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Photoemission spectromicroscopy in materials science and in neurobiology

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The combination of photoemission spectroscopy and high lateral resolution is rapidly evolving from feasibility tests to experiments. We discuss several important recent developments and results.

1. INTRODUCTION

Photoemission spectromicroscopy [1-5] has rapidly evolved from feasibility tests to real experiments. We will discuss some of the most significant recent results, obtained both in the "scanning" and "electron-imaging" versions of this technique [1-5].

For many years, the photoelectric effect has been a source of extremely valuable information on the electronic, chemical and electronic structure of a variety of systems [6]. The amount and quality of information depends primarily on the degree of sophistication of the technique for its extraction. In the old days, the only relevant parameter was the electron energy, and "photoemission" was a synonym of photoelectron energy distribution curves, that provided information on the density of electronic states [6].

The advent of synchrotron radiation unlocked several other parameters, the most important of which were the photon energy and the angle of emission. This transformed photoemission from an "energy spectroscopy" into a "wavevector spectroscopy" [6]. This huge progress notwithstanding, most of the information potentially carried by the photoelectric effect remained untapped and waiting for more powerful extraction techniques.

The past two years have brought again significant progress, mostly in two directions. First of all, the resolution standard improved by approximately one order of magnitude, reaching ≈10 meV of energy resolution -- which makes it possible to explore entirely new classes of collective phenomena. The best known consequence of this improvement is the study of high-temperature superconductors and the symmetry of their collective electronic state [7].

Second, it has become possible to combine photoelectron (energy) spectroscopy and high lateral resolution, which produces a new technique known as *photoelectron spectromicroscopy*.[1-5] The progress of this technique has been quite spectacular, mostly based on advanced synchrotron sources but with some relevant exceptions [8].

The purpose of this article is not to discuss the technical details of these techniques, that have been analyzed in detail by other publications [1-5,8]. We will try instead to use some recent results and prove that the case for spectromicroscopy is compelling. These recent results are not those of feasibility tests, but of real experiments.

Perhaps the most relevant of them in materials science is the discovery by Coluzza et al. [9] that photoemission spectra of insulators are systematically affected by local charging effects. These makes it very difficult to use

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space-averaging spectra, since they can affect the lineshape, spin-orbit branching ratio and the apparent peak position.

Also relevant are the first spectromicroscopy results on clean semiconductor surfaces and on semiconductor interfaces, obtained by Cerrina et al. [10] and by Gozzo et al. [11,12]. These have revealed substantial lateral variations of important properties such as the clean-surface band bending, the Schottky barriers and the heterojunction band lineups.

Finally, we will discuss the first systematic application to a real biology problem: the study of the uptake of aluminum by neuron cultures, performed by De Stasio et al. in cooperation with Mercanti and Ciotti [13-15].

2. MATERIALS SCIENCE RESULTS

Coluzza et al. [9] used a SCIENTA ESCA 300 spectromicroscope (which can reach a spatial resolution of 27 micron) to systematically investigate a number of insulating systems. They found that their core-level photoemission peaks are affected by *local* charging effects, which cause rigid shifts in energy. The shifts' magnitude dramatically changes from place to place on the scale of 30-300 micron.

Photoemission core peaks taken without lateral resolution can, therefore, be the superposition of different local components. This affects the apparent peak's lineshape, position in energy and spin-orbit branching ratio. The consequences are far-reaching: virtually every conventional photoemission spectrum of insulating materials could be affected.

Local charging effects are evident, for example, in the single-crystal NaCl Cl2p and Na1s spectra of Fig. 1, taken with a charge-neutralizing flood gun. The three lower sets of spectra concern three different adjacent 40 × 300 micron^2 areas on a straight line (similar results were obtained for spectra from 40 × 40 micron^2 spots). The spatial differences in peak energy position are evident and equal for the two core levels, suggesting an electrostatic effect, such as, indeed, charging.

The topmost curves of Fig. 1 are normalized averages of the spatially-resolved spectra, and provide a rough idea of the effects of spatial integration in a conventional photoemission experiment. We see, in particular, that the apparent linewidth is larger than that of the spatially-resolved components.

Similar results were found for all of the insulating systems that were explored, specifically: layers of silicon oxide on Si(100) [9], granular Sc_2O_3 pellets [9], CsI single crystals [16], zeolite [9], diamond films [17], and Cu-containing superconducting oxides [16]. No shifts were found for clean gold and silver films.

The causes of the electrostatic shifts' spatial variations are not clear, and could be different for different samples and/or different experiments. The experimental conditions can play a role, for example, the possible mismatch between flood gun and x-ray beam even after flood gun optimization. The intensity distribution of the photon beam could also play a role, although we did not find a correlation with the spatially-changing rigid shifts.

