



Synthesis :: Materials :: Corrosion :: Environment :: Energy

**YUCORR**

Analyse :: Discover :: Coat :: Green :: Protect :: Save :: Sustain

---

INTERNATIONAL CONFERENCE  
MEĐUNARODNA KONFERENCIJA

---

MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF  
CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

---

*STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE,  
ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE*

---

**PROCEEDINGS**

---

***KNJIGA RADOVA***

Under the auspices of the  
MINISTRY OF SCIENCE, TECHNOLOGICAL DEVELOPMENT  
AND INNOVATION OF THE REPUBLIC OF SERBIA

*Pod pokroviteljstvom  
MINISTARSTVO NAUKE, TEHNOLOŠKOG RAZVOJA I  
INOVACIJA REPUBLIKE SRBIJE*

May 28-31, 2023 :: Divčibare, Serbia

---

CIP - Katalogizacija u publikaciji  
Narodna biblioteka Srbije, Beograd

620.193/.197(082)(0.034.2)  
621.793/.795(082)(0.034.2)  
667.6(082)(0.034.2)  
502/504(082)(0.034.2)  
66.017/.018(082)(0.034.2)

INTERNATIONAL Conference YUCORR (24 ; 2023 ; Divčibare)

Meeting point of the science and practice in the fields of corrosion, materials and environmental protection [Elektronski izvor] : proceedings = Stečište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine : knjiga radova / XXIV YuCorr International Conference, May 28-31, 2023, Divčibare, Serbia = XXIV YuCorr [Jugoslovenska korozija] Međunarodna konferencija = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.] ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] ; [editors, urednici Miroslav Pavlović, Marijana Pantović Pavlović, Miomir Pavlović]. - Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM = Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM, 2023 (Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM = Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM). - 1 elektronski optički disk (CD-ROM) ; 12 cm  
Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Radovi na engl. i srp. jeziku. - Tiraž 200. - Bibliografija uz većinu radova. - Abstracts.

ISBN 978-86-82343-30-1

a) Премази, антикорозиони -- Зборници b) Превлаке, антикорозионе --  
Зборници v) Антикорозиона заштита -- Зборници g) Животна средина --  
Заштита -- Зборници d) Наука о материјалима -- Зборници

COBISS.SR-ID 119553545

## **XXIV YUCORR – International Conference | Međunarodna konferencija**

### **PUBLISHED BY | IZDAVAČ**

SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOZAM)

UDRUŽENJE INŽENJERA SRBIJE ZA KORIJU I ZAŠTITU MATERIJALA (UISKOZAM),

Kneza Miloša 7a/II, 11000 Beograd, Srbija, tel/fax: +381 11 3230 028, [office@sitzam.org.rs](mailto:office@sitzam.org.rs); [www.sitzam.org.rs](http://www.sitzam.org.rs)

**FOR PUBLISHER | ZA IZDAVAČA** Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOZAM

**SCIENTIFIC COMMITTEE | NAUČNI ODBOR:** Prof. dr M. G. Pavlović, Serbia – President

Prof. dr Đ. Vaštag, Serbia; Dr M. M. Pavlović, Serbia; Prof. dr D. Vuksanović, Montenegro; Prof. dr D. Čamovska, N. Macedonia; Prof. dr M. Antonijević, Serbia; Prof. dr S. Stopić, Germany; Prof. dr R. Zejnilović, Montenegro; Prof. dr L. Vrsalović, Croatia; Dr N. Nikolić, Serbia; Dr I. Krastev, Bulgaria; Prof. dr B. Grgur, Serbia; Prof. dr M. Gvozdrenović, Serbia; Prof. dr S. Hadži Jordanov, N. Macedonia; Prof. dr R. Fuchs Godec, Slovenia; Prof. dr J. Stevanović, Serbia; Dr V. Panić, Serbia; Dr M. Mihailović, Serbia; Prof. dr V. Marić, B.&H.; Prof. Dr C. Stojanović, B.&H.; Prof. dr J. Jovičević, Serbia; Prof. dr D. Jevtić, Serbia; Dr M. Pantović Pavlović, Serbia; Dr F. Kokalj, Slovenia; Prof. dr M. Gligorić, B.&H.; Prof. dr A. Kowal, Poland; Prof. dr M. Tomić, B.&H.; Prof. Dr B. Arsenović, B.&H., Dr S. Blagojević, Serbia

