Technical Physics Letters, 2025, Vol. 51, No. 3

13

Field electron emission from a carbon nanotube amino acid composite layer

© O.Yu. Tsybin[1], M.A. Baranov[1], M.E. Popov[1,2], S.V. Filippov[2], A.G. Kolosko[2],
E.O. Popov[2]

[1] Peter the Great Saint-Petersburg Polytechnic University, St. Petersburg, Russia
[2] Ioffe Institute, St. Petersburg, Russia
E-mail: popov_me@spbstu.ru

Received October 21, 2024
Revised November 20, 2024
Accepted November 27, 2024

The paper presents a study of the field emission properties of a new nanocomposite material based on a mixture of carbon nanotubes and organic substance (valine amino acid). On the surface of a thin composite layer covering an electrically conductive metal cathode there was experimentally revealed a developed network of active electron emission sites. Valine not only enhanced field emission properties of the composite surface, but also acted as a binder thus providing high adhesion and strength of the nanocomposite coating.

Keywords: electron field emission, carbon nanotubes, amino acid, valine.

DOI: 10.61011/TPL.2025.03.60735.20161

Biomolecular functionalization of nanocarbon materials makes possible their new unique applications in physics, chemistry, biology, medicine and electronics. The use of carbon nanotubes (CNTs) looks promising; their combination with biological molecules opens up possibilities for developing new types of biosensors and bioaccumulators [1–5].

Coupling of CNTs with biomolecules may reduce the non-constructive CNT agglomeration caused by van-der-Waals forces between them. On the other hand, covalent bonds between the functional groups and CNT carbon skeleton can improve the CNT adhesion to the substrate [5]. Both of these factors together determine the possibilities of using such substances in vacuum electronics, among others, in important design solutions for field electron emitters and cathodes.

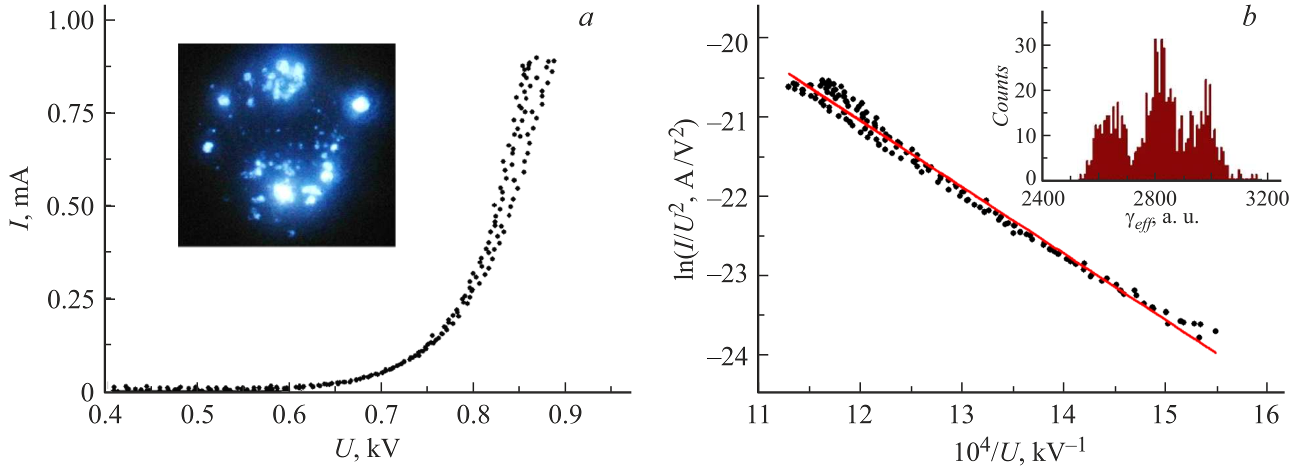
CNT based field cathodes are characterized by low threshold voltages and quite high emission currents arising due to the current load distribution over a multitude of conductive pointed protrusions above the cathode surface [6].