Possible *intrinsic* causes of the spatial variations include inhomogeneities in the specimen's local resistivity (either bulk or surface), and in the surface morphology, which could for example produce spatially-varying electrostatic charging or shadowing effects of the photon beam and/or the flood gun.

Whatever their causes, the observed spatially-varying rigid shifts makes it difficult to derive fine chemical information from the lineshape analysis of spatially-integrated spectra of insulators -- and may force a revision of many accepted notions on such spectra.

The case for spatial resolution in materials-science photoemission, that is already quite compelling based on the above results on insulators, is further enhanced by a series of results on semiconductor surfaces and interfaces [10-12]. Photoemission spectroscopy has been very extensively used to study and measure energy barriers at such surfaces and interfaces [6]. For example, it has been used to measure Schottky barriers.

All of these studies, however, did not touch the issue of the possible lateral variation of the barriers. The first spatially resolved experiments have almost always revealed that the barriers change from place to place on the scale of microns [10-12]. This is true for the three major classes of barriers: those due to band bending at clean surfaces [10], the Schottky barriers [11] and the heterojunction band discontinuities.

The results obtained until now concern, of course, only a very few systems, most of them rather specialized [10-12]. It is not possible, therefore, to assess how general these findings are. If they will prove indeed to be general, then they may require a revision of the standard way to consider semiconductor interface barriers. Such barriers would have to be considered as local rather than non-local entities, and one would have to adopt a "microscopic" rather than a "macroscopic" point of view about them.

3. NEUROBIOLOGY RESULTS

The scientific case for photoelectron spectromicroscopy is even more compelling if one considers that lateral resolution makes it possible for the first time to use the photoelectric effect in the study of biological systems. Microchemical analysis is an essential tool in biology. Photoelectron techniques have had a minimal impact in this field, primarily because of their limited spatial resolution.

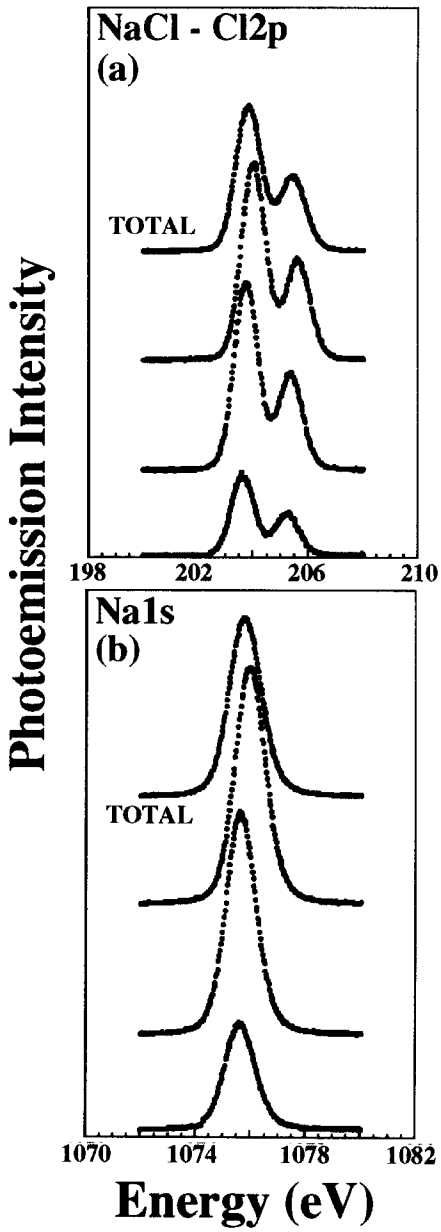

Figure 1. Spatially-resolved Alk$_\alpha$ photoemission spectra taken on single-crystal NaCl, for (a) the Cl2p and (b) the Na1s core levels. Spectra from three different adjacent 40×300 micron^2 areas along a line are shown, together with their normalized sum. The spectra were taken with a flood gun. Data from Coluzza et al. [9].

The situation is radically changing with the advent of spectromicroscopy. The most significant results have been obtained with the XSEM instrument developed by Brian Tonner and coworkers [18]. The first systematic XSEM investigation in biology concerned the distribution of toxic elements like aluminum in neural specimens [19], which are suspected to be involved in neuropathologies such as the Alzheimer's and Parkinson's diseases.

Figure 2 shows an XSEM micrograph of a portion of a rat cerebellar neuron culture on a gold substrate [20]. Note that the lateral resolution (better than 0.5 micron) enables one to identify the details of each cell in the neuron network.

