



## In situ photoelectron spectroscopy at the liquid/nanoparticle interface

Matthew A. Brown <sup>a,\*</sup>, Inga Jordan <sup>b</sup>, Amaia Belouqui Redondo <sup>a</sup>, Armin Kleibert <sup>c</sup>,  
Hans Jakob Wörner <sup>b</sup>, Jeroen A. van Bokhoven <sup>a,c</sup>

<sup>a</sup> Institute for Chemical and Bioengineering, ETH Zurich, CH-8093 Zurich, Switzerland

<sup>b</sup> Laboratory of Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland

<sup>c</sup> Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

### ARTICLE INFO

#### Article history:

Received 26 November 2012

Accepted 21 January 2013

Available online 28 January 2013

#### Keywords:

Liquid microjet

In situ X-ray photoelectron spectroscopy

Time-resolved photoelectron spectroscopy

Liquid/solid interface

Nanoparticles

Colloidal suspension

### ABSTRACT

In this prospective, an overview of in situ photoelectron spectroscopy at the liquid/nanoparticle (NP) interface is presented. Recently it was shown that by using a liquid microjet in combination with synchrotron radiation electronic structure measurements at the aqueous solution/nanoparticle interface can be realized. We discuss unique aspects of this experiment including the liquid microjet source while outlining potential applications and opportunities. A special section is devoted to laboratory based in situ ultrafast pump-probe photoelectron spectroscopy at the liquid/nanoparticle interface. In situ photoelectron spectroscopy at the liquid/nanoparticle interface has potential to benefit researchers across several disciplines including chemistry, physics, biology, materials science and nanomedicine.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

The liquid/solid interface is ubiquitous in nature, essential to (electro-) catalysis and colloidal science, and at the heart of many fundamental atmospheric chemistry processes. The liquid/solid interface is however very difficult to investigate on an atomic/molecular level because it is buried between two condensed phases. Many believe that the development of new approaches for investigating this buried interface is the next big challenge for the surface science community [1,2]. In this light, common analytical tools have been successfully adapted to liquid/solid interfaces, each with their strengths and limitations. Among the most successful to date are vibrational spectroscopies such as infrared (IR) [3,4] and sum frequency generation (SFG) [5], while other techniques such as XAS [6], nuclear magnetic resonance (NMR) [7] and quartz crystal microbalance (QCM) [8] are emerging as strong candidates. A comprehensive list of spectroscopic techniques available for the characterization of liquid/solid interfaces complete with a list of their strengths and limitations can be found elsewhere [1]. The application of X-ray photoelectron spectroscopy (XPS) to in situ measurements at the liquid/solid interface has been largely discredited for technical reasons [2] that have been overcome with the development of the liquid microjet, high brilliance synchrotron radiation facilities and modern day state-of-the-art electron spectrometers [9]. In the traditional sense where one considers the solid under investigation to have the form of a single crystal substrate characteristic of UHV surface science [10–12], probing the liquid/solid interface

using soft X-ray photoelectron spectroscopy is almost certainly out of the question. However, if one instead considers the solid to have the form of a nanoparticle (NP) and this NP is suspended in solution, then immediately XPS at the liquid/NP interface becomes a reality using the liquid microjet in combination with synchrotron radiation [13,14].

Faubel introduced his liquid microjet in 1997 [15], and in doing so reinvigorated [16,17] the research field of electronic structure measurements at the vapor/liquid interface. The design of Faubel's liquid microjet enables in situ soft X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS) studies of high vapor pressure solutions, in particular aqueous solutions, by creating a free flowing equilibrated filament in vacuum. Now, some 20 years onward of Faubel's invention several international groups have built their research programs based on liquid microjets [18–20]. A search of the liquid microjet literature reveals a broad scientific record of studies including the electronic structure of liquid water [21,22], spatial distributions of atmospherically relevant atomic [23] and molecular ions [24] in aqueous solutions, and the structures of acid base equilibria pairs of organic molecules [25]. There are now too many scientific papers that have resulted from using the liquid microjet to provide an exhaustive list and the reader is encouraged to see recent reviews on the subject [26–28]. All of these papers, however broad their specific application, share a common theme, which is that they are studies of solutes in solutions or solvents themselves at the vapor/liquid interface.

