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In situ photoelectron spectroscopy at the liquid/nanoparticle interface

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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.

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

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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 μm or smaller. For this reason our studies have used nozzles with diameters that vary from 28 to 50 μm. 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 ~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].

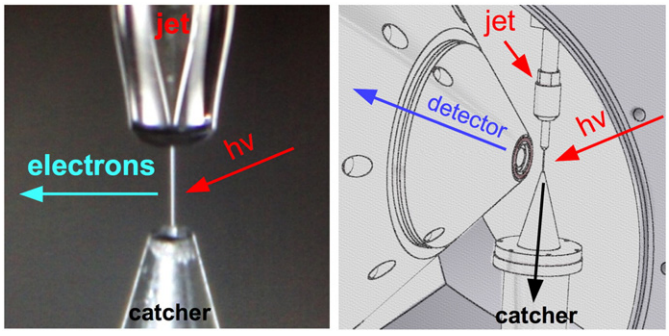

Fig. 1. (Left) A 50 *um* liquid microjet in operation at the Swiss Light Source. The direction of liquid flow is from top to bottom. The liquid is expanded at a velocity of ~50 m/s into the measurement chamber through a micron sized quartz nozzle. The liquid filament is then irradiated with X-rays before 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

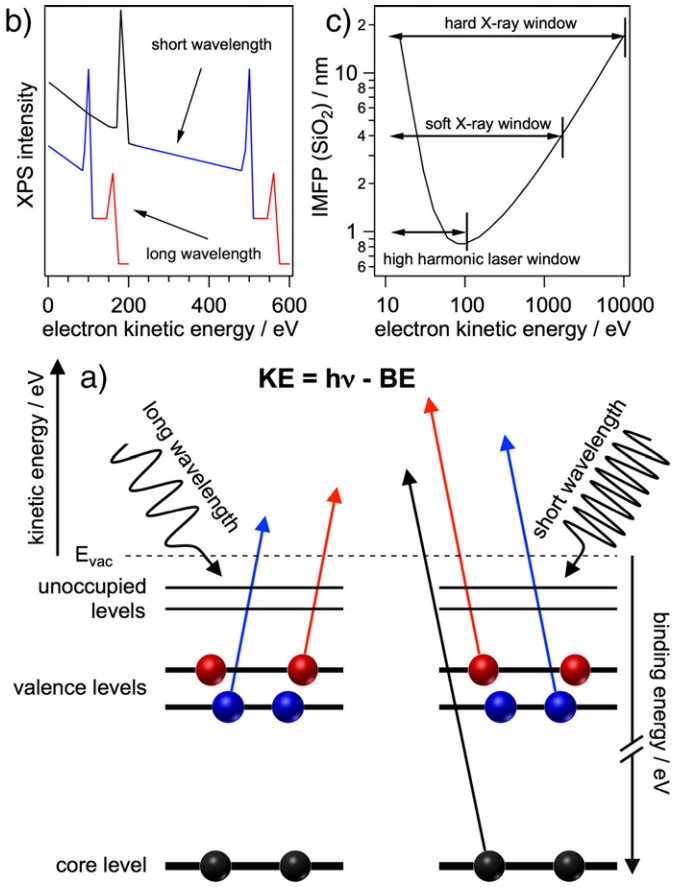

Fig. 2. In the simplest description an XPS experiment is the detection of the kinetic energy of primary (and secondary) electrons emitted from the sample following irradiation by monochromatic photons and provides element-specific, local atomic/molecular environment information. The kinetic energy of the photoelectrons are governed by the Einstein equation, KE = hν – BE, where BE is the orbital binding energy and hν 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 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.

in photoelectrons being emitted at kinetic energies near the minimum of the IMFP curve (Fig. 2c, ca. 80 eV) the surface sensitivity of the experiment can be maximized. At high incident X-ray energies the signal is more heavily weighted by bulk contributions. It is however, important to remember that photoelectron spectroscopy is an integrated technique, and while performing the experiment at high electron kinetic energy is generally accepted to yield information primarily on the bulk electronic structure, information originating from the interface is also contained in the signal, and appropriate techniques need to be taken to ensure the proper interpretation of the results.

