Short Communication

Problems in Determination of Ag Charge State Atoms in Silver Nanoparticles by X-Ray Photoelectron Spectroscopy -

Alexander Naumkin*

A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 119991, Russian Federation

***Address for Correspondence:** Alexander Naumkin, A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 119991, Russian Federation, Russia, Tel: +749-913-59217; Fax: +749-913-55085; E-mail: naumkin@ineos.ac.ru

Antibacterial properties of silver are widely used for centuries to treat a wide class of diseases. Currently, there is an increased interest in the use of Silver Nanoparticles (Ag NPs) for medical purposes, the effect of which differs from massive silver particles or objects. Numerous studies have been devoted to the discovery of a correlation between the characteristics of Ag NPs and their useful properties. For these purposes, a large number of methods are used to characterize certain properties of Ag NPs. But since the treatment involves direct contact with the tissue, the data on the surface properties of nanoparticles and composites based on them are of particular interest. In this case, one of the effective methods of analysis is X-ray photoelectron spectroscopy. This method is surface-sensitive with an information depth of about 10 nm and provides information about the elemental composition of the surface and the chemical state of atoms. Unfortunately, in a large number of works devoted to the study of Ag NPs by XPS, the data needed to establish a correlation between the chemical composition of the surface and the antibacterial properties of Ag NPs are often absent.

Often, authors determine the presence of silver atoms in the material or only their concentration.

The conclusion about the chemical state of silver atoms is carried out without taking into account surface charging or on the basis of approximate values of binding energies [1-7], and the results of the curve-fitting procedure are given without specifying the widths of the peaks. It should be noted that when recording the Ag 3d spectra of pure silver and its oxides under the same conditions, the widths of the peaks differ noticeably. According to [8-10] FWHM of the Ag $3d_{5/2}$ peaks for Ag, Ag_2O and AgO are 1.2, 1.53 and 1.75 eV, respectively.

The use of incorrect data on the binding energy leads to incorrect conclusions about the chemical state of silver atoms [11-13]. At present, the most accurate values of the Ag $3d_{5/2}$ peak binding energies for solid silver are 368.327 and 368.299 eV for Al Kα and Mg Kα, respectively. The corresponding kinetic energies for Ag $M_4N_{45}N_{45}$ peak and Auger parameters are 357.855, 357.902, 726.182 and 726.201 eV, respectively [14]. The binding energies above 368.327 and 368.299 eV should be assigned to the Ag^0 state, while those below them - to Ag^+ or Ag^{2+} states. The first assignment is based on the cluster size effect, which reflects the binding energy dependence on particle size [15-18]. The set of BE, KE and AP compiled in accordance with NIST XPS Database rules [19] is presented elsewhere [20].

It is well known that when analyzing silver nanoparticles, some problems arise that do not always allow us to determine in which chemical state silver atoms are and which of them is responsible for antibacterial properties. The purpose of this communication is to attract the attention of researchers to the features of the interpretation of Ag 3d photoelectron spectra of Ag NPs.

The main problem is the difficulty of distinguishing the states of Ag^0 and Ag^+, since the binding energies of photoelectron peaks are fairly close. The surface charge of the sample as a result of the photoemission of electrons also introduces additional uncertainty. To take it into account, as a rule, the C 1s spectrum is used with attribution the binding energy in the range of 284.6 - 285.2 eV to the main peak. This range is quite large and does not allow determining the binding energy of the Ag $3d_{5/2}$ peak with the required accuracy. The modified Auger parameter, which is the sum of the binding energy of the Ag $3d_{5/2}$ photoelectron peak and kinetic energy of the Ag $M_4N_{45}N_{45}$ Auger peak, is widely used to determine the chemical state of silver atoms. But in this case, there are two problems as well.

The first is the difference in the information depth of photoelectrons and Auger electrons, i.e. the summation of signals from near-surface layers of various thicknesses occurs. In this case, Auger electrons are more surface-sensitive than photoelectrons. The second problem is that the time of registration of the Auger spectrum is usually much longer than the time of registration of the photoelectron spectrum due to a wider range, which can lead to the decomposition of silver oxides if they are present in the subsurface layer.