In connection with the requirement for mechanical stability of the emitter material under the impact of ponderomotive forces, various options for fixing CNTs on the cathode surface are used. These are formation of cluster structures (e.g. emitters based on cone-shaped CNT agglomerates [7]), creation of special buffer layers that increase the adhesion (e.g. adding a Ti layer [8]), and also using various substances binding CNTs to the substrate (the so-called binders). Binders are applied prior to placing CNTs on the cathode surface (e.g. emitters obtained by transferring CNTs from a homogeneous film to the AuSn and SnAg islands by direct contact [9]) or after it (e.g., infiltration of vertically oriented CNTs with polydimethylsiloxane molecules and their subsequent polymerization [10]); also, binders are mixed with CNTs thus forming a suspension from which a nanocomposite coating is then formed (e.g. emitters created by pneumatic spraying onto the substrate of a mixture of CNTs and polymethyl-methacrylate polymer solution [11]). Paper [12] has demonstrated an improvement in the CNT cathode emission properties due to using electrochemically controllable coagulation of dispersed CNT molecular complexes with ribonucleic acid. However, a wide range of such scientific and technological tests have not yet provided efficient solutions.

In this study we have developed a nanocomposite mixture of CNTs with amino acids among which the composition with valine was distinguished due to its positive properties; field emission properties of a cathode with such a composite layer were examined for the first time.

The experimental field cathode was constructed as a substrate in the form of a round metal plate 10 mm in diameter coated with the CNT/valine nanocomposite. The coating was created by applying onto the plate a drop of the composite suspension with subsequent evaporation of the solvent. The suspension consisted of two components: CNTs suspended in orthoxylene (0.1 mg of CNTs per ml) and valine solution in orthoxylene (1 mg of valine per ml); they both were treated with ultrasound for several hours. CNT concentration in the nanocomposite was 10 wt.%. As CNTs, carbon nanotubes Tuball (produced by OCSiAl, Novosibirsk) were used. Side contacts of CNTs on the metal substrate provide the contact resistance of about 1 kΩ, while end CNT contacts may be significantly more conductive [13,14].

In the experiments, valine ($HO_2CCH(NH_2)CH(CH_3)_2$, EMD Millipore Corporation, Japan) was used without additional purification. Valine belongs to the group of simple aliphatic non-polar α-amino acids having the major alkyl side chain C_α and existing in various conformers. Electron



Results of the field emission experiment with the CNT/valine nanocomposite layer on the cathode. *a* — IV characteristic (the inset presents the glow pattern); *b* — Fowler-Nordheim IV characteristic (FN IV) (the inset illustrates statistics of the effective field gain).

transfer through the polypeptide matrices of such proteins is a key process in biological systems responsible for energy conversion and signal transduction. The charge transfer process is sensitive to the sequence of amino acids making up the protein and to their conformation; therefore, it may serve as a tool for controlling the conductivity of such nanocomposites. Studies [15,16] have shown that the self-organizing polypeptide matrix is electronically conductive not only in solution, but also in the dry state over hundreds of nanometers. Thus, we assumed that high electrical conductivity of amino acid polypeptides, e. g. valine, is expected to improve the CNT nanocomposite conductive properties and enhance the field emission.

The emission properties were studied using a computer-aided method of multichannel detection and recording of field emission data [17]. The parameters to be measured were the measuring chamber vacuum, applied voltage and emission current, as well as the pattern of emission activity distribution over the cathode surface (the so-called glow pattern). Glow patterns were formed on the phosphor coating of the transparent anode (glass with the transparent conductive ITO-coating). IV characteristics were recorded in the pulse voltage mode with high-speed signal recording (a single IV curve was measured during 20 ms, this value being equal to the high voltage pulse period); this allowed achieving higher voltages than in the constant power supply mode. The voltage and emission current levels are further used to designate pulse amplitudes of the applied voltage and corresponding emission current.

A special program for the data recording and online processing allowed construction of the I-V curves in the Fowler–Nordheim coordinates, estimation of the effective field enhancement factor and emission area, and also construction of their statistics at a relatively stable level of emission current [18]. Another possibility was online conduction of the test for cold field emission (the so-called Forbes test) [19].

