

# Applications of X-ray Photoelectron Spectroscopy for Catalytic and Photocatalytic Studies

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## Abstract

*The study of the external surface and interfaces of catalysts is very relevant in the characterization of active phases and supports and in the interaction between active phase-support. X-ray Photoelectron spectroscopy (XPS) is a very useful tool for knowing the chemical surface composition and the chemical state of the constituent elements of catalysts. In this lecture, the application of this technique in environmental catalysis, including photocatalysis will be presented with illustrative examples.*

## 1.- Introduction

In heterogeneous catalysis, the surface properties of the catalysts are always important, but so is having the means to measure those properties. The behaviour of a catalyst can only be fully understood if there is information about the surface composition (i.e., types of atoms present and their concentrations) and about the chemistry of the surface (chemical state of the atoms). X-ray photoelectron spectroscopy (XPS) is currently the most widely used surface analytical technique, where the surface to be analysed is irradiated with soft X-ray photons. When a photon of energy  $h\nu$  interacts with an electron at a level with a binding energy  $E_B$ , the energy of the photon is completely transferred to the electron, resulting in the emission of a photoelectron with a kinetic energy (see Eq 1), where  $\phi$  is the work function of the spectrometer, which is small and almost constant.

$$E_{\text{Kin}} = h\nu - E_B - \phi \quad (1)$$

The XPS can analyse all elements of the periodic table with the exception of hydrogen and helium. Although XPS is primarily concerned with photoelectrons and their kinetic energies, the departure of electrons by other processes also occurs. An emitted photoelectron leaves behind an internal hole in the atom thus producing the Auger process. These Auger electrons are very sensitive when they come from the valence band. The reasons why XPS is a surface specific are because an electron with kinetic energy moving through a solid matrix has a probability of traveling a certain distance before losing some or all of its energy as a result of an inelastic collision. The important consequence of the dependence of  $\lambda$  (inelastic mean free path) on kinetic energy is that the ranges of secondary electron kinetic energies used in XPS are very small (from 2 to 6 monolayers). This means that in practice the photoelectrons or Auger electrons that escape into the vacuum and are detected come from the surface of the catalyst. This is the reason why XPS is surface specific.

The application of XPS in oxidative catalysis is very common. Especially in the study of active phases and supports, as well as a better knowledge of the interactions of the active phases with the catalytic support.

## 2.- Illustrative examples

In a recent study [1] of the ethylene photodegradation with four different composites ( $\text{Cu}/\text{C}_3\text{N}_4$ ,  $\text{Cu}/\text{TiO}_2$ ,  $\text{Ni}/\text{C}_3\text{N}_4$ ,  $\text{Ni}/\text{TiO}_2$ ) under UV-Vis illumination. The photocatalytic composites were characterized by XPS. Figure 1 clearly shows the identification of the different functional groups on the surface of the studied composites. The different oxidation states of the metallic active phases are also identified, and the XPS results confirm the formation of the composites, and all atomic elements have been identified. In the case of Cu-containing catalysts, the presence reduced Cu on sample  $\text{Cu}/\text{TiO}_2$  and of Cu(II) on sample  $\text{Cu}/\text{C}_3\text{N}_4$  are observed (Figure 1c). This is relevant because sample  $\text{Cu}/\text{TiO}_2$  is an efficient catalyst but sample  $\text{Cu}/\text{C}_3\text{N}_4$  is not.

