Chemical Mapping of Graphene-Based Material with X-ray Photoelectron Spectroscopy (XPS) Using Principal Component Analysis (PCA)

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Abstract

XPS has been extensively used to characterize the surface chemistry of materials. It plays a unique role in giving access to qualitative, semi-quantitative/quantitative information as well as speciation and the presence of chemical functional groups on the surface of any material. PCA is the analysis of variability in a particular set of data. The first principal component accounts for as much of the variability in the data as possible and has the largest eigenvalue. Large image data sets obtained by XPS can be analyzed using PCA in order to extract the most significant information. The goal of PCA in an area scan of XPS is to find images which are correlated or anti-correlated. Images are acquired as a function of binding energy in an images-to-spectra experiment. Small area spectra can be obtained from any part of the sample by plotting image pixel intensity for a single pixel or a group of pixels versus binding energy. In the present study, the graphene-based material was synthesized via oxidation of graphite by Brodie Method. Then, chemical mapping has been produced with PCA on the basis of spectral information. For this purpose, XPS area scan has been performed and then the data sets were subjected to PCA in order to present the compositional inhomogeneities on the surface of synthesized graphene-based material.

Keywords: Chemical mapping, X-ray photoelectron spectroscopy, principal component analysis, multivariate analysis, graphene, graphene oxide.

Grafen Temelli Malzemelerin PCA Kullanılarak XPS ile Kimyasal Haritalanması

Öz

XPS, malzemelerin yüzey kimyasının karakterize edilmesinde yaygın olarak kullanılmaktadır. Kalitatif, yarı kantitatif/kantitatif bilgilerin yanı sıra herhangi bir malzemenin yüzeyindeki kimyasal fonksiyonel gruplar ve türleme hakkındaki bilgilere ulaşmada önemli bir rol oynamaktadır. PCA, belirli bir veri setindeki değişkenliğin analizidir. Örnekler ve değişkenler arasındaki ilişkileri anlamak için en güçlü grafik araçlarını sağlamaktadır. İlk ana bileşen, verilerdeki değişkenliğin mümkün olduğunca çoğunu oluşturur ve en büyük özdeğere sahiptir. En önemli bilgileri elde etmek amacıyla, XPS tarafından elde edilen büyük görüntü veri setlerini pca kullanarak analiz edilebilmektedir. XPS verilerinden elde edilen bir alan taramasında PCA' nın amacı, birbiri ile ilişkili ya da ilişkili olmayan görüntüleri bulmak ve bu ilişkilerden sorumlu olan pikselleri görselleştirmektir/tanımlamaktır. Görüntüler, bir görüntü-spektrum deneyinde bağlanma enerjisinin bir fonksiyonu olarak elde edilir. Küçük alan spektrumları, tek bir piksel veya bir piksel grubu ile bağlanma enerjisine karşı görüntü piksel yoğunluğunu çizerek numunenin herhangi bir kısmından elde edilebilir. Bu çalışmada, grafen bazlı malzeme, Brodie yöntemi ile grafitin oksidasyonu yoluyla sentezlenmiştir. Daha sonra, spektral bilgiye dayalı olarak PCA ile kimyasal haritalama oluşturulmuştur. Bu amaçla, XPS alan taraması gerçekleştirilmiş ve sentezlenen grafen bazlı malzeme yüzeyindeki homojensizlikleri göstermek için veri setlerine PCA uygulanmıştır.

Anahtar Kelimeler: Kimyasal haritalama, X-Işını Fotoelektron Spektroskopisi, temel bileşenler analizi, çok değişkenli analiz, grafen, grafen oksit

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1. Introduction

Many scientists have used images in science for a long time as large amounts of data in complex systems can easily be represented by visualization. In these cases, multivariate analysis (MVA) might be a very useful tool. The simplest image obtained via MVA has two-pixel indices (e.g. i x j, width and height in the image plane) and a variable index. MVA characterizes the composition of these set of pixels (Wise and Geladi 2000).

In traditional, univariate analysis, each variable is treated as independent from each other and analyzed separately whereas MVA deals with the simultaneous analysis of one or more sets of data. (Lee and Gilmore 2009; Vickerman and Gilmore 2011). MVA methods could also be applied to large data sets of XPS (X-ray Photoelectron Spectrsocopy) (Béchu, et al. 2016). In the last two decades, XPS spectra and images are increasingly being used in the surface analysis of different types of materials (Artyushkova and Fulghum 2002). Detailed analysis of high resolution of survey and elemental spectra can provide certainly much of information required by the researchers in this area.

XPS imaging/mapping can be useful to identify regions of different chemical structure on a sample surface (Gurker, et al. 1983). It is useful here to define what is meant by "Chemical Mapping" in the present study. As it might be considered, elemental images tell the analyst where elemental signals come from in the scanned area but not about the details of their chemical state (Crist B.B.,2019). Chemical state imaging takes a similar approach, however, focuses on a single element region in the XPS spectrum with a narrow energy window. At each pixel, a spectrum (survey or partial) can be extracted that gives the details of the chemical region of the surface (Barlow, et al. 2015).

