High-resolution Electronic and Chemical imaging of wonder nanomaterials beyond graphene

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Abstract. Despite the great progress made recently in spectroscopic imagery and even the remarkable success achieved, the challenge still remain concerning the precise determination of the chemical and electronic imagery of advances materials, which usually are available as heterogeneous large crystals or tiny homogeneous monocrystals. Here we report, a recently developed novel X-ray microscope, labelled, k-microscope or NanoARPES (Nano Angle Resolved Photoelectron Spectroscopy) particularly well suited to provide both high resolved chemical and electronic information in the real and reciprocal space of complex materials with nano-scale resolution.

1. Introduction
In today’s state-of-the-art material science, length scales from the nano- to the mesoscopic scales control and characterise chemical and electronic properties of matter. In recent decades we have witnessed exponential advances in the development of different areas of new nanotechnologies. These advances, seen particularly important in nanoelectronics, nanomagnetism and nanochemistry, among others, affect almost every aspect of our lives and are major players in our evolution towards the ‘information and automation age’.

New materials are often initially isolated or synthesized as small crystallites, which makes difficult their precise exploration. Also, it can be difficult to produce materials without fluctuations in their chemical composition, bringing out heterogeneities at variable scales. Polycrystalline materials, with chemically homogeneous and well-structured grains are also frequent, where the crystalline orientation is challenging to unravel as well as its consequences on the transport and magnetic properties are unknown. In the field of nano-objects also, even if these smart “building blocks” may show remarkable properties, they would have remained unexploited if, we had not developed new tools capable of viewing and scrutinizing objects on a wide range of scales, from a few microns to a few tens of nanometers.

Recently, great progress has been made as a result of the rapid expansion in the range of modern microscopies. However, if they have achieved nanometer spatial resolution, the challenge still remains to provide powerful high-energy-resolution spectroscopic tools for probed nano and micro-areas, as illustrated in Fig. 1. The challenge is to quantify and analyze the electronic properties of advanced materials on a nano and micrometer scale. For such a result, analysis of the electronic structure must be comprehensive, not only with regard to detection of core
levels, but especially to study the structure of delocalized valence bands, directly responsible for chemical bonds, electrical transport and the thermal and mechanical properties.

Traditionally, ARPES is the only technique capable of making sufficiently precise measurements of the dispersion of the band structure of materials in reciprocal space. The state of the art ARPES equipments installed at synchrotron radiation sources is such that it can offer energy and angular resolution of better than 5 meV and 0.1°, respectively. Yet, until now, no instrument has been capable of performing spatially resolved ARPES experiments on the nanometer scale.

In this paper, we present the first results of the NanoARPES microscope recently installed on the ANTARES beamline at the French Synchrotron SOLEIL[1]. With a spatial resolution of several tens of nanometers, this sophisticated instrument is able to carrying out the direct imaging of core levels and their chemical shifts, band electronic structures in reciprocal space and constant energy surfaces in reciprocal space, especially the Fermi surfaces.

2. Principle and performance of \textit{k-microscope}

The \textit{k-microscope} is a scanning photoemission microscopy, which combines linear and angle sweeps of the sample to perform precise electronic band structure determination by using ARPES and chemical imaging by core level detection, respectively. As shown in Fig. 2, the photon source has been combined with an advanced microscope, which has precise sample handling abilities. Moreover, it is fully compatible with a high angular and energy resolution hemispherical analyzer and a set of Fresnel Zone Plates (FZP) able to focalise the beam spot up to a few tenths of nanometers, depending on the spatial resolution of the selected FZP. More detailed instrumental and conceptual design of the instrument have been described in several previous publications[2, 3, 4, 5]. The main difference between the ANTARES microscope and other conventional ARPES instruments is that for the \textit{k-microscope}, the specimens are mounted on the high-precision plate that ensure their nano-positioning in the \textit{x} and \textit{y} directions. The microscope has two operating modes, discontinuous punctual NanoARPES detection and sequential spectroscopic imaging. The first mode is like conventional but with a focalised nano-spot size, while for the second mode, the nano-spot of X-ray is raster scanned relative to the sample to produce an image with one pixel at a time. The complete set-up consists of fourteen independent axis piezo stages, which focus the beam and perform the sample scanning with nanometric precision. Moreover, the sample position relative to the focal distance of the FZP for experiments at constant and variable photon energy is controlled by an automatic feedback interferometric system.
3. Chemical and electronic imaging of graphene polycrystalline films on copper foils grown by chemical vapour deposition