The next feature is the manifestation of the size effect in photoelectron spectra, i.e. dependence of the position of the photoelectron peak on the size of nanoparticles. It consists in increasing the binding energy of the photoelectron peak with decreasing particle size. In some cases, the size effect helps to distinguish the Ag^0 state, since the Ag^+ and Ag^{2+} states are characterized by a shift to the low-energy region. The decrease in the size of Ag NPs leads to an increase in the binding energy and peak width and can reach 1.4 eV [21]. These changes are due to the influence of the initial state contribution and final state effect. Lopez-Salido et al found that for Ag NPs on HOPG the latter is about 0.1 eV and it is independent on the particle size, while the positive shift is mostly determined by the initial state contribution [22]. From general point of view the final state effect should depend on the conductivity of a support and it may play a significant role when such supports as chitosan and cellulose are used for biomedical applications. Another reason for positive energy shift may be related to different secondary emission coefficients of Ag NPs and non-conducting neighboring regions. Therefore, a combination of various processes should be taken into account to describe the positive binding energy shift. It should be stressed again that the shift is characteristic of Ag^0 state.

Another feature is the possible manifestation of differential charging, when areas with different electrical conductivities and the secondary electron emission coefficient acquire a different surface potential, which influences the position of the photoelectron peak. This phenomenon is traditionally considered as negative, but, nevertheless, it can be used for surface analysis in the controlled differential charging mode, when a positive or negative mixing voltage is applied to the sample holder. In this case, the photoelectron spectra from regions with good conductivity will shift by a larger amount than from regions with poor conductivity. Since surface atoms are more active than bulk atoms, the possibility of their reaction with the environment becomes very high, and for nanoparticles one should expect a core-shell structure.

Summarizing the written above, it should be noted that for understanding the antibacterial properties of silver nanoparticles, reliable information about their chemical composition and interaction with the support is needed. When analyzing the chemical composition of Ag-containing composite by XPS, the following procedures must be met:

- Calibration of the energy scale of the spectrometer.

- Accounting for surface charging. In the case of using the C 1s spectrum, a state with a well-defined binding energy must be deconvoluted in it. One of the most reliable sources for the binding energies of chemical groups is [23].

- When deconvoluting different states in the Ag 3d spectra, one should take into account the difference in the peak the widths of Ag^0, Ag^+ and Ag^{2+} states.

- When registering the Auger spectrum, determine the position

of the peak used to determine the Auger parameter, then move to another area of the sample not exposed to X-rays and record the spectrum in a narrow energy range. The subsequent registration of the photoelectron spectrum used to take into account surface charging.

Applying a bias voltage to the sample holder in the presence of a good electrical contact may allow the detection of areas with different physical and chemical characteristics.

REFERENCES

1. Gurunathan S, Han JW, Kwon DN, Kim JH. Enhanced antibacterial and anti-biofilm activities of silver nanoparticles against gram-negative and gram-positive bacteria. Nanoscale Res Lett. 2014; 9: 373. https://goo.gl/CWyktr

2. Fayaz AM, Balaji K, Girilal M, Yadav R, Kalaichelvan PT, Venketesan R. Biogenic synthesis of silver nanoparticles and their synergistic effect with antibiotics: a study against gram-positive and gram-negative bacteria. Nanomedicine. 2010; 6: 103-109. https://goo.gl/eBDb2o

3. Xu H, Shi X, Ma H, Lv YH, Zhang LP, Mao ZP. The preparation and antibacterial effects of dopa-cotton/ AgNPs. Appl Surf Sci. 2011; 257: 6799-6803. https://goo.gl/5XvVhc.

4. Li G, Liu H, Zhao H, Gao Y, Wang J, Jiang H, et al. Chemical assembly of TiO2 and TiO$_2$@ Ag nanoparticles on silk fiber to produce multifunctional fabrics. J Colloid Interface Sci. 2011; 358: 307-315. https://goo.gl/rsqoGi.

5. Chen SF, Li JP, Qian K, Xu WP, Lu Y, Huang WX, et al. Large scale photochemical synthesis of M@TiO$_2$ nanocomposites (M = Ag, Pd, Au, Pt) and their optical properties, CO oxidation performance, and antibacterial effect. Nano Res. 2010; 3: 244-255. https://goo.gl/sX4oom

6. Gurunathan S. Biologically synthesized silver nanoparticles enhances antibiotic activity against gram-negative bacteria. J Industr Eng Chem. 2015; 29: 217-226. https://goo.gl/MWs484.