A major advantage of in situ XPS, compared with for instance IR, SFG, XAS, NMR and QCM, is that it is inherently surface sensitive, provides high sensitivity (sub-monolayer electronic structure information can be easily detected with XPS), and can be used across a very broad energy range which allows access to element-specific valence or core states with varying probe depth. In situ XPS is however not without its limitations. Energy analyzers adapted to the non-traditional vacuum environment of the liquid microjet must be used and are expensive and synchrotron radiation facilities, while growing in number, are limited.

4. General considerations of XPS at the liquid/nanoparticle interface

Bearing in mind that the liquid/NP interface is a buried interface the main limiting aspect of XPS at the liquid/NP interface is the signal intensity that can be obtained. As was shown in our 2011 study [13] for a NP that resides at the vapor/liquid interface, photoelectrons generated from the surface of the NP, but below the vapor/liquid interface, are strongly attenuated by the solvent and contribute a fraction of the signal intensity (this is photoelectron kinetic energy dependent) they would in vacuum when the water layer is absent.

The spatial distribution of the NP's in solution relative to the vapor/liquid interface also plays a significant role in determining the signal intensity that can be recorded. This is demonstrated in Fig. 3 by calculating the relative XPS signal intensity for a 10 nm NP at four different IMFP's (the signal intensity for each IMFP has been set equal to unity when the NP resides in contact with the vapor phase, d = 0) as a function of NP distance below the vapor/liquid interface. The signal intensity is most affected for low IMFP's as the NP moves away from the vapor/liquid interface, where the surface sensitivity of the experiment is highest. If we assign 30% signal intensity as a cutoff, under which the signal is too low to perform in situ measurements then it is easy to see the added benefit of performing experiments using hard X-ray excitation energies where the photoelectron kinetic energy is greater than ca. 2000 eV and IMFP's are above ca. 5.0 nm.

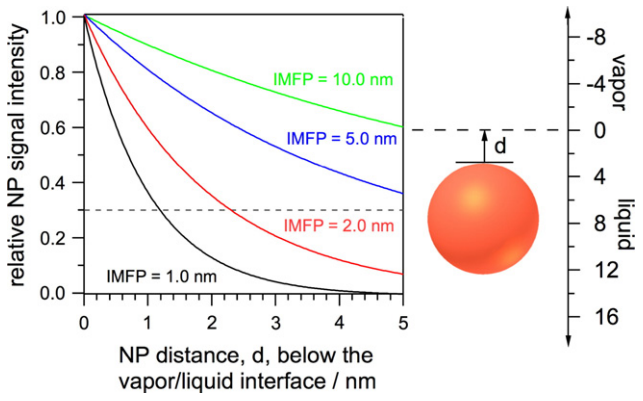

Fig. 3. Relative XPS signal intensity at four different IMFP's, 1.0, 2.0, 5.0 and 10.0 nm, as a function of particle distance below the vapor/liquid interface. The diameter of the particle is 10.0 nm. For each IMFP the intensity at d = 0 has been set to unity. There is a clear benefit to using hard X-ray energies when the nanoparticle resides several nm's below the vapor/liquid interface.

5. The liquid/nanoparticle interface

Our first in situ XPS study at the liquid/NP interface focused on charge-stabilized (ligand-free) colloidal silica in aqueous solution [13]. We were able to identify a distinct electronic structure in the Si 2p spectrum, seen as a shoulder to the low binding energy side of the main Si 2p peak at pH 10, that is not seen in ex situ vacuum measurements. Based on the acid–base equilibrium of silica-silanol groups the low binding energy structure was assigned as deprotonated silanol, ≡Si–O$^-$, whereas the main component was assigned to tetrahedral coordinated bulk silica. We also reported measurements as a function of photoelectron kinetic energy (probing depth) and were able to conclude that deprotonated silanol groups are present only at the water/silica interface and not in the interior of the NP's.