The experiments showed that the threshold voltage of the cathode under consideration was $\sim 300\,\mathrm{V}$ (necessary to achieve the preset current level of $1.5\,\mu\mathrm{A}$). Recording of the glow patterns started at the voltage of $\sim 400\,\mathrm{V}$ and current of $\sim 20\,\mu\mathrm{A}$. Knowing the established inter-electrode distance between flat surfaces of the emitter and anode ($d_{sep} = 370\,\mu\mathrm{m}$), it is possible to estimate the threshold emission onset field which appeared to be as low as $0.81\,\mathrm{V}/\mu\mathrm{m}$.

The maximum current obtained in the experiments amounted up 1.6 mA at the voltage of $\sim 920\,\mathrm{V}$. The voltage was not raised higher because of the risk of damaging the ITO-coating.

The Figure presents the IV characteristic with the maximum current of $\sim 1.5\,\mathrm{mA}$; the curve is constructed in the linear and semi-logarithmic Fowler –Nordheim coordinates (FN IV characteristic). The insets demonstrate the glow pattern and statistics of the effective field enhancement factor. The obtained statistics exhibits an anomalous effect, namely, the presence of three peaks at once, which get formed simultaneously in the process of data acquisition. Probably, three independent areas of the emitting surface were active; they differed in the parameters of local enhancement of the microscopic electric field strength and provided different partial field emission fluxes in the vacuum gap between the composite layer and anode. This assumption is supported by both the field gain statistics and glow pattern of the anode's phosphor coating (see Fig. *a*).

Local properties of the composite layer surface were determined by the fact that electrons might be emitted into vacuum not only from the energy level corresponding to pure CNT ($\sim 4.6\,\mathrm{eV}$ [20]) but also from the level corresponding to the highest occupied molecular orbital of valine which was about 8.72 eV (the effective gas phase valine work function, the potential of ionization potential from NH_3 HOMO) [21].

Along with this, it seems possible that just the polymer islands of valine molecules covering CNTs provided the nanocomposite coating with high electron energy levels and parameters of local field enhancement and release of electrons into vacuum.-

When the measured emission current was $\sim 1.5\,\mathrm{mA}$, all the recorded I-V characteristics passed the test for cold field emission. At the given CNT work function (4.6 eV), the emission proceeded in the range of dimensionless local fields f of 0.36 to 0.45, which, according to the test, does not go beyond the mode of „classical cold field emission“ [19]. This evidences that the developed composite cathode is quite promising to be used in vacuum microelectronics.

Funding

O.Yu. Tsybin, M.A. Baranov, and M.E. Popov, who have formulated the problems, designed the samples to be studied and analyzed the results, express their gratitude to the Russian Science Foundation for financial support of this study (Project № 21-72-20029 „Supercomputer modeling and biomolecular film structure technology“ (https://rscf.ru/project/21-72-20029).

S.V. Filippov, A.G. Kolosko and E.O. Popov have performed emission analysis of the samples in the framework of developing the experimental research method under State Assignment № 0040-2019-0024 and FFUG-2024-0031.

Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] J. Wang, Electroanalysis, **17**(1), 7 (2005). DOI: 10.1002/elan.200403113

[2] J.R. Siqueira, L. Caseli, F.N. Crespilho, V. Zucolotto, O.N. Oliveira, Biosens. Bioelectron., **25** (6), 1254 (2010). DOI: 10.1016/j.bios.2009.09.043

[3] W. Putzbach, N.J. Ronkainen, Sensors, **13** (4), 4811 (2013). DOI: 10.3390/s130404811

[4] L. Ma, H.L. Zhuang, S. Wei, K.E. Hendrickson, M.S. Kim, G. Cohn, R.G. Hennig, L.A. Archer, ACS Nano, **10** (1), 1050 (2016). DOI: 10.1021/acsnano.5b06373

[5] R. Yadav, K. Kumar, P. Venkatesu, in *Handbook of carbon nanotubes*, ed. by J. Abraham, S. Thomas, N. Kalarikkal (Springer, Cham, 2021). DOI: 10.1007/978-3-319-70614-6_65-1