7. An J, Wang DS, Yuan XY. Synthesis of stable silver nanoparticles with antimicrobial activities in room-temperature ionic liquids. Chem Res in Chinese Universities. 2009; 25: 421-425.

8. Hoflund GB, Weaver JF, Epling WS. Ag Foil by XPS, Surf Sci Spectra. 1994; 3: 151-156. https://goo.gl/zX17NZ.

9. Hoflund GB, Weaver JF, Epling WS. Ag$_2$O XPS spectra. Surf Sci Spectra. 1994; 3: 157-162. https://goo.gl/5dQUS6.

10. Hoflund GB, Weaver JF, Epling WS. AgO XPS spectra. Surf. Sci. Spectra. 1994; 3: 163-168. https://goo.gl/Mp1pj8.

11. Zhang F, Wu X, Chen Y, Lin H. Application of silver nanoparticles to cotton fabric as an antibacterial textile finish. Fibers and Polymers. 2009; 10: 496-501. https://goo.gl/qLSAoG.

12. Pagliai M, Caporali S, Muniz-Miranda M, Pratesi G, Schettino V. SERS, XPS, and DFT study of adenine adsorption on silver and gold surfaces. J Phys Chem Lett. 2012; 3: 242-245. https://goo.gl/xc3RRK.

13. Kumar SA, Abyaneh MK, Gosavi SW, Kulkarni SK, Pasricha R, Ahmad A, et al. Nitrate reductase-mediated synthesis of silver nanoparticles from AgNO3. Biotechnology Lett. 2007; 29: 439-445. https://goo.gl/tqU13h.

14. Seah MP. AES: energy calibration of electron spectrometers. IV. A re-evaluation of the reference energies. J Electron Spectrosc Relat Phenom. 1998; 97: 235-241. https://goo.gl/ekaCwB

15. Egelhoff Jr, WF. Electronic structure evolution of Au, Ag, and Cu deposited on Al (100). J Vac Sci Technol. 1982; 20; 668-670.

16. Egelhoff Jr WF. Core-level binding-energy shifts at surfaces and in solids. Surf Sci Reports. 1987; 6: 253-415. https://goo.gl/2bVV7E.

17. Peters S, Peredkov S, Neeb M, Eberhardt W, Al-Hada M. Size-dependent XPS spectra of small supported Au-clusters. Surf Sci. 2013; 608; 129-134. https://goo.gl/EhS5bH.

18. Wertheim GK. Core-electron binding energies in free and supported metal clusters. Z Phys B Condens Matter. 1987; 66: 53-63. https://goo.gl/3cJJVb.

19. Naumkin AV, Kraut-Vass A, Gaarenstroom SW, Powell CJ. NIST X-ray photoelectron spectroscopy database, version 4.1. 2012. https://goo.gl/CZtyA6

20. Samoilova N, Krayukhina M, Naumkin A, Yamskov I. Eco-friendly preparation of a magnetic catalyst for glucose oxidation combining the properties of nanometal particles and specific enzyme. Monatshefte für Chemie-Chemical Monthly. 2018; 149: 1179-1188. https://goo.gl/aDWmZS.

21. Shin HS, Choi HC, Jung Y, Kim SB, Song HJ, Shin HJ. Chemical and size effects of nanocomposites of silver and polyvinyl pyrrolidone determined by X-ray photoemission spectroscopy. Chem Phys Lett. 2004; 383: 418-422. https://goo.gl/oYP9BK.

22. Lopez-Salido I, Lim DC, Dietsche R, Bertram N, Kim YD. Electronic and geometric properties of Au nanoparticles on Highly Ordered Pyrolytic Graphite (HOPG) studied using X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). J Phys Chem B. 2006; 110: 1128-1136. https://goo.gl/Ndti8s.

23. Beamson G, Briggs D. High resolution XPS of organic polymers: The Scienta ESCA300 Database. Chichester: Wiley; 1992. https://goo.gl/K4f2qv