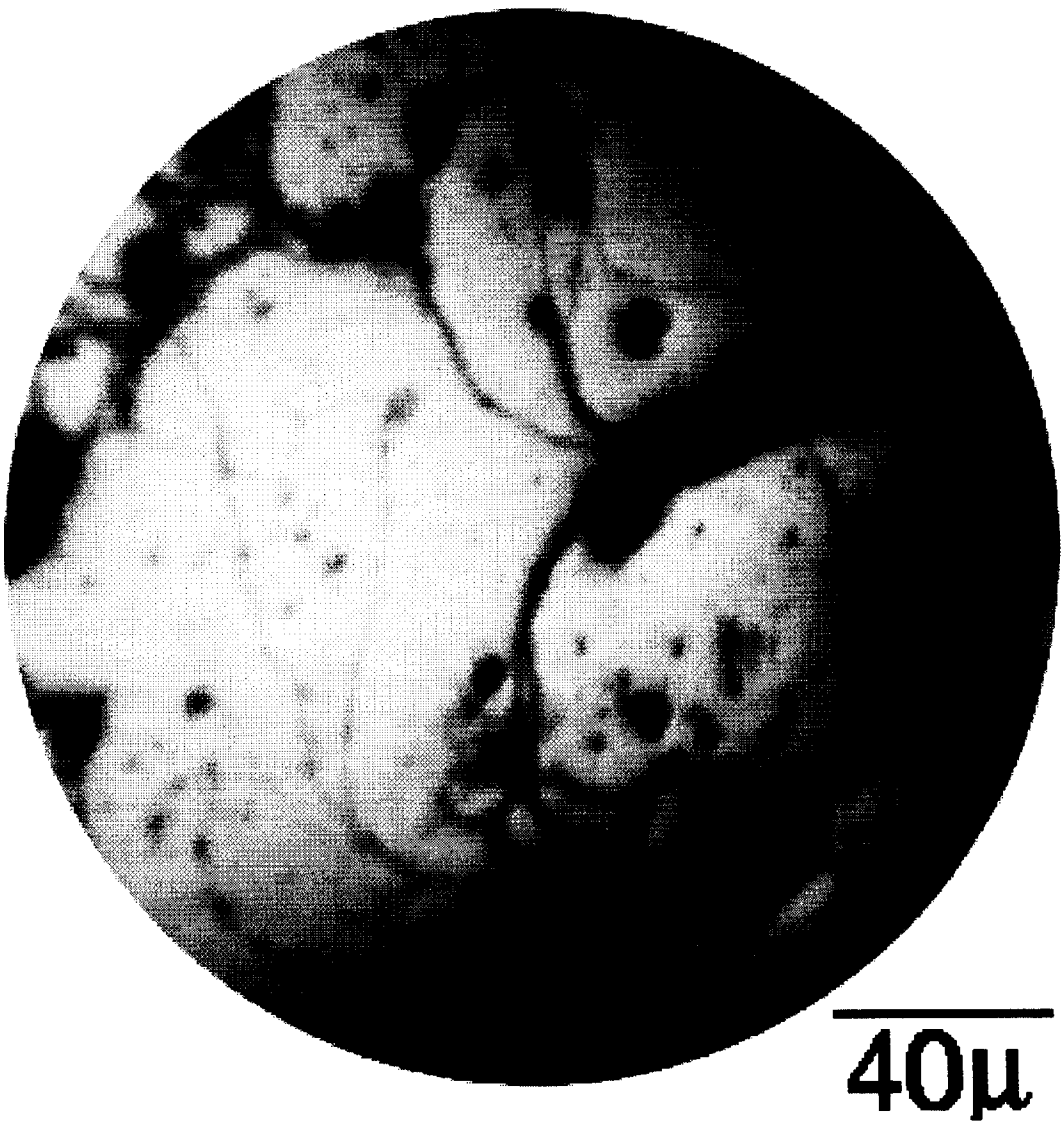

Figure 2. (a) XSEM microimage from a rat cerebellar granule cell culture. Data from De Stasio et al. [20].