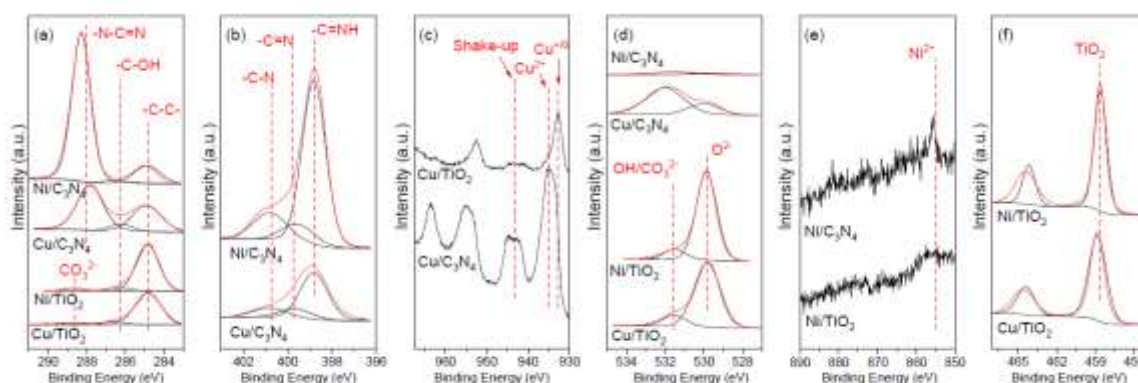


Figure 1. High-resolution XPS spectra of: C 1s (a) N 1s (b), Cu 2p (c), O 1s (d), Ni 2p (e) and Ti 2p (f).

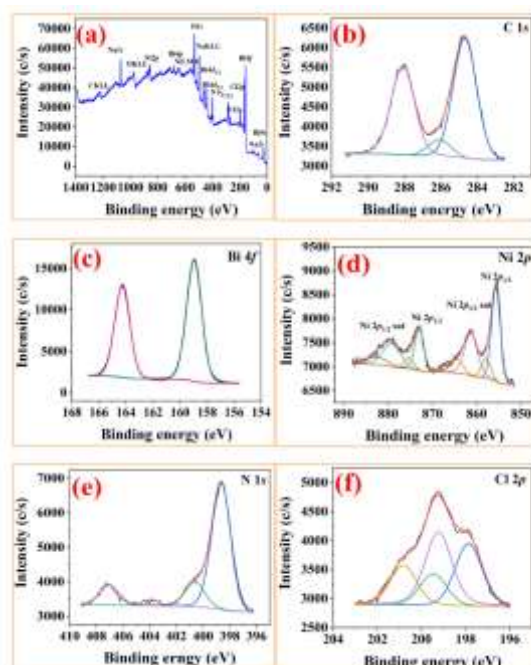


Figure 2. Survey spectrum (a), and high resolution C 1s (b), Bi 4f (c), Ni 2p (d), N 1s (e) and Cl 2p (f) spectra of  $\text{BiVO}_4\text{-Ni(II)/C}_3\text{N}_4(1.5)$ .

XPS was used in the study of novel Bi-based bifunctional photo electrocatalysts used to remove dibenzothiophene from n-heptane as model fuel [2]. Figure 2 shows the survey spectrum of the most efficient photo-electrocatalyst where all elements are identified. The Bi

4f spectrum (Fig. 2c) shows the doublet Bi 4f<sub>7/2</sub>- Bi 4f<sub>5/2</sub> with binding energies at 159.0 and 164.2eV, respectively, typical of Bi(III). The high-resolution N 1s spectrum presented in Fig. 2e shows three contributions at 398.6, 400.6, and 407.0 eV, where the first two are assigned to C-N-C and (C)<sub>3</sub>-N groups, respectively, and the contribution at high binding energy (407.0eV) to the presence of nitrate.

In the following example, a thin layer of sub-stoichiometric TiO<sub>2-x</sub> has been deposited, aiming at inducing a vacancy doped homojunction between two different oxygen rich/deficient TiO<sub>2</sub> layers, where vertically aligned titania nanorods (TNRs) have been deposited through a hydrothermal growth in acidic conditions on a pre-seeded glass conducting substrate. Sub-stoichiometric TiO<sub>2-x</sub> layer (50 nm nominal thickness) has been deposited on top of TNRs via radiofrequency magnetron sputtering at three different stoichiometries, tuning the oxygen partial pressure in sputtering argon atmosphere at 10 %, 15 % and 20 %, respectively. Photocatalytic activity has been investigated in the photodegradation of an aqueous solution of methylene blue, both under UV and simulated solar light irradiation [3]. The Ti 2p<sub>3/2</sub> signal is always symmetric and Ti(IV) species are the main ones. However, after a mild etching with an Ar<sup>+</sup> plasma, the presence of sub-stoichiometric titania is observed too after removing the surface contamination, as shown by the lower BE 2p doublet overlapping the Ti(IV) signals.