**ORGANIZING COMMITTEE | ORGANIZACIONI ODBOR:** Dr Miroslav Pavlović – president

**Dr Nebojša Nikolić – vice president; Dr Marija Mihailović – vice president**

Prof. dr Miomir Pavlović; Dr Vladimir Panić; Jelena Slepčević, B.Sc.; Prof. dr Milica Gvozdrenović; Zagorka Bešić, B.Sc.; Gordana Miljević, B.Sc.; Miomirka Anđić, B.Sc.; Dr Marija Matić; Dr Marijana Pantović Pavlović; Dr Dragana Pavlović; Dr Sanja Stevanović; Lela Mladenović – secretary

**EDITORS | UREDNICI:** Dr Miroslav Pavlović, Dr Marijana Pantović Pavlović, Prof. dr Miomir Pavlović

**SCIENTIFIC AREA | OBLAST:** CORROSION AND MATERIALS PROTECTION | KOROZIJA I ZAŠTITA MATERIJALA

**PAGE LAYOUT | KOMPJUTERSKA OBRADA I SLOG:** Dr Marijana Pantović Pavlović

**CIRCULATION | TIRAŽ:** 200 copies | primeraka

**PUBLICATION YEAR | GODINA IZDANJA:** 2023

**ISBN 978-86-82343-30-1**

## Long-term air exposure surface modification-XPS first principle approach study

### *Ispitivanje promena na površini nakon dugotrajnog izlaganja vazduhu polazeći od prvih principa-XPS*

Mirjana Medić Ilić<sup>1,\*</sup>, Bojana Kuzmanović<sup>1</sup>, Bojana Paskaš Mamula<sup>1</sup>, Katarina Batalović<sup>1</sup>, Nenad Bundaleski<sup>1,2</sup>

<sup>1</sup>*Vinča Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade, P.O. Box 522, 11001, Belgrade, Serbia*

<sup>2</sup>*CEFITEC, Faculdade de Ciências e Tecnologia – Universidade Nova de Lisboa, 2829-516 Caparica, Lisboa, Portugal*

\**mirjanamedic@vinca.rs*

#### **Abstract**

*Within the scope of this paper, a potential impact of noble metal particles on the surface of N-TiO<sub>2</sub> and its catalytic properties is observed through correlation with contamination layer thickness. Owing to 'first principle' approach study, without additional experimental measurements or permanent damage to the surface of the samples, it is possible to obtain significant novel information based on a single measurement of the XPS spectra. Presented research demonstrated how the surface contamination layer in the case of samples based on N-TiO<sub>2</sub> is related to the nature of two studied noble metals, indicating that Pd might serve as an important co-modifier to suppress surface contamination.*

**Keywords:** *X-ray Photoelectron Spectroscopy (XPS); surface structure; surface layers thicknesses; N-TiO<sub>2</sub>*

#### **Izvod**

*Kroz ovaj rad će biti sagledan uticaj čestica plemenitih metala na strukturu površine titanijum dioksida dopiranog azotom i katalitička svojstva kroz uticaj na debljinu sloja nečistoća. U ovakvom pristupu koji polazi od „prvih principa“ je bez dodatnih eksperimentalnih merenja i trajnog oštećenja površine uzoraka moguće dobiti značajne nove informacije korišćenjem rezultata jednom izvedenog merenja rendgenskog fotoelektronskog spektra. Dobijeni rezultati ukazuju na to da promene na površini uzoraka na bazi N-TiO<sub>2</sub>, do kojih dolazi zbog prisustva Pd, utiču na suzbijanje površinskih organskih nečistoća*

**Ključne reči:** *Фотоелектронска спектроскопија рендгенским зрачењем (XPS); површинска структура; дебелина површинских слојева; N-TiO<sub>2</sub>*