Surface analysis of materials using imaging techniques often represents a challenge because the analytical signals depend not only on the surface composition but also upon the local topography (Briggs and Grant 2003). The contrast in images acquired in XPS may result from changes in elemental/chemical composition and sample topography (Artyushkova and Fulghum 2004). Therefore, photoelectron intensities will be low and the images will be black where the elements or the compounds of interest are absent in those regions analyzed. It means that there will be a chemical contrast in the chemical mapping of the surface. In addition, identification of chemical phases in multicomponent samples will then require the differentiation in terms of their surface chemistry. In these cases, MVA methods are easily used to aid the analysts.

Principal component analysis (PCA) is a multivariate technique for reducing matrices of data to their lowest dimensionality. The goal of PCA is to extract "principal components" that capture the largest amount of variance within the multi-dimensional data set (Abdi and Williams 2010). Multivariate image data set contains pixels, where each pixel contains a complete spectrum consisting of variables (binding energies) and each pixel is treated as a separate sample. For example, in XPS the intensities on more than one variable are recorded during each measurement. Hence, PCA successfully highlights major trends and variations in the images.

MVA has been used for a number of years in surface analysis, most notably in the techniques of secondary ion mass spectrometry (SIMS), X-ray photoelectron

spectroscopy (XPS), Auger electron spectroscopy (AES) and Raman spectroscopy, as raw data obtained from these techniques are multivariate in nature (Barlow, et al. 2015; Briggs and Grant 2003; Cumpson, et al. 2016; Hofmann 1986; Kalegowda and Harmer 2012; Zhang, et al. 2005).

Sastry (1997) has well summarized the application of PCA to XPS in his article. He has mainly focused on the role of noise in the spectra. Then, Artyushkova and Fulghum (2001) have published a work regarding the identification of some polymeric compounds in XPS spectra and images. They have evaluated different MVA algorithms that could be applied to XPS spectra and images to some chemical components. They have tried to resolve chemically meaningful components existing in a multicomponent system. Yet, they have mainly focused on the theory behind MVA.

Another study published by Artyushkova and Fulghum (2002) have also pointed out how multivariate image analysis methods could be applied to XPS. This study has successfully demonstrated the extraction of hidden information from a structure. Moreover, Artyushkova and Fulghum (2004) have performed another study regarding the mathematical topographical correction of XPS images using MVA methods. They have used different samples one of which is the fossilized carbonate rock and the other is a flat polymer blend.

Barlow, et al. (2015) have performed a study for identification of novel carbons in XPS imaging. They have used multivariate auger feature imaging (MAFI) as a new approach to identify graphite film mounted on carbon tape via XPS imaging. Finally, Cumpson, et al. (2016) have also applied PCA for multispectral optical imaging to data obtained with XPS and ToFSIMS.

In addition to the literature, the present study reported the chemical mapping of different carbon-based materials with XPS using PCA. In the present study, the authors aimed to present the applicability and strength of XPS imaging. Due to the powerful feature of imaging XPS, scientists could achieve the information reagrding both elemental and chemical state imaging to map the localization of a given moiety As X–Y coordinates are used, it reveals the elemental distribution and therefore chemical state of the samples surface. A simple discussion was made on how the scanned survey spectra and elemental snapshot spectra were used for the identification of different components in a scanned surface area. For this purpose, the fisrt sample was prepared as a test sample to tell how the methodology could be realized and the second sample was used to apply the same methodology and then confirm its applicability to real samples.

2. Material ve Method

2.1. *Preparation of test sample*

In the present study, two samples were used to emphasize the significance of chemical mapping with XPS. First one was a test sample and it was prepared in order to make the progress of the processes clear to obtain a meaningful chemical mapping. The second sample was a graphene-based electrode prepared in our laboratory.

For the preparation of test sample, double coated carbon conductive tape (Ted Pella 16073-1, USA) was mounted on the sample stage. Then, a piece of commercial aluminum foil was placed on the top of the carbon tape. One side of the commercial aluminum foil

was covered with a microfiber cloth whereas the other side was exposed to air for 24 hours. Finally, some amount of calcium carbonate (CAS Number 471-34-1 Sigma-Aldrich, Germany) was spread over the carbon tape with the aid of a micro-spatula.

2.2. *Preparation of graphene oxide based electrode*

For the preparation of the graphene-based electrode, first graphene oxide was synthesized. It was synthesized by using Brodie Method (Brodie 1859; Dreyer, et al. 2010) from spectroscopically grade pure graphite (Merck). In this method, 2.0 g pure graphite and 17.0 g $NaClO_3$ (CAS Number 7775-09-9 Sigma-Aldrich, Germany) were mixed in a beaker. Then, 50 mL concentrated HNO_3 (CAS Number 7697-37-2 Sigma-Aldrich, Germany) was added into the mixture slowly which was kept in an ice bath during the process. Then, this mixture was continuously mixed at room temperature for 24 hours. At the end of this process, 500 mL ultrapure water was added. The obtained material was washed with ultra pure water and centrifuged until it reached a pH value of 7.0. After, it was dried at 60 ºC. Finally, 0.05 g of synthesized graphene oxide was pretreated with 3 mL of N, N-dimethyl formamide (DMF, CAS Number 68-12-2 Sigma-Aldrich, Germany). In the end, a suspended mixture in black color was obtained.

