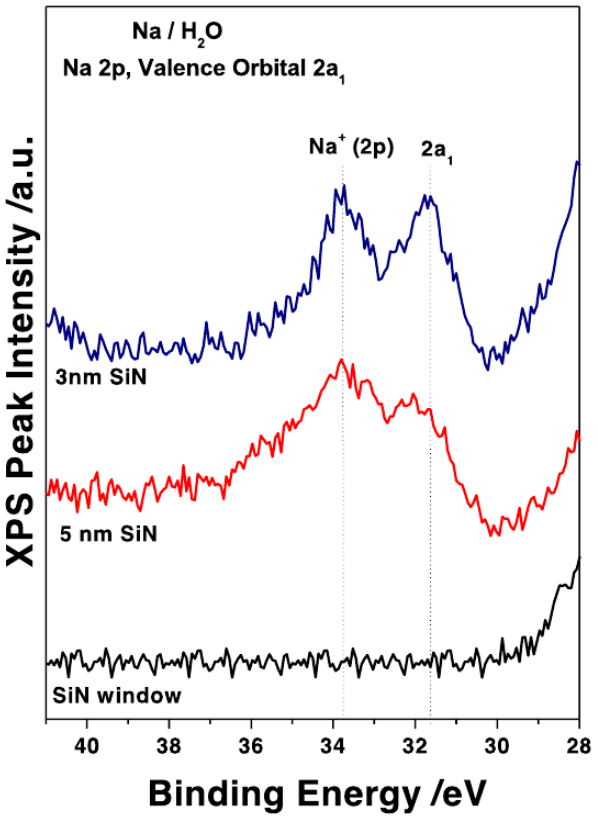


Figure 5. Liquid water orbital $2a_1$ recorded from the solution inside the E-cell. The ionic state Na^+ (2p) was also recorded from the solution indicating the presence of dissolved ions into the water.

IV. Conclusions

We have demonstrated a robust in-situ experimental method for probing the chemical state of iron oxide nanoparticles in aqueous environments using XPS through ultrathin SiN membranes. Our findings reveal that Fe_2O_3 nps interact strongly with liquid water, leading to partial reduction of Fe^{3+} to Fe^{2+} and even lower oxidation states, which cannot be captured by traditional XPS analysis of dried samples. Depth-resolved measurements show a stratified structure composed of an outer hydroxide layer, a Fe_2O_3 core, and a stable FeOx intermediate. Additionally, the detection of liquid-phase molecular orbitals and dissolved Na^+ ions confirms the presence and analyzability of the liquid environment inside the e-cell. This work validates the use of SiN-based e-cells for in-situ XPS analysis of solid-liquid interfaces and opens new possibilities for studying redox reactions, surface chemistry, and ionic species in fields ranging from catalysis and energy storage to environmental science.

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