#### **Introduction**

The surface of materials plays a prominent role in heterogeneous catalysis. Oxidation and impurities formed during the synthesis and aging of the materials interfere with the material's functionality, and understanding all the factors that influence catalyst performance is therefore of high significance. In this paper, we consider attractive photocatalytic material, N-doped TiO<sub>2</sub> in order to examine whether the presence of surface deposited Pd and Pt affects the surface structure and, indirectly, its catalytic properties. All the samples presented in this paper have a non-uniform in depth surface structure, which is a characteristic of most samples in general. When we talk about X-ray Photoelectron Spectroscopy (XPS), there are several standard ways of the sample in-depth analysis. A commonly

used procedure is sputter depth profiling i.e. successive ion sputtering and acquiring of spectra [1], which makes a permanent change of the surface structure caused by ion bombardment thus affecting the experimental result. In order to perform analysis without surface damage, the AR-XPS technique can be used, but in practice, there are often limiting factors concerning the size of the sample and the roughness [2]. Non-uniformity of the surfaces, for instance due to long-term air exposure, and the need for detailed information concerning the sample surface motivated us to develop a model for quantitative analysis of in-depth non-uniform surfaces [3]. Here, the major idea was to reexamine the XPS data of N-TiO<sub>2</sub> based samples starting from the 'first principles', in order to reveal the details of the samples surface structure. Potential impact of metal particles on the changed surface structure is observed through correlation with impurity (contamination) layer thickness.

## Experimental details

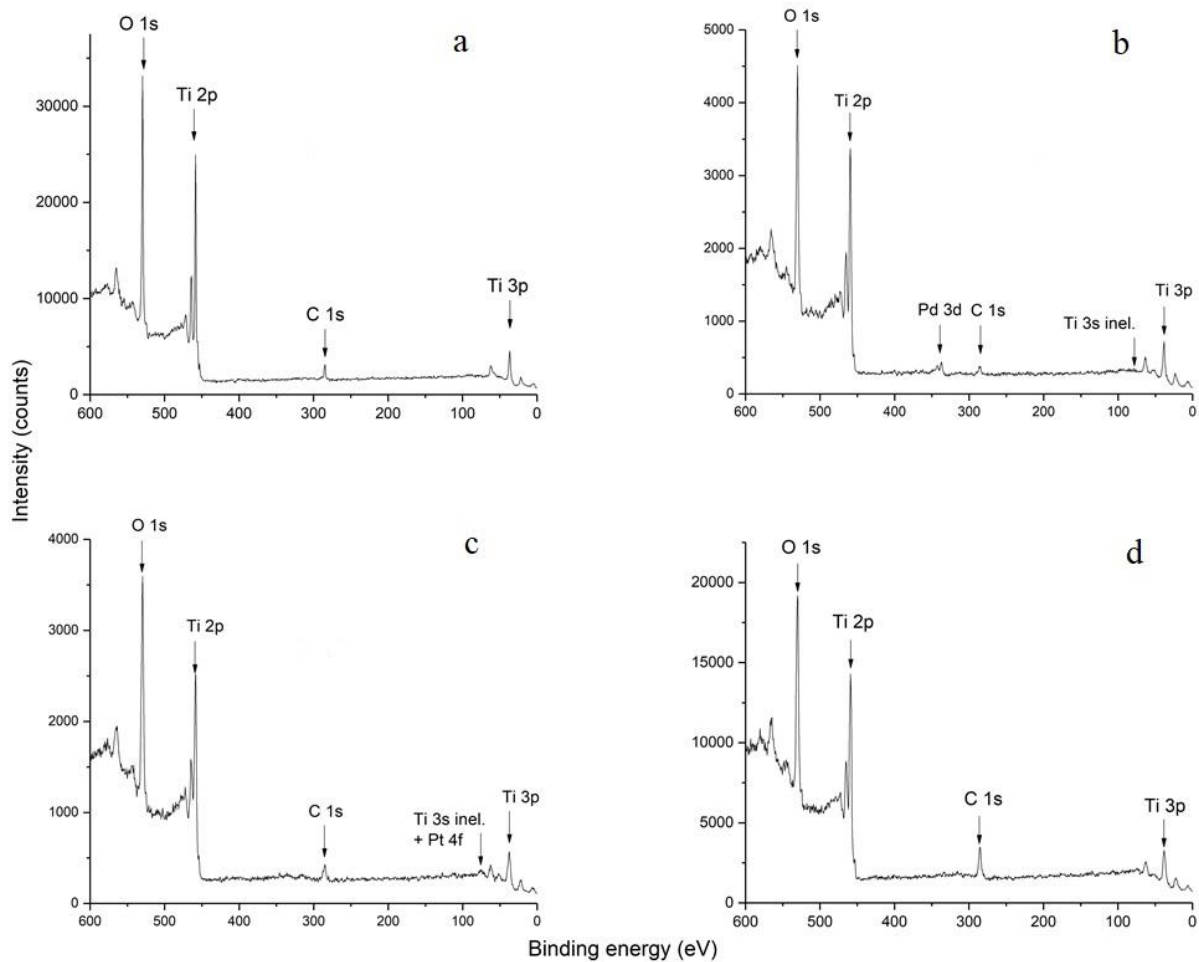
N-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) was prepared via a solvothermal method, using urea (Acros Organics, purity 99%) as the dopant source and titanium(IV) isopropoxide (Acros organics, purity 98%) as titanium source (molar ratio of N/Ti was 10%). Noble metals were deposited at the surface of N-TiO<sub>2</sub> using photoreduction from the solution to reach 0.10wt% of Pt (N-TiO<sub>2</sub>/Pt) and 0.05wt% of Pd (N-TiO<sub>2</sub>/Pd) in the final samples. The solution was filtered, dried, and finally calcinated at 440 °C for one hour.

