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THE ELECTROCHEMICAL BEHAVIOUR OF Au-PEDOT/rGO MODIFIED ELECTRODE IN URIC ACID

(Sifat Elektrokimia Elektrod Bermodifikasi Komposit Au-PEDOT/rGO dalam Asid Urik)

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Abstract

The development of gold nanoparticle/poly(3,4-ethylene dioxythiophene)/reduced graphene oxide (denoted as Au-PEDOT/rGO) sensor is necessary for the detection of UA as the irregular amount of UA in the human body may cause several diseases such as gout, heart disease, kidney stone and hypertension. In this work, Au-PEDOT/rGO nanocomposite was synthesized by a facile chemical technique. The morphology, composition, and structure of Au-PEDOT/rGO composite were confirmed by FTIR, SEM, and XRD characterization. FTIR spectrum showed the presence of C-O-C stretching and C-S stretching of the thiophene ring. The attachment of Au with PEDOT and rGO was confirmed by SEM. XRD analysis showed the presence of Au(111), Au(200), Au(220), Au(311) and Au(222) corresponding to Au-PEDOT/ rGO composite. This proved that Au-PEDOT/rGO has been successfully synthesized. The electrochemical behavior of Au-PEDOT/rGO/GCE was evaluated by cyclic voltammetry (CV) in 1.0 M KCl with 5 mM $K_4[Fe(CN)_6]$ and the results demonstrated that Au-PEDOT/rGO/GCE has a better electrical conductivity for detection of UA in the real sample. DPV measurements showed a linear relationship between oxidation peak current and concentration of UA in phosphate buffer (pH 7) over the concentration range 0.10 µM

until 25.0 µM. The limit of detection of UA is 0.05 µM, and the limit of quantification of UA is 0.22 µM. Thus, Au-PEDOT/rGO electrode composite is a worthy alternative for the detection of UA in human's urine.

Keywords: conducting polymer, gold nanoparticles, reduced graphene oxide, uric acid

Abstrak

Pembangunan sensor buat zarah nano aurum/poli(3,4-etilenadioxitiofena/grafin oksida terturun (dilabel sebagai Au-PEDOT/rGO) adalah diperlukan untuk pengesanan UA kerana jumlah UA yang tidak normal dalam tubuh manusia boleh menyebabkan beberapa kondisi penyakit seperti gout, penyakit jantung, batu ginjal dan darah tinggi. Dalam kajian ini, komposit nano Au-PEDOT/rGO telah disinthesis melalui teknik kimia mudah. Morfologi, komposisi, dan struktur komposit Au-PEDOT/rGO telah disahkan melalui teknik pencirian FTIR, SEM, dan XRD. Spektrum FTIR menunjukkan kehadiran regangan C-O-C dan regangan C-S bagi ikatan tiofena manakala penggabungan Au kepada lembaran PEDOT dan rGO telah dibuktikan melalui SEM. Analisis XRD menunjukkan kehadiran Au(111), Au(200), Au(220), Au (311) dan Au(222) sepadan dengan komposit Au-PEDOT/rGO. Keputusan tersebut telah mengesahkan bahawa Au-PEDOT/rGO telah berjaya disintesis. Sifat elektrokimia Au-PEDOT/rGO telah dinilai melalui voltammetri berkitar (CV) di dalam 1.0 M KCl bersama dengan 5 mM $K_4[Fe(CN)_6]$ dan hasil kajian menunjukkan bahawa Au-PEDOT/rGO memiliki konduksi elektrik yang bagus untuk pengesanan UA di dalam sample nyata. Analisis DPV menunjukkan hubungan linear antara puncak pengoksidaan arus dan kepekatan UA di dalam penimbal fosfat (pH 7) diantara julat kepekatan 0.10 µM hingga 25.0 µM. Had pengesanan yang diukur bagi UA ialah 0.05 µM manakala had pengukuran UA adalah 0.22 µM. Oleh itu, komposit Au-PEDOT/rGO merupakan alternatif yang berbaloi untuk mengesan UA dalam air kencing manusia.

Kata kunci: polimer pengalir, zarah nano aurum, grafin oksida terturun, asid urik