Around the same time, Björneholm and coworkers [14] used XPS in combination with the liquid microjet to study ligand stabilized 70 nm silica particles in aqueous solution. Their study demonstrated two important concepts. First, the hydrophobic nature of the ligand strongly enhanced the surface (vapor/liquid interface) concentration of the NP's and allowed to study dilute suspensions (~15 nM). Second, by using a ligand with distinct spectroscopic signatures they were able to show that the ligand-NP interface can be interrogated using in situ XPS.

With NP's coming in nearly every size, shape and composition imaginable the liquid/NP interface presents a nearly endless array of differing combinations that can be studied at an atomic/molecular level using in situ XPS. In Fig. 4 we highlight some of the systems that are of particular interest to this field of study and discuss them accordingly.

In situ XPS has been [13,14], and will continue to be used to study homogeneous NP's in liquid solutions. These studies can identify surface versus bulk electronic structures as a function of NP size, the influence of solution pH on surface structure and speciation, and the role of electrolyte concentration in regulating surface charge density [38]. Nanoparticles that are not soluble and/or stable in aqueous environments can be studied in organic solvents, which are fully compatible with the liquid microjet.

The adsorption of (reactant) molecules, or the identification of structured solvent layers at the NP interface can also be determined using in situ XPS. As an example of the latter case, the adsorbed water layer at the silica NP surface, both its hydrogen bonding structure and properties, plays a crucial role in directing microscopic wetting and spreading [39]. These phenomena remain poorly understood at the atomic level because of the lack of microscopic probes available for the liquid/solid interface and in situ XPS in combination with the liquid microjet provides great opportunity to explore these types of NP interfaces. The quantitative nature of XPS also makes it ideal to determine surface coverage, be it of a self-assembled monolayer (SAM) on the surface of a NP [40] to wanted or unwanted doping/impurities within the NP structure.

By varying the probe depth of the experiment core-shell type NPs can be studied and the structure of the solid–solid interface determined. These studies will be used to help understand and finally to control the properties of various systems in liquid solutions ranging from quantum dots to magnetic NPs. The latter are of great interest for applications in fields such as catalysis [41], magnetic fluids [42], data storage [43], and biomedicine [44] and chemical methods are nowadays available to produce large amounts of such particles [45]. However, long term instability, agglomeration, undesired chemical reactivity and non-uniform properties even in mono-disperse systems are still issues that need to be solved [46]. XPS at the liquid/NP interface is a promising tool to study these phenomena in an environment that is relevant to the applications. The possibility to identify surface and bulk properties will enable to understand the impact different layers play in the functionalization or passivation of the magnetic properties. For instance, oxide layers may help to obtain chemically inert nanoparticles such as CoO (shell)/Co(core). However, the CoO shell is known to be antiferromagnetic which in turn induces a magnetic coupling between the shell and ferromagnetic core of the nanoparticle