In this prospective we highlight recent developments as well as future opportunities related to performing in situ XPS at the liquid/NP interface. Our goal is two-fold: First, to make the reader aware of current developments in the field, and second, to inspire more research groups to enter

\* Corresponding author. Tel.: +41 446323048.

E-mail address: [matthew.brown@chem.ethz.ch](mailto:matthew.brown@chem.ethz.ch) (M.A. Brown).

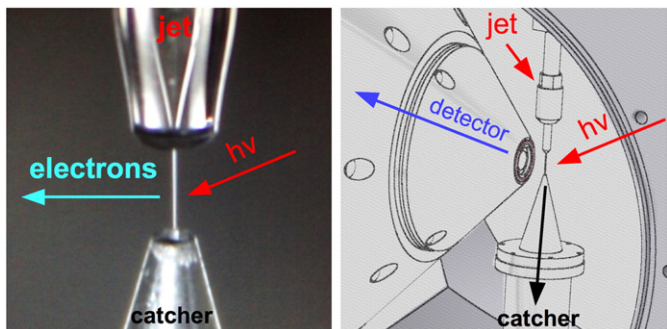
this field at its infancy when advances and innovations brought about by creativity and diversity are strongly needed. This prospective is divided as follows: First we review the principles of the liquid microjet as an injection source of NP-containing suspensions and discuss select aspects of XPS that are needed for these experiments. We then highlight the existing literature of in situ XPS at the liquid/NP interface and give examples of potential future applications of this new experiment. We devote a separate section to ultrafast processes at the liquid/NP interface before concluding with an outlook.

## 2. The liquid microjet

The liquid microjet is shown in Fig. 1 and a complete description has been reported previously [26–28]. Here, we briefly describe some of the important aspects of the liquid microjet that are specifically related to performing in situ XPS measurements at the liquid/NP interface.

Nanoparticle suspensions are often more viscous and turbid than neat solvents or solutes in solutions and therefore present a challenge for expansion through the liquid microjet nozzle which has a diameter typically of 20  $\mu\text{m}$  or smaller. For this reason our studies have used nozzles with diameters that vary from 28 to 50  $\mu\text{m}$ . The increased diameter of these nozzles greatly reduces the frequency of clogging and provides stability on the order of hours. A drawback to the increased nozzle diameter is that the volumetric flow rate of the solution under study is higher. A typical flow rate for NP suspensions has been 0.75 ml/min, or about 25% higher than used for solvents and solutes in solutions [25]. A comprehensive in situ XPS study of a NP suspension where one collects a survey spectrum as well as several high-resolution narrow regions scans at differing electron kinetic energies requires a volume on the order of 100–200 ml. For the moment this makes certain specialized (and expensive) NP's unrealistic for study by in situ XPS. Several possibilities are available to overcome this issue, with the most obvious being to recycle the NP suspensions by 'catching' them and re-injecting the sample for further measurements [29]. Our liquid microjet chamber at the Swiss Light Source [18,30] is set up for this possibility but conclusive and comprehensive studies addressing the effects of radiation on the NP suspensions must first be established before the solutions can be recycled.