References

1. Yu, H., Zhang, Z., Shen, T., Jiang, J., Chang, D. and Pan, H. (2018). Sensitive determination of uric acid by using graphene quantum dots as a new substrate for immobilisation of uric oxidase. *IET Nanobiotechnology*, 12(23): 191-195.
2. Soares, F., Paula, F. D. S., Franco, D. L., Torres, W. and Ferreira, L. F. (2017). Electrochemical detection of uric acid using graphite screen-printed electrodes modified with prussian blue/poly(4-aminosalicylic acid)/uricase. *Journal of Electroanalytical Chemistry*, 806: 172-179.
3. Ndrepepa, G. (2018) Uric acid and cardiovascular disease. *Clinica Chimica Acta*, 484(3): 150-163.
4. Black, C. N., Bot, M., Peter, G., Snieder, H. and Penninxm B. W. J. H. (2017). Uric acid in major depressive and anxiety disorders. *Journal of Affective Disorders*, 225: 684-690.
5. Kand, R., Drábková, P. and Hampl, R. (2011). The determination of ascorbic acid and uric acid in human seminal plasma using an HPLC with UV detection. *Journal of Chromatography B*, 879: 2834-2839.
6. Long, Q., Fang, A., Wen, Y., Li, H., Zhang, Y. and Yao, S. (2016). Biosensors and bioelectronic rapid and highly-sensitive uric acid sensing based on enzymatic catalysis-induced upconversion inner filter effect. *Biosensors and Bioelectronic*, 86: 109-114.
7. Wei, Y., Liu, Y., Xiu, Z., Wang, S., Chen, B., Zhang, D. and Fang, Y. (2020). Simultaneous detection of ascorbic acid, dopamine, and uric acid using a novel electrochemical sensor based on palladium nanoparticles/reduced graphene oxide nanocomposite. *International Journal of Analytical Chemistry*, 1-13.
8. Su, C. H., Sun, C. L. and Liao, Y. L. (2017). Printed combinatorial sensors for simultaneous detection of ascorbic acid, uric acid, dopamine and nitrite. *ACS Omega*, 2(8): 4245-4252.
9. Tukimin, N., Abdullah, J. and Sulaiman, Y. (2018). Electrodeposition of poly(3,4-ethylenedioxy thiophene)/reduced graphene oxide/manganese dioxide for simultaneous detection od uric acid,

dopamine and ascorbic acid. *Journal of Electroanalytical Chemistry*, 820: 74-81.
10. Muhamad, N. B., Khairul, W. M. and Yusoff, F. (2019). Synthesis and characterization of poly(3,4-ethylenedioxythiophene) functionalized graphene with gold nanoparticles as a potential oxygen reduction electrocatalyts. *Journal of Solid State Chemistry*, 275(4): 30-37.
11. Li, Y., Du, Y., Dou, Y., Cai, K. and Xu, J. (2017). PEDOT-based thermoelectric nanocomposites-a mini review. *Synthetic Metals*, 226: 119-128.
12. Lawal, A. T. (2019). Graphene-based nano composites and their applications. A review. *Biosensors and Bioelectronics*, 2019: 111384.
13. Rosli, A. R., Loh, S. H. and Yusoff, F. (2019). Synthesis and characterization of magnetic fe_3o_4/ reduced graphene oxide and its application in determination of dopamine. *Asian Journal of Chemistry*, 31(12): 2785-2792.
14. Berisha, L., Shabani, E., Maloku, A., Jashari, G. and Arbneshi, T. (2020). Electrochemical determination of dopamine and uric acid in blood serum using anionic surfactants at carbon paste electrodes. *Malaysian Journal of Analytical Sciences*, 24(1): 97-106.
15. Jin W. and Maduraiveeran, G. (2017). Electrochemical detection of chemical pollutants based on gold nanomaterials. *Trends in Environmental Analytical Chemistry*, 14(4): 28-36.
16. Harun, N. A., Kassim, S., Tahrin, R. A. A. and Rusdi, N. F. (2018). Bimetallic (Au-Ag) in 3D hot spots as highly sensitive substrate for high performance surface-enhanced raman scattering (SERS). *ASM Science Journal*, 11(1): 86-95.
17. Kassim, S., Padmanabhan, S. C., Salaun, M. and Pemble, M. E. (2011). PMMA gold metallodielectric photonic crystals and inverse opals: preparation and optical properties. *AIP Conference Proceeding*, 263: 1-4.
18. Kaur, M., Kaur, H., and Kukkar, D. (2018). Synthesis and characterization of graphene oxide using modified Hummer's method. *AIP Conference Proceeding*, 1953(1): 030180.
19. Johra, F. T. and Jung, W. (2016). Low temperature synthesis of RGO-Au nanocomposite for apparently reduced time and its application as a chemical sensor. *Applied Surface Science*, 362: 169-175.
20. Liu, Z., Xu, J., Yue, R., Yang, T. and Gao, L. (2016). Facile one-pot synthesis of Au-PEDOT/rGO nanocomposite for highly sensitive detection of caffeic acid in red wine sample. *Electrochimica Acta*, 196: 1-12.
21. Yan, Q., Zhi, N., Yang, L., Xu, G., Feng, Q., Zhang, Q. and Sun, S. (2020). A highly sensitive uric acid electrochemical biosensor based on a nano-cube cuprous oxide/ferrocene/uricase modified glassy carbon electrode. *Scientific Reports*, 10: 10607.
22. Ali, A., Zhang, Y., Jamal, R., and Abdiryim, T. (2017). Solid-state heating synthesis of poly(3,4-ethlylenedioxythiophene)/gold/graphene composite and its application for amperometric determination of nitrite and iodate. *Nanoscale Research Letter*, 12(568): 1-10.
23. Muhammad, N. B., and Yusoff, F. (2018). The physical and electrochemical characteristic of gold nanoparticles supported PEDOT/graphene composite as potential cathode material in fuel cells. *Malaysian Journal of Analytical Sciences*, 22(6): 921–930.
24. Gualandi, I., Tonelli, D., Mariani, F., Scavetta, E., Marzocchi, M. and Fraboni, B. (2016). Selective detection of dopamine with an all PEDOT:PSS organic electrochemical transistor. *Scientific Reports*, 6 (10): 1-10.
25. Sekli-belaidi, F., Temple-boyer, P. and Gros