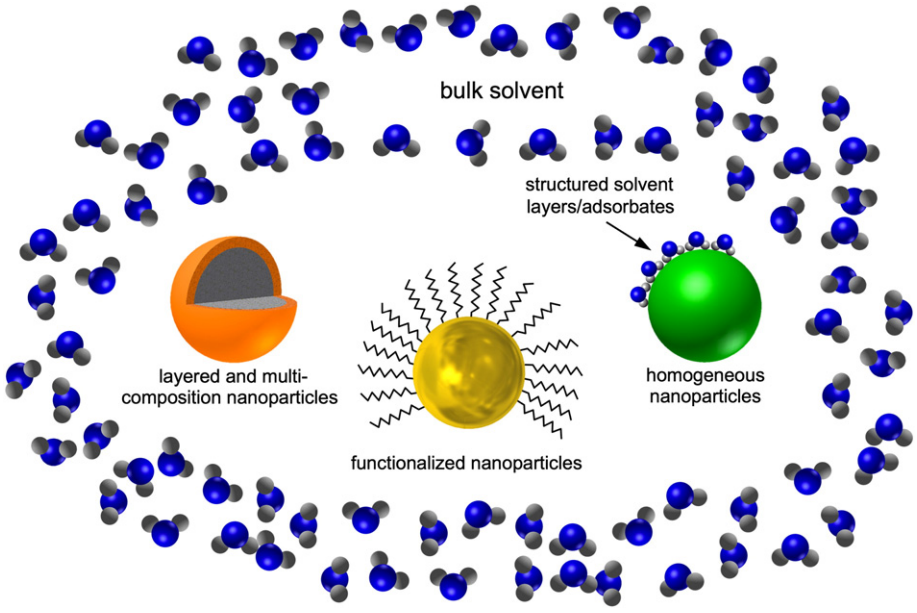

Fig. 4. In situ XPS at the liquid/NP interface provides an opportunity to study a variety of NP type systems in liquid solutions. Some of the potential systems are shown here and include homogeneous NPs, layered and multi-composition NPs, and functionalized NPs.

[47]. This effect significantly alters the particles effective magnetic anisotropy when compared to pure metallic Co NPs. Knowing the properties at the core/shell interface (interdiffusion, chemical order, stoichiometry) will greatly help to optimize or suppress the coupling effect depending on the desired application of the particles.

In situ XPS may also be used to follow chemical reactions (and syntheses) in the liquid phase by taking advantage of the intrinsic time resolution provided by the continuous delivery of the liquid through the liquid microjet. Here a chemical reaction would be initiated in the supply reservoir of the liquid microjet and the liquid continuously injected into the measurement chamber to yield time dependent (on the time scale of minutes and longer) electronic structure information. To date, this remains to be explored but provides potential opportunities. For instance, the synthesis of complex nanostructures can be followed in situ as the reactants are transformed into the final NP structure [46] to yield detailed information on the intermediate electronic states. Such investigations will help to further optimize chemical synthesis methods used to prepare functional NPs. Most interesting here are synthetic strategies that work at room temperature and ambient pressure such as co-precipitation [46], which is capable of producing iron oxide nanoparticles at large scale using water as the solvent. A critical, yet poorly understood step of the synthesis process is the addition of organic ions that are required to stabilize the particles. The addition of oleic acid, for example, is believed to result in two competing mechanisms at the NP surface, one that promotes and the other that prevents nanoparticle growth. A detailed understanding of the early stage of particle growth and the effect of the organic ions in the synthesis process will help to improve size and shape control in respective iron oxide nanoparticles which are particularly important for applications in medical diagnostics and therapeutics. Finally, while not shown schematically in Fig. 4 we expect in situ XPS to attract interest from the biological and nanomedicine communities to study, for instance, the interaction of NP's with proteins and cells in their native aqueous environment.

6. Ultrafast processes at the liquid/nanoparticle interface

Many fundamental processes occur on time scales that are too fast to be revealed by static XPS and require the additional dimension of time. By combining the liquid microjet with a pump-probe experiment ultrafast in situ photoelectron spectroscopy at the liquid/NP interface will be realized. Probing excited states of solvated particles and mapping the temporal evolution of their electronic structure then becomes possible.

In a time-resolved photoelectron experiment the excited state of interest is prepared by a pump pulse and subsequently ionized by a probe pulse. The time-of-flight distribution of the photoelectrons is recorded as a function of the delay between the pump and probe pulses [48]. The time resolution of the experiment is only limited by the cross-correlation function of the pump and probe pulses and is independent of the time it takes to record a spectrum. This type of experiment requires significantly different infrastructure compared to static XPS measurements that are done using a synchrotron radiation source and a hemispherical energy analyzer. The general setup is shown in Fig. 5. The X-ray source used in static measurements is replaced by a source of high-order harmonics generated in a rare gas target by femtosecond pulses from a titanium:sapphire laser system. The pump pulses are generated by nonlinear optical frequency conversion. The time delay between the pump and probe pulses is controlled by a delay line. The hemispherical energy analyzer is replaced by a time-of-flight (magnetic bottle) spectrometer. Information on the orbital binding energies and the population dynamics of selected vibronic states can be extracted from the photoelectron time-of-flight spectrum and the corresponding signal intensity as a function of the pump-probe delay time.