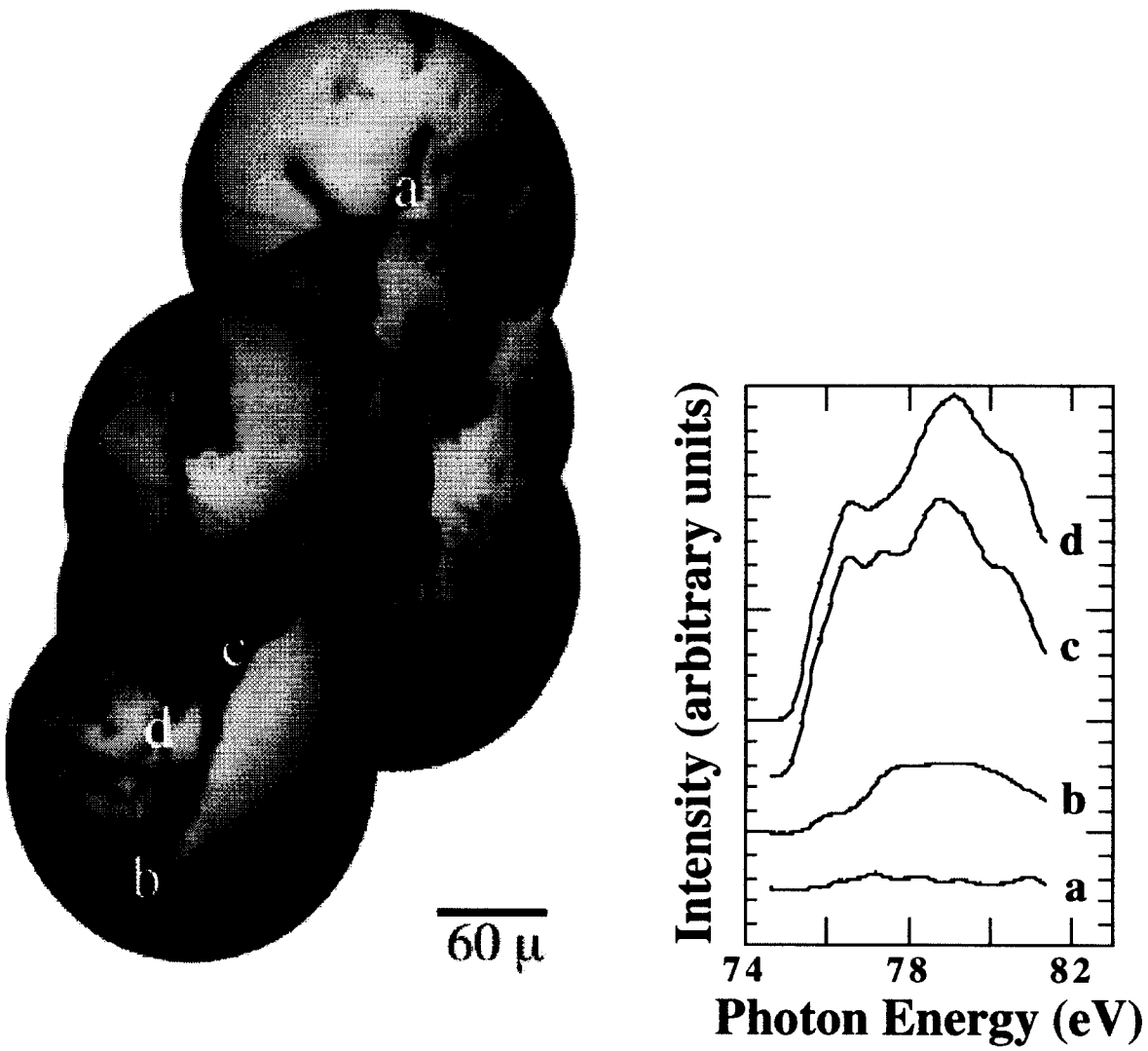

Figure 3. (a) XSEM microimage from a Purkinje neuron culture. (b) Aluminum-edge XSEM spectra taken in the marked areas of Fig. 2a. Data from De Stasio et al. [15].

The spatial distribution of aluminum was explored by taking XSEM absorption spectra in the spectral region of the Al2p edge in different portions of the specimens. Figure 3 shows an example of this approach,[15] with a micrograph and spectra taken at specific points, revealing the presence or absence of aluminum.

The most significant conclusions of these studies are the following. Aluminum is very localized in the culture. In the case of granule cell cultures, aluminum was *not* found in the granule cells, but only in very few (3 out of $\approx 10^5$) cells, identifiable from their morphology as Purkinje or glial cells [14].

The data suggest, therefore, a special role of such cells in the uptake of aluminum. We recently tested [15] this intriguing hypothesis: Mercanti and Ciotti developed an innovative method to produce cultures that predominantly contain Purkinje neurons [21]. We exposed three of these cultures to aluminum ions in solution, and found by XSEM a statistically much larger cells with aluminum than in the previous studies. The results of Fig. 3 concern indeed one of these cultures [15].

4. CONCLUSIONS

In summary, a series of materials science and neurobiology results demonstrate that photoelectron spectromicroscopy is already beyond its infancy stage, and is in fact a mature technique, absolutely required in both domains. The future expansion of this technique is likely to be accelerated by the advent of the new ultrabright synchrotron sources ELETTRA [22] and ALS, and by the foreseen commissioning of even brighter sources like the SLS in Switzerland and SOLEIL in France. At any rate, the few examples that we discussed clearly show that lateral resolution in photoemission is no longer a luxury, but an essential feature, very much like the photon energy tunability or angular resolution.

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