[6] R.G. Forbes, Solid-State Electron., **45** (6), 779 (2001). DOI: 10.1016/S0038-1101(00)00208-2

[7] H.M. Oh, J.H. Ryu, N.Y. Bae, E.H. Lee, A.N. Ha, W.M. Bae, J. Jang, K.C. Park, in *Int. Vacuum Nanoelectronics Conf.* (IEEE, 2010), p. 127–128. DOI: 10.1109/IVNC.2010.5563137

[8] S. Srividya, S. Gautam, P. Jha, P. Kumar, A. Kumar, U.S. Ojha, J.S.B.S. Rawat, S. Pal, P.K. Chaudhary, Harsh, R.K. Sinha, Appl. Surf. Sci., **256** (11), 3563 (2010). DOI: 10.1016/j.apsusc.2009.12.155

[9] A. Kumar, V.L. Pushparaj, S. Kar, O. Nalamasu, P.M. Ajayan, R. Baskaran, Appl. Phys. Lett., **89** (16), 163120 (2006). DOI: 10.1063/1.2356899

[10] Y.J. Jung, S. Kar, S. Talapatra, C. Soldano, G. Viswanathan, X. Li, Z. Yao, F.S. Ou, A. Avadhanula, R. Vajtai, S. Curran, O. Nalamasu, P.M. Ajayan, Nano Lett., **6** (3), 413 (2006). DOI: 10.1021/nl052238x

[11] H. Jung, S.Y. An, D.M. Jang, J.M. Kim, J.Y. Park, D. Kim, Carbon, **50** (3), 987 (2012). DOI: 10.1016/j.carbon.2011.10.001

[12] L.T. Cheng, M. Zheng, W. Mahler, D. Roach, A. Fennimore, G. Reynolds, I.H. Kim, C.S. Lee, H.S. Kim, SID Symp. Digest Tech. Papers, **39** (1), 155 (2008). DOI: 10.1889/1.3069457

[13] P. Wilhite, A.A. Vyas, J. Tan, J. Tan, T. Yamada, P. Wang, J. Park, C.Y. Yang, Semicond. Sci. Technol., **29** (5), 054006 (2014). DOI: 10.1088/0268-1242/29/5/054006

[14] F. Banhart, Nanoscale, **1** (2), 201 (2009). DOI: 10.1039/B9NR00127A

[15] S.Y. Yew, G. Shekhawat, N. Wangoo, S. Mhaisalkar, C.R. Suri, V.P. Dravid, Y.M. Lam, C.R. Suri, V.P. Dravid, Y.M. Lam, Nanotechnology, **22** (21), 215606 (2011). DOI: 10.1088/0957-4484/22/21/215606

[16] I. Ron, L. Sepunaru, S. Itzhakov, T. Belenkova, N. Friedman, I. Pecht, M. Sheves, D. Cahen, J. Am. Chem. Soc., **132** (12), 4131 (2010). DOI: 10.1021/ja907328r

[17] E.O. Popov, A.G. Kolosko, S.V. Filippov, E.I. Terukov, R.M. Ryazanov, E.P. Kitsyuk, J. Vac. Sci. Technol. B, **38** (4), 043203 (2020). DOI: 10.1116/6.0000072

[18] A.G. Kolosko, E.O. Popov, S.V. Filippov, Y. Gotoh, J. Vac. Sci. Technol. B, **37** (3), 031803 (2019). DOI: 10.1116/1.5090461

[19] A.G. Kolosko, S.V. Filippov, P.A. Romanov, E.O. Popov, R.G. Forbes, J. Vac. Sci. Technol. B, **34** (4), 041802 (2016). DOI: 10.1116/1.4946834

[20] V. Barone, J.E. Peralta, J. Uddin, G.E. Scuseria, J. Chem. Phys., **124** (2), 024709 (2006). DOI: 10.1063/1.2150213

[21] A.N. Zavilopulo, A.I. Bulhakova, S.S. Demes, E.Yu. Remeta, A.V. Vasiliev, Eur. Phys. J. D, **75**, 287 (2021). DOI: 10.1140/epjd/s10053-021-00294-2

Translated by EgoTranslating