To demonstrate the capabilities of the \textit{k-microscope}, we present the first results obtained from a specimen of single layer graphene film grown by chemical vapour deposition (CVD) on polycrystalline copper foils\cite{6}. As it is shown in Fig. 2, by collecting exclusively the “sp” copper states (those confined in the red box of Fig. 2b), the location, shape and orientation of Cu grains and their grain boundaries could be precisely determined. Fig. 2c shows one of the resulting NanoARPES images, in which the grain structure of the copper substrate can be clearly identified. If instead of copper states, we record the $\pi^*$ states (green box of Fig. 2b), the resulting nano-ARPES image provides the size, distribution and orientation of the graphene grains covering the copper grains, as can be observed in Fig. 2d. As the graphene $\pi$ and $\pi^*$ bands are only close to the Fermi level at the $K$ points of the graphene grains investigated, the NanoARPES image detects not only the presence of the pristine grains, but also their orientation.

In Figure 3, ARPES results show that both multi- and single-grain ARPES spectra present a well-defined conical Dirac dispersion, with n-type extrinsic doping. Due to the continuous orientation distribution of the graphene grains, corroborated by LEED and the Fermi surface results, the multi-grain ARPES data, taken along any $\Gamma K$ direction display “filled Dirac cones”, (see Fig. 3e), which is a consequence of the Dirac cone overlapping from grains adjacently oriented. Comparison between panel (b) and (c) of figure 3 shows that individual pristine graphene grains should be measured in order to determine correctly the existence and size of the Dirac gap. Multigrain Dirac cone shows apparent gaps up to 80\% bigger than the real gap.

![Figure 2](image)

\textbf{Figure 2.} (a) Schematic of the different components of the ANTARES \textit{k-microscope}. (b) ARPES data showing the $d$ and sp bands of the copper substrate together with the massless band $\pi$ of graphene. (c) real-space image of the copper states intensity (red box states of panel(b)) obtained by NanoARPES mapping presented on a linear scale as a false-color image. The inset of panel (c) shows the sample optical image where the copper border grains are visible. Panel(d) shows the real-space image of graphene grains distribution, obtained by monitoring the graphene states intensity (green box states of panel (b)).
Figure 3. Panel (a) shows the Fermi surface map of the graphene multigrain film recorded with a spot size of \(\sim 100 \text{ um}\) and a photon energy of 100 eV, covering several individual graphene grains randomly oriented. Panel (b) depicts multi-grain energy-momentum dispersion relations of \(\pi\) and \(\pi^*\) bands near \(E_F\), using circularly polarized light of 30 eV. Panel (c) shows the \(E(k)\) dispersions measured by NanoARPES, along the high symmetry direction \(\Gamma K\), in a single pristine graphene. Finally, panels (d) and (e) show the reciprocal space of single- and multi- graphene grain, respectively, where the superposition of Dirac cones of graphene grains randomly oriented has been schematized.

due to the random orientation of the graphene grains.

The results presented here indicate that by employing NanoARPES, we are able to measure the complete electronic structure, of polycrystalline graphene films, which is impossible to tackle by conventional ARPES. This allows to use NanoARPES for future studies in a wide domain of heterogeneous materials.

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5. References

[1] Avila J. and Asensio M C. 2014 Synchrotron Radiation News 27 24-30
[2] Bostwick A. et.al 2014 Synchrotron Radiation News 25 19-25
[3] Avila J. et al. 2013 Journal of Physics Conference Series (SR12012) 425 192023
[4] Avila J. et al. 2013 Journal of Physics Conference Series (SR12012) 425 132013
[5] Chen C Y et al. J. Phys.: Condens. Matter 29 183001
[6] Avila J. et al. 2013 Scientific Reports 3 , 2439