XPS analysis was carried out on a SPECS customized UHV surface analysis system with PHOIBOS 100 spectrometer for energy analysis, dual anode Al/Ag monochromatic source, and electron flood gun. XPS spectra were taken using a monochromatic Al K $\alpha$  line (photon energy of 1486.74 eV) in FAT 40 mode with an energy step of 0.5 eV and dwell time of 0.2 s. The samples, in a powder form, have been supported on a copper adhesive tape and analysed 'as received'.

## Experimental results and surface layer thickness calculation

Survey XPS spectra of all investigated samples are presented in Fig. 1, where the most prominent photoelectron lines are denoted. Characteristic O, C and Ti photoelectron lines are clearly visible in each spectra (Fig. 1), as well as the typical Pd photoelectron line (Fig. 1b). The nitrogen N 1s line with very low intensity was also detected during higher energy resolution measurements and a prolonged acquisition time, though not visible in the survey spectrum of each sample. It should be pointed out that the Pt 4f line is overlapping with the inelastic contribution of Ti 3s photoelectron line (Fig. 1c and 1d). The elemental surface compositions of investigated samples, determined from the intensities of the characteristic XPS lines, using the appropriate relative sensitivity factors [4], are given in Table 1.

Different chemical phases present at the surface can be well estimated based on chemical peak shifts of the photoelectron lines. The thickness of the oxide layer can be calculated from the previously proposed compositions of the bulk and oxide phase, using the experimental intensity ratio of the two line contributions [4], as long as all line components can be clearly distinguished. While in the case of the O 1s line of the sample N-TiO<sub>2</sub> (Fig. 1a), there are contributions of Ti-oxides [5] in the samples with Pd and Pt, this line contains additional components originating from these metals. At the same time, samples with photo-deposited Pd or/and Pt have the main photoelectron lines of Pd and Pt with very low intensity (Fig. 1b) that overlaps with other lines (Fig. 1c) or below the detection limit of the XPS instrument (Fig. 1d). Therefore, oxide layer thicknesses calculation wasn't performed, but an equivalent approach was applied to obtain the contamination layer thicknesses.