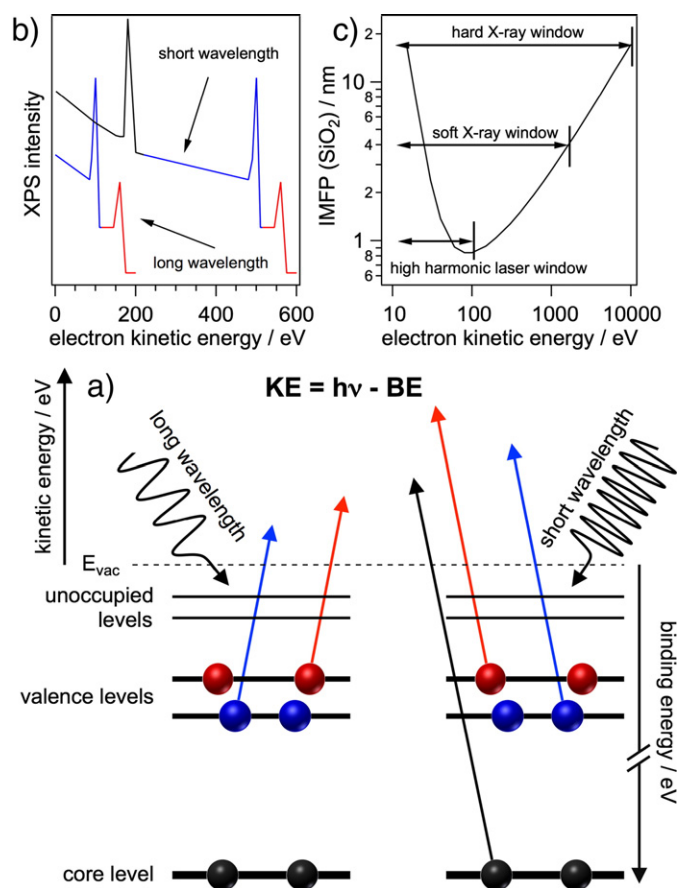
One advantage of the liquid microjet is that the interface is continuously refreshed at a rate of  $\sim 50$  m/s and remains contamination-free [23]. Our XPS measurements [13,23–25] have shown no sign of adventitious carbon impurities that plague many interfacial liquid studies that are done in the static regime [31] and allows for in situ XPS measurements on clean interfaces. In addition, because the interface is continuously refreshed there is no sign of beam damage that is often observed in static measurements at the vapor/liquid interface [32,33].



**Fig. 1.** (Left) A 50  $\mu\text{m}$  liquid microjet in operation at the Swiss Light Source. The direction of liquid flow is from top to bottom. The liquid is expanded at a velocity of  $\sim 50$  m/s into the measurement chamber through a micron sized quartz nozzle. The liquid filament is then irradiated with X-rays before being 'caught' by the catcher and removed from the measurement chamber. (Right) The liquid microjet, incident photons, and the electron detection axis are all normal to one another.

## 3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy [34] is one of the most powerful techniques to determine the electronic structure of solid-state materials. In the simplest description an XPS measurement is the detection of the kinetic energy of primary (and secondary) electrons emitted from the sample following irradiation by monochromatic photons and provides element-specific, local atomic/molecular environment information (Fig. 2a). From the energy distributions of the photoelectrons (chemical shift), details about the local electronic structure, and hence of the geometric structure of a given atomic/molecular species, within its distinct chemical environment can be inferred. Performing XPS measurements with a tunable incident photon source, provided for example by a synchrotron, provides additional benefits. By varying the incoming photon energy, the kinetic energy of the emitted photoelectrons can be varied, which in turn controls the surface sensitivity of the experiment according to the energy dependent inelastic mean free path (IMFP) of the electrons (Fig. 2c) [35,36]. Using incident X-ray energies that result



**Fig. 2.** In the simplest description an XPS experiment is the detection of the kinetic energy of primary (and secondary) electrons emitted from the sample following irradiation by monochromatic photons and provides element-specific, local atomic/molecular environment information. The kinetic energy of the photoelectrons are governed by the Einstein equation,  $KE = hv - BE$ , where  $BE$  is the orbital binding energy and  $hv$  the energy of the incident photon. (a) Performing XPS measurements using a variable incident X-ray source such as a synchrotron provides the additional benefits of being able to access deeper lying core levels and the ability to control the surface sensitivity, or probe depth, of the experiment. By using long(er) excitation wavelengths (schematically represented by 200 eV in (b)) the photoelectron signal originates primarily from the surface of the sample because of the short inelastic mean free path of the photoelectrons. At low incident photon energies lower lying core-levels may not be accessible as the photon energy is below the orbital threshold. At short(er) excitation wavelengths (schematically represented by 600 eV in (b)) the photoelectron signal begins to tend towards bulk sensitivity and core-levels become accessible. An inelastic mean free path curve for  $\text{SiO}_2$  is shown in (c) [37] with the typical KE windows that can be collected using high harmonics from tabletop laser systems, soft X-ray and hard X-ray synchrotron beamlines.

Download English Version:

<https://daneshyari.com/en/article/5422486>

Download Persian Version:

<https://daneshyari.com/article/5422486>

[Daneshyari.com](https://daneshyari.com)