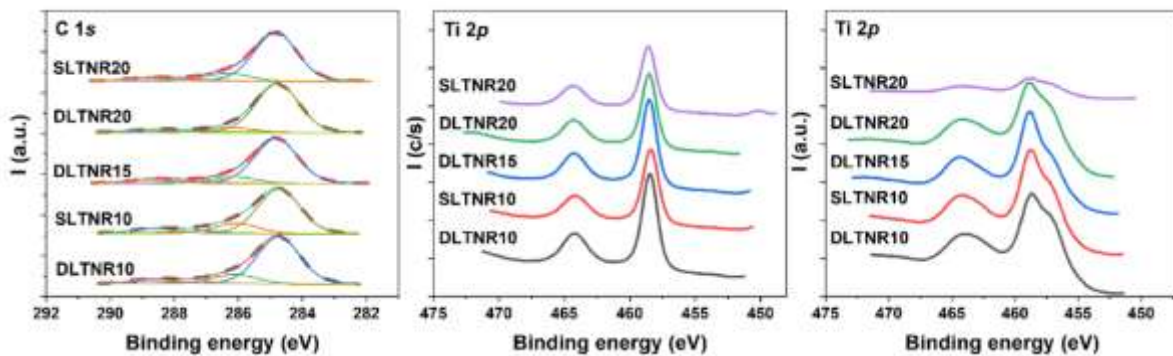


Figure 3. High resolution spectra of C 1s, Ti 2p before and after mild Ar<sup>+</sup> sputtering for removing surface contamination.

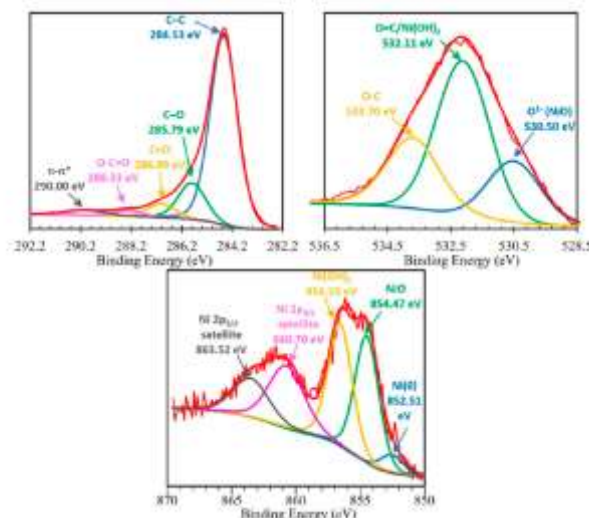


Figure 4. High resolution C 1s, O 1s and Ni 2p spectra of TPNi

In the last example, Ni-doped ordered nanoporous carbons prepared from chestnut wood tannins for the photocatalytic degradation of methylene blue was also studied by XPS (Figure 4) to identify the different chemical states. The deconvolution of the C 1s spectrum revealed the nature of the different bonds: C-C (284.5 eV), C-O (285.8 eV), C=O (287.0 eV), and O-C=O (288.3 eV). The deconvolution of the O 1s spectrum shows the presence of contributions at 530.5, 532.1 and 533.7 eV, that are assigned to O<sup>2-</sup> in NiO, C=O in carbonyl and carboxylic groups and C-O in phenols, ethers and lactones, respectively. Three Ni species were identified in the Ni 2p spectrum: Ni<sup>0</sup> at 852.2 eV, NiO at 854.5 eV and Ni(OH)<sub>2</sub> at 856.6 eV.

## CONCLUSIONS

The use of XPS as an important tool for the study of materials for oxidative catalysis is presented in four illustrative examples, showing the relevance of this technique to know the chemical state of the constituent elements of the catalysts.

## REFERENCES

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