**Figure 1.** Survey XPS spectra of as-received samples (a)  $N\text{-TiO}_2$ , (b)  $N\text{-TiO}_2/\text{Pd}$ , (c)  $N\text{-TiO}_2/\text{Pt}$ , and (d)  $N\text{-TiO}_2/\text{Pd}+\text{Pt}$ .

In the further surface analysis of the tested samples, Ti 2p and Ti 3p lines (see Fig. 1) were selected as representative. The kinetic energies of these lines differ by more than 400 eV, and each has its own relative sensitivity factor, RSF. Since both lines originate from the same element, any of them could be used for quantitative analysis, but the result would be the same only if the surface is free of contamination. The difference between the obtained quantitative results comes from the layer of organic impurities, whose thickness can be determined precisely based on the intensity ratio of these lines. Intensity ratio,  $I_0(\text{Ti } 2p) / I_0(\text{Ti } 3p)$ , is equal to the ratio of the corresponding relative sensitivity factors  $\text{RSF}(\text{Ti } 2p) / \text{RSF}(\text{Ti } 3p)$  only when the sample is homogeneous in depth. When the sample is covered with a contamination layer of thickness  $d$ , this ratio will be:

$$\frac{I_m(\text{Ti } 2p)}{I_m(\text{Ti } 3p)} = \frac{I_0(\text{Ti } 2p)}{I_0(\text{Ti } 3p)} \cdot \frac{A_T(\text{Ti } 2p)}{A_T(\text{Ti } 3p)} \quad (1)$$

where  $A_T(I) = \exp(-d/\lambda(I))$  is the corresponding attenuation factor [6] of the organic layer determined by the thickness of the layer  $d$  and the effective attenuation length  $\lambda$ . It can be easily shown that:

$$d = \frac{\ln\left(\frac{I_m(\text{Ti } 2p)/I_m(\text{Ti } 3p)}{\text{RSF}(\text{Ti } 2p)/\text{RSF}(\text{Ti } 3p)}\right)}{\left(\frac{1}{\lambda(\text{Ti } 3p)} - \frac{1}{\lambda(\text{Ti } 2p)}\right)} \quad (2)$$

It should be noted that the thickness  $d$  corresponds only to the organic layer of the Ti-containing phase. In Table 1 we present the calculated thicknesses  $d$  with the composition results obtained using the RSF (i.e. assuming that the samples are uniform), revealing a considerably larger amount of organic impurities is present at the surface of the two samples containing Pt. This could be a consequence of the fact that the Pt on the surface acts as a catalyst for various reactions at the surface, among them also the oxidation of hydrocarbons [7].

**Table 1.** Surface composition based on relative sensitivity factors (RSF) and contamination layers thicknesses calculated using Equation 2.

Sample	Composition (%)					Contamination layer thickness (nm)
	C	N	O	Ti	Pd/Pt	
N-TiO <sub>2</sub>	11.72	1.00	61.28	26.00	-	2.14
N-TiO <sub>2</sub> /Pd	6.95	1.01	63.73	27.58	0.72	2.65
N-TiO <sub>2</sub> /Pt	15.32	0.48	58.93	23.82	1.46	5.43
N-TiO <sub>2</sub> /Pd+Pt	17.42	0.50	57.42	24.48	0.17 (Pt)	3.46

Considering that the matrix in all samples is the same (N-TiO<sub>2</sub>), the contamination layer thicknesses are expected to be consistent with the C amount. Thereby, observed variations can be related to the presence of deposited Pt and Pd particles. Platinum creates favorable conditions for hydrocarbons contamination, which is in agreement with the experimentally determined increase in C amount of the N-TiO<sub>2</sub>/Pt sample and especially N-TiO<sub>2</sub>/Pd+Pt. On the other hand, the presence of Pd seems to 'clean' the surface. It is interesting to look into the differences in C quantity for N-TiO<sub>2</sub>/Pt and N-TiO<sub>2</sub>/Pd+Pt samples, and relate them to the thickness of the contamination layer. Since the highest amount of C is seen in N-TiO<sub>2</sub>/Pd+Pt, where Pt is present in traces, there is a possibility that the hydrocarbons on the surface are laterally non-uniformly distributed. That way, it could be that C accumulates around the Pt and thus attenuates its signal. The small contamination layer thickness of 'only' 3.46 nm on the N-TiO<sub>2</sub> matrix with 17.42% C in the N-TiO<sub>2</sub>/Pd+Pt sample, also supports this interpretation.