An ultrafast pump-probe photoelectron spectroscopy experiment is perfectly suited to observe processes that are associated with a change in orbital binding energy such as electron transfer and/or structural changes. For instance, transition metal complexes can be prepared in electronically excited states by the pump pulse, which then undergo geometrical changes due to vibronic coupling that give rise to measureable changes in orbital binding energies [49]. Light-induced charge transfer to a reactant bound on the surface of a NP catalyst can also be investigated. This includes, for example, electron transfer from the valence d-band of a supported transition metal catalyst into the anti-bonding orbital of a reactant/adsorbate, whereby the bond is weakened and a pathway towards a chemical reaction is opened [50]. An obvious field where ultrafast in situ photoelectron spectroscopy at the liquid/nanoparticle interface will thrive is in dye-sensitized solar cells based on NP's [51]. With time-resolved photoelectron spectroscopy information about the binding energies, the time scale and efficiency of electron transfer from the electronically excited state of the dye into the semiconductor valence band, and

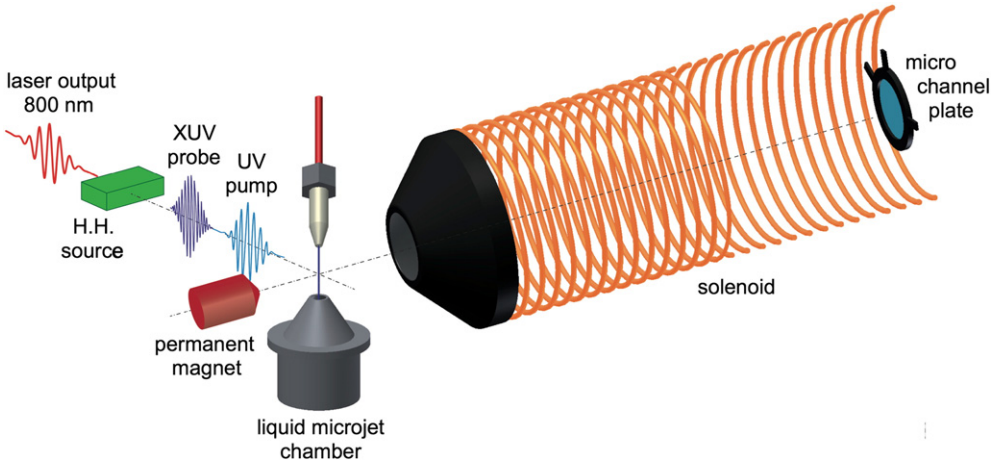

Fig. 5. The general setup of a liquid microjet pump-probe photoelectron spectroscopy experiment. A Ti:Sapphire laser combined with high-harmonic generation and nonlinear frequency conversion is used to generate both the pump and probe pulses. A delay line controls the time delay between the pulses. The photoelectron detector is a time-of-flight spectrometer equipped with a micro channel-plate (MCP) detector.

finally the quantum yield of the dye should be accessible. Depending on the interaction between the NP and the dye various electron transfer mechanisms are conceivable and time-resolved photoelectron spectroscopy would help to reveal and understand them.

We expect the results of such experiments to have important implications for the understanding and tailoring of the electronic structure and dynamics of nanoscale systems that have found a wide range of scientific and technological applications in photochemistry, solar cells and heterogeneous catalysis.

7. Conclusion

We have provided an overview of in situ photoelectron spectroscopy at the liquid/nanoparticle interface using a liquid microjet. In situ photoelectron spectroscopy is a powerful surface-sensitive analytical tool that has potential to benefit researchers across several diverse disciplines. To exploit its full potential in situ photoelectron spectroscopy needs to attract a larger user pool that fosters cross collaboration among different research communities. There is also need for more dedicated endstations for such experiments at synchrotron and free electron laser facilities around the world.

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