Bare glassy carbon electrode (GCE) was polished with a slurry of alumina and then sonicated for 2 minutes in ethanol and ultrapure water (Milli-Q 18.2 MΩ cm, Millipore System Inc.), respectively. After this procedure, 10 µL of graphene oxide suspension was injected on the pre-conditioned bare GCE surface. The electrode was then kept in the oven at 55˚C for 1 hour

to evaporate the solvent (DMF) present in the suspension.

The prepared graphene-based electrode was then mounted on the sample stage of X-ray spectrometer using double coated carbon conductive tape (Ted Pella 16073-1, USA) prior to XPS mapping.

2.3. *XPS analysis conditions and data acquisition*

In order to produce a map using K-Alpha, the sample stage has been scanned which have several advantages. Qualitative and quantitative data have been obtained having a spectrum from each pixel. Moreover, spatial resolution could be adjusted by X-ray spot size which does not change during the acquisition. With the aid of snapshot spectra for each element selected, one can apply peak fitting in order to define the chemistry of surface. At the end of the mapping, high-quality images could be obtained. Application of PCA and overlaying the images collected from each pixel have been realized by the advanced features present in the Avantage 5.9912 data system that K-Alpha has.

XPS mapping was realized by K-Alpha (Thermo Fisher Scientific, UK), equipped with a multi-channel detector and micro focusing monochromator. The spatial resolution could be determined with the operator-selected X-ray spot size.

The monochromated X-ray (Al Kα) spot size was fixed at 50 µm. The survey spectra were recorded with as pass energy of 50 eV. Base pressure in the analysis chamber was 2 x 10-⁹ mbar. The multichannel detector allowed snapshot spectra for the elements selected at each pixel of the map. XPS mapping resulted in the acquisition of spectra at each pixel, in an array of 25 x 40 pixels with a step size of 50 µm. Figure 1 shows the images of the prepared test sample whereas Figure 5 shows the graphene-based electrode mounted on the

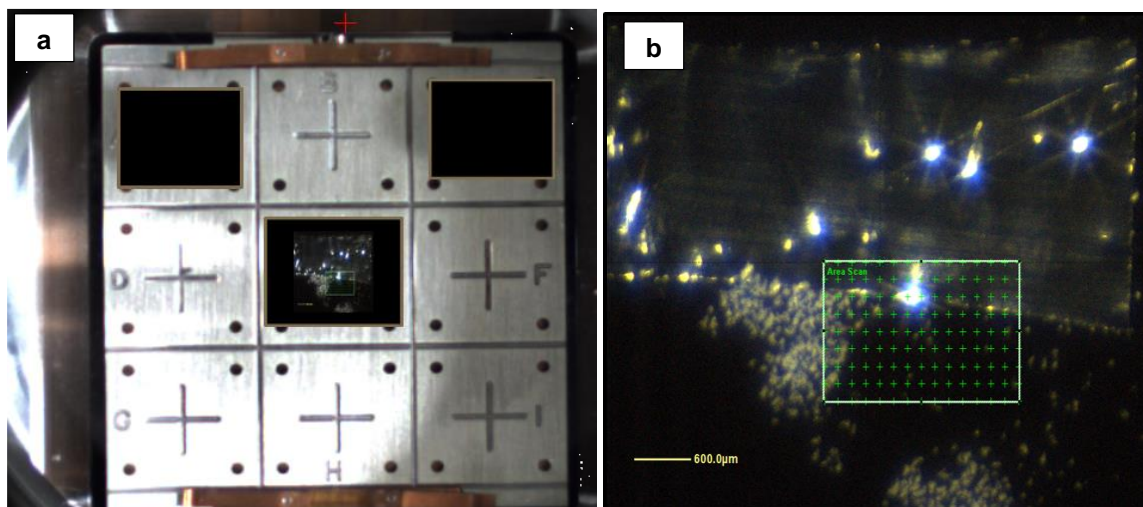stage and the area of the samples analyzed in
K-Alpha.

Figure 1. Optical image of test sample (a) mounted on sample stage (b) area of test sample
analyzed

3. Research Findings

Traditionally, in univariate analysis, each variable is treated as independent from each other and analyzed separately whereas multivariate analysis (MVA) deals with the simultaneous analysis of one or more sets of data. In MVA, variable obtained from an experiment are generally evaluated as "correlated" or "uncorrelated" (Vickerman and Gilmore 2011). Principal component analysis (PCA) is also a multivariate technique that reduces matrices of data to their lowest dimensions. It is clear that the aim of PCA is to extract "principal components" which have the largest amount of variance within the multi-dimensional data set.

In this study, optical images of test samples and the analysis area were taken by XPS camera. In order to find the maximum number of principal components eigenvalue diagram of test sample was obtained. Then PCA profiles of samples were constructed. After,

XPS survey spectra of principal components were used. Finally, overlaid principal component profiles of samples obtained for chemical mapping.

4. Result and Discussion

The optical images for the test sample taken by XPS camera were depicted in Figure 1. In PCA, one of the ways to determine the number of factors needed to describe the data satisfactorily is examining the eigenvalue plot. An eigenvalue is a number that tells us where most variation in the data and more information is present. For the XPS mapping of the test sample, it can be deduced that four factors are required to explain all the features of the data set acquired as presented in Figure 2. It is obvious that dimension reduction using PCA helps us in simplifying the whole spectral data set by finding the dominant dimensions within it.
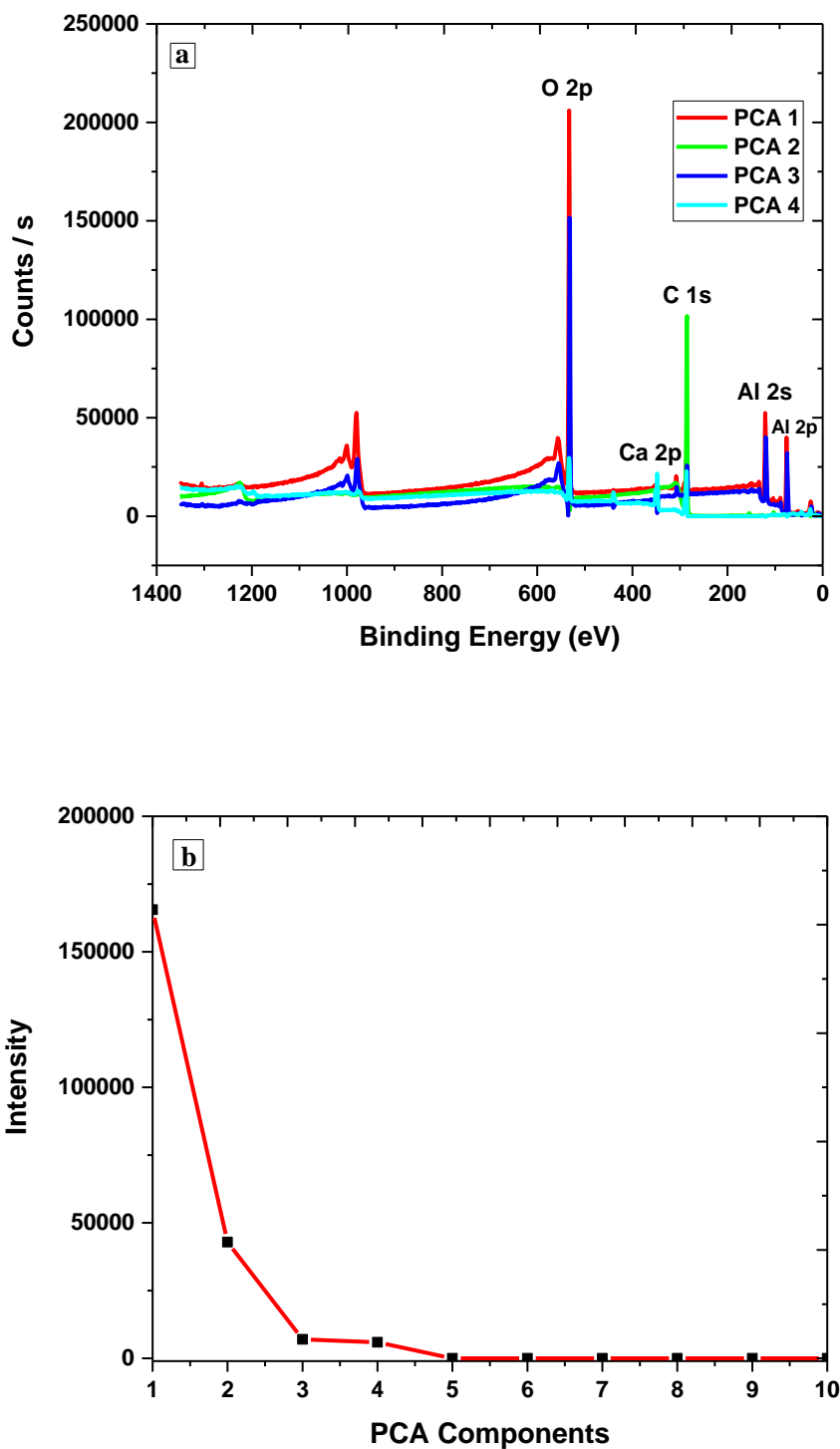
Figure 2. **(a)** XPS survey spectra of principal components for test sample **(b)** Eigenvalue diagram obtained from XPS spectra of test sample

After the application of PCA using Avantage 5.9912 software in K-Alpha, one can get the PCA profiles in the form of images as demonstrated in Figure 3. Photoelectron images contain concentration information at each pixel in the image thus indicating the spatial differences in concentration. These areas show intensity variations related or

unrelated to chemical composition. The intensity of the pixels will then be different for each photoelectron image which results in different contrast among the images. The intensities depend on the binding energy (BE) and shadowing. Heterogeneities present in the scanned area will give us an idea about the chemical composition of materials.
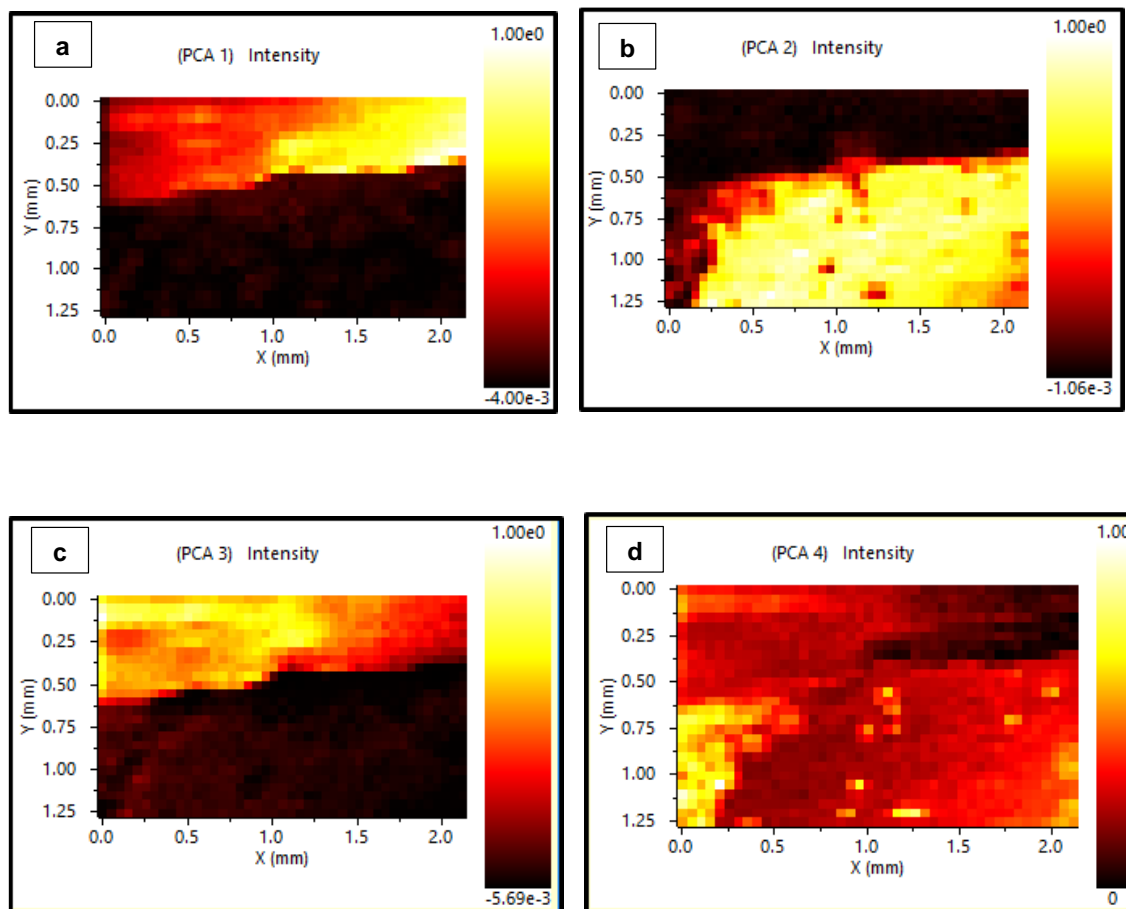

Figure 3. PCA profiles for the XPS mapping of test sample (a) PCA 1: Foil with aluminum oxide (b) PCA 2: Carbon tape (c) PCA 3: Foil with metallic aluminum (d) PCA 4: Calcium carbonate

In the present study, bright yellow pixels in each image expresses the presence of principal components whereas the dark pixels mean the absence of the principal component in question. When all the PCA profiles are overlaid, an optical image of the mapped area of test sample could be achieved as shown in Figure 4. A chemical map of the test sample was generated by acquiring full spectral data sets at each mapping pixel. It is very simple to automatically correlate the data by using Avantage 5.9912 Data System. Comparison of two images in Figure 4a and Figure 4b reveals that each component is present and located in the same position of the selected area.
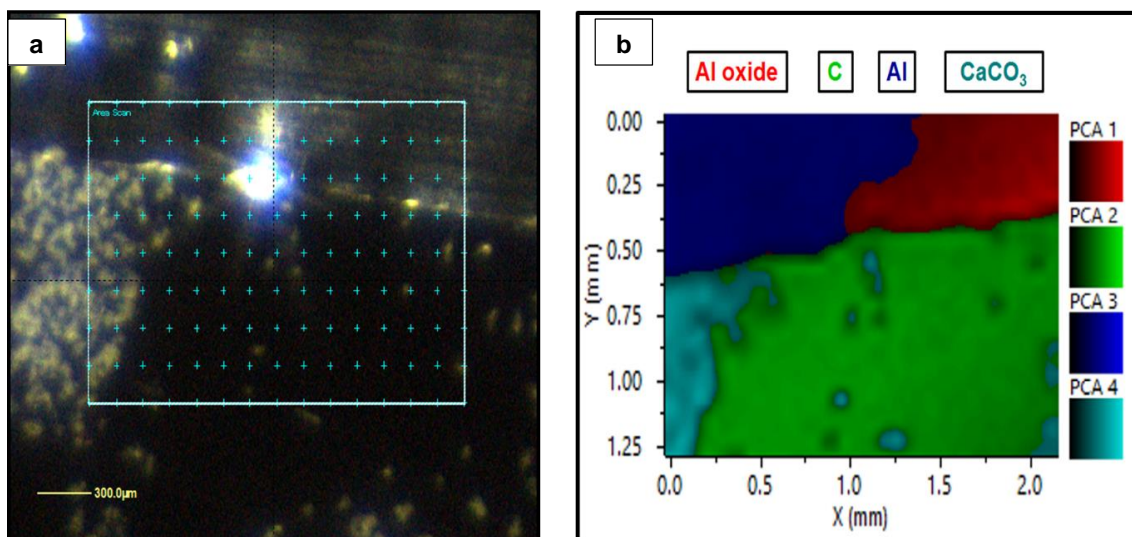
Figure 4. Chemical mapping of test sample with XPS (a) Optical image of test sample of selected area (b) Overlaid optical images using principal components

As illustrated in Figure 2, XPS survey spectra of principal components for test sample could also be attained using statistical analysis applied. As each principal component was examined, the presence of elements that compose those principal components has been observed easily. For instance, first PCA corresponds to aluminum oxide on foil. Al 2p3/2 peak (75.5 eV), Al 2s peak (120.2 eV) and O 1s peak (532.6 eV) can be easily seen from the XPS survey spectra of principal components. When the survey spectra for PCA 2 is examined, it can be derived that it is C tape due to the presence of C 1s peak at 284.8 eV. XPS survey spectrum of PCA 3 corresponds to metallic Al due to the presence of Al 2p3/2 peak at 72.8 eV and Al 2s peak at 118.1 eV. Since the other side of the aluminum foil was exposed to air for 24 hours, it has less aluminum oxides as can be seen from the survey spectra. For the last principal component (PCA 4), results reveal that calcium carbonate exists in the scanned area. The presence of Ca 2p3/2 peak (346.9 eV), C 1s peak at 289.2 eV due to metal carbonates and O 1s peak at 531.3 eV indicate that there are calcium carbonate particles spread over the indicated part of the surface of the test sample (Scientific, H.,2014). These results show that two images are in good agreement when PCA has been used for the identification of compounds on the surface. The snapshot spectra for all elements for the test sample can be examined from Figure S1, S2, and S3.

With the same methodology, graphene oxide based electrode surface was also scanned to obtain the chemical mapping. The optical images of graphene oxide based electrode mounted on the sample stage and the scanned area by XPS were demonstrated in Figure 5. This time, three principal components were determined to be present as could be understood from the eigenvalue diagram depicted in Figure 6. It is apparent that the location of each PCA is definite again as in the case of the test sample. It means that it is possible to elucidate the presence of phase-separated regions from the set of images without doing any other experiments based on the PCA.
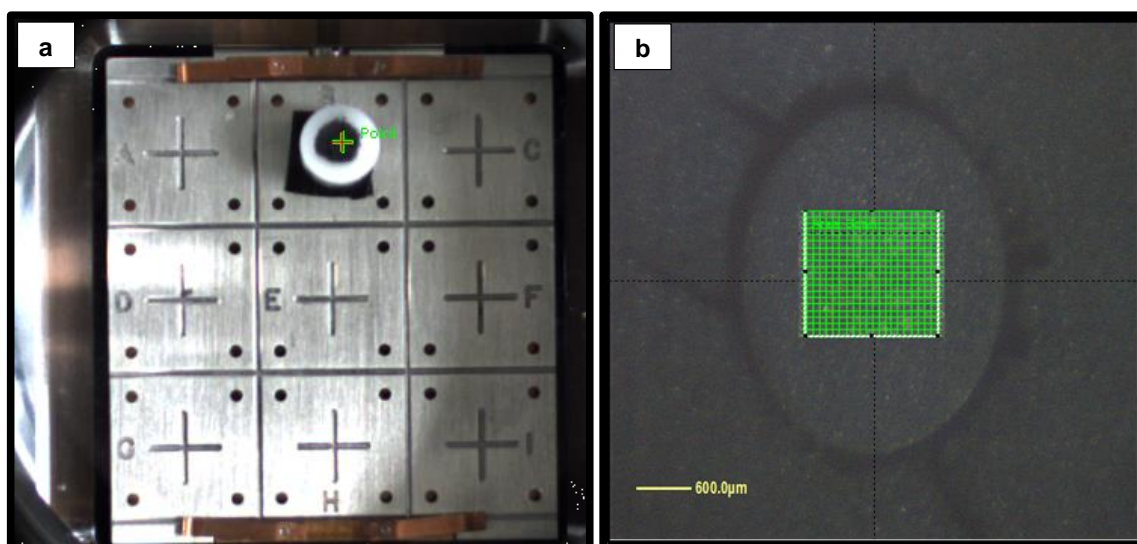
Figure 5. Optical image of graphene-based electrode (a) mounted on the sample stage (b) selected area

The prepared electrode was first analyzed by XPS by applying point analysis. It was really interesting that different signals were collected after three point analyses from different parts of the surface. Then, it was decided to make an area scan in order to image the surface of the sample since it was the most useful way of understanding the distribution of chemistries across this surface and finding the type and/or limits of contamination.

Figure 7 provides the overlay of each principal component profiles (data not shown) for the graphene-based electrode. The scanned area is approximately 1.25 mm x 2.0 mm. This time XPS mapping was used to elucidate the homogeneity and contamination levels in the scanned area. As discussed previously in the experimental section, graphene was synthesized by using Brodie Method. The obtained chemical map was also verified with the presence of C, O and F peaks in Figure 6 which is the XPS survey spectra of principal components for the graphene-based electrode. C 1s spectrum at 284.0 eV shown in both the survey spectra (Figure 7) and Figure S4 indicates the presence of sp2 bonding which

corresponds to graphene. On the other hand, Figure S5 reveals that the existence of C 1s spectrum at 284.8 eV (sp3 bonding) and a decrease of sp2 character mean that there occurs graphene oxide. The distinction between sp2 and sp3 carbon in XPS spectra of the sample analyzed can be easily made as demonstrated in Figure S4 and Figure S5. Finally, some contamination was also determined which might stem from politetrafloroetilen (Teflon material in which the prepared electrode was placed) during the preparation of electrode prior to XPS analysis. It was deduced from C 1s peak for -CF2- (298.5 eV) and C-H, C-C groups around 285 eV (Briggs and Beamson 1991) which are present in the survey spectra. In addition, F 1s peak (-CF2-CF2-) at 689.1 eV is also present in the survey spectrum which supports Teflon contamination. According to the chemical mapping of the selected area of the graphene-based electrode, the regions can be clearly identified that they are different from one another (Scientific, H.,2014).
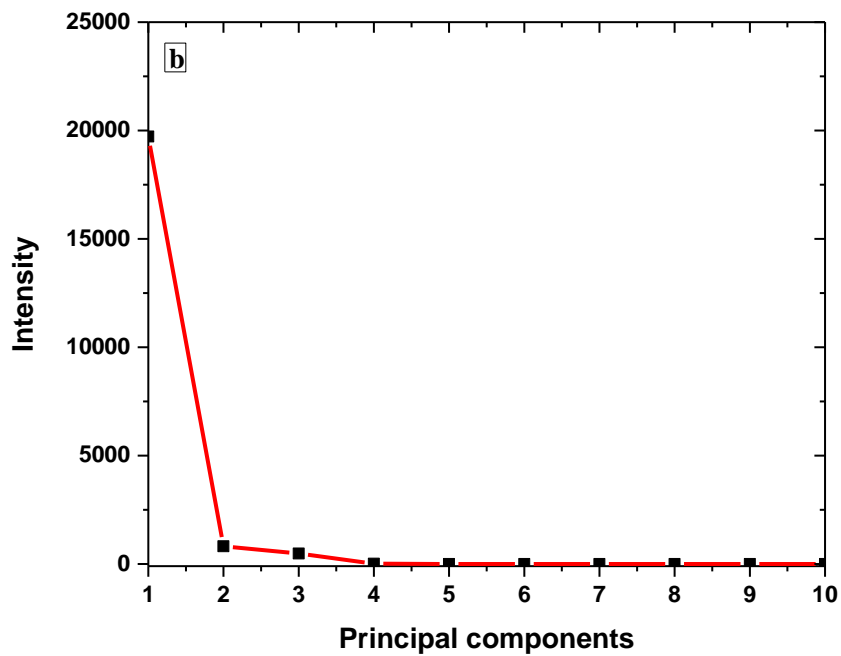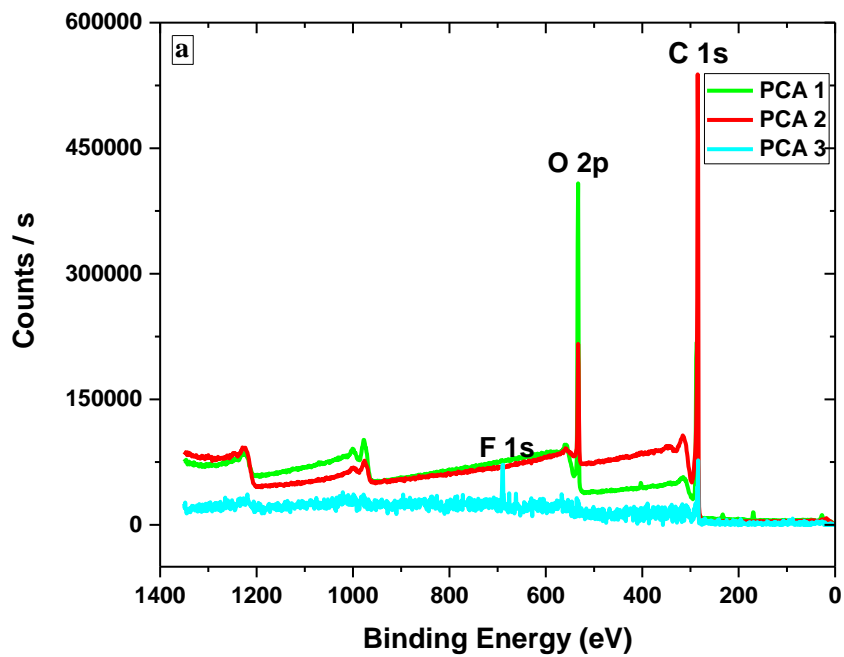
Figure 6 (a) XPS survey spectra of principal components for graphene-based electrode
(b) Eigenvalue diagram obtained from XPS spectra of graphene-based electrode
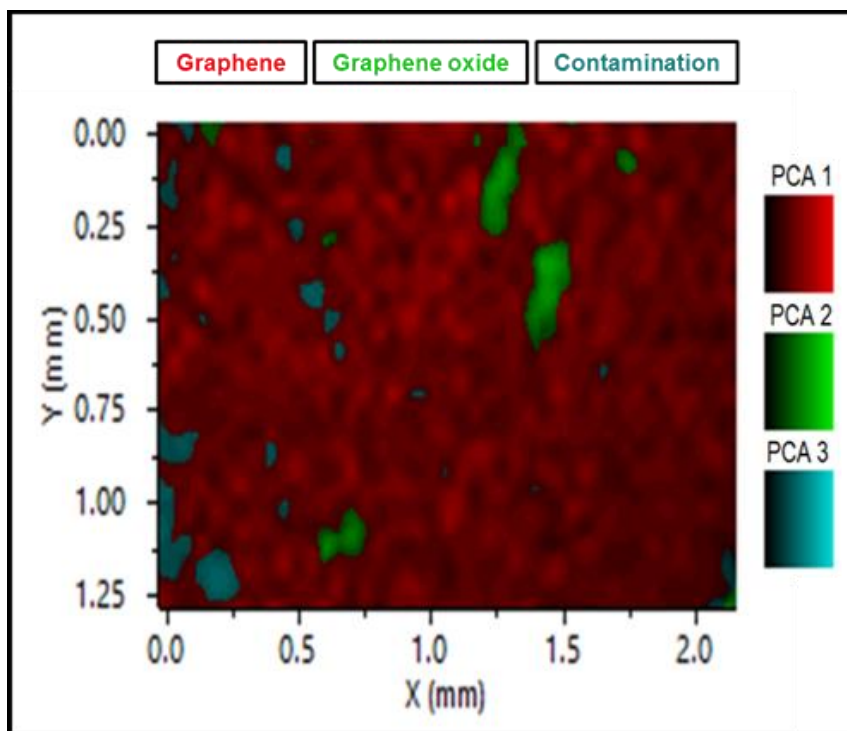
Figure 7. Overlaid principal component profiles of graphene-based electrode surface
PCA 1: Graphene PCA 2: Graphene oxide (c) PCA 3: Contamination

Multivariate analysis can be applied to any set of data which involves measurement having more than one variable. After a spectroscopic analysis as in the case of XPS, massive amounts of data have been obtained and the most important information is hidden in these numbers. For this reason, scientists often need data mining. This means an attempt to find the required information embedded in this complex data. When multivariate analysis has been applied, this hidden information has been extracted. Then, it shows the most important groupings. It also visualizes different regions in the data obtained.

PCA, which is one of the most important multivariate methods, reveals the relationships between the samples and the variables. PCA applied to the multispectral data set allows for the identification of components based on the principal component image and evaluation of survey spectra together. It is possible to elucidate the

presence of separated regions without any additional information or experiments.

The goal of this present work was to show how chemical mapping with XPS using PCA might be very useful in identification of regions analyzed. XPS images obtained by this methodology demonstrates that the appropriate application of surface chemometrics can extract hidden information from complex data. The results presented in this study state that multivariate methods can provide significant information regarding the chemical mapping after XPS analysis of a defined area. Each variable's contribution has been defined for both the test sample and the graphene-based electrode.

We have demonstrated the application of PCA to area scan realized by XPS and how the surface chemistry has been identified. This is very important for many reasons. First, the compositional inhomogeneities and the contamination on the scanned area could be

clearly seen. In addition, all the compounds that compose the mapping could be identified region by region which is called the "Chemical Mapping".

The future of XPS imaging is promising. In future XPS users will be able to maximise the available information from their samples and, as quantitative imaging and associated multivariate analysis becomes more prevalent, the application of standard XPS data analytical routines, such as curve fitting, could be routinely applied to image data. Finally, the present study showed a tool for chemical identification of regions of a scanned sample by XPS using PCA.

5. Acknowledgement

6. References

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