The main difference in the behavior of Pd and Pt as surface modifiers comes from the charge transfer trend, as shown in earlier DFT studies [8]. Charge transfer is from the surface to Pt, leaving some unoccupied N states near the Fermi level. Contrary, Pd donates charge to the surface, leading to the occupation of the previously empty N states. Therefore, for various molecular species adsorbed at the surface, Pt acts as a charge source. However, regarding the photocatalytic performance in the hydrogen generation reaction, it was shown that a combination of both metals on top of N-TiO<sub>2</sub> outperforms Pt/N-TiO<sub>2</sub> [5]. Our presented research is a certain supplement to these results, demonstrating how the surface contamination layer is also related to the nature of two studied noble metals and indicating that Pd might serve as an important surface co-modifier to reduce surface contamination.

## Conclusion

The samples presented in this paper and the great majority of samples, in general, have in-depth non-uniform surface structure, which is especially present after long-term air exposure. Thus, an approach based on the 'first principles' was successfully applied to obtain the thicknesses of contamination layers. The major idea was to reexamine the XPS data of N-TiO<sub>2</sub>-based samples, in order to reveal the catalytic properties of noble metals and their potential impact on the samples' surface structure. A potential influence is observed through the correlation of surface composition and contamination layer thicknesses. While Pd might be an important co-modifier for reducing surface impurity formation, platinum creates favorable conditions for hydrocarbon contamination.

## Acknowledgements

The funding for this research is provided by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, under Grant. No. 451-03-47/2023-01/200017.

## References

1. J. F. Watts and J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES*, Wiley, 2003.
2. C. J. Powell, A. Jablonski, Progress in quantitative surface analysis by X-ray photoelectron spectroscopy: Current status and perspectives, *J. Electron Spectros. Relat. Phenomena*, **178–179**, 331–346, 2010.
3. N. Bundaleski, I. Radisavljević, N. Ivanović, Z. Rakočević, M. Medić Ilić, N. Romčević, O. M. N. D. Teodoro, Local, electronic and surface structure of multi-component Fe-doped CdTe(S) systems, *Surf. Sci.*, **681**, 76–86, 2019.
4. S. Hofmann, *Auger- and X-Ray Photoelectron Spectroscopy in Materials Science*, Springer, 2013.
5. K. Batalović, N. Bundaleski, J. Radaković, N. Abazović, M. Mitrić, R. A. Silva, M. Savić, J. Belošević-Čavor, Z. Rakočević, C. M. Rangel, Modification of N-doped TiO<sub>2</sub> photocatalysts using noble metals (Pt, Pd) – a combined XPS and DFT study, *Phys.Chem.Chem.Phys.*, **19**, 7062–7071, 2017.
6. C. J. Powell and A. Jablonski, Electron effective attenuation lengths for applications in Auger electron spectroscopy and X-ray photoelectron spectroscopy, *Surf. Interface Anal.*, **33**, 211–229, 2002.
7. M. Taleblou, M. F. Camellone, S. Fabris, S. Piccinin, Oxidation of Gas-Phase and Supported Pt Nanoclusters: An Ab Initio Investigation, *J. Phys. Chem. C*, **126**, 10880–10888, 2022.
8. K. Batalović, J. Radaković, N. Bundaleski, Z. Rakočević, I. Pašti, N. V. Skorodumova, C. M. Rangel, Origin of photocatalytic activity enhancement in Pd/Pt-deposited anatase N-TiO<sub>2</sub> – experimental insights and DFT study of the (001) surface, *Phys. Chem. Chem. Phys.*, **22**, 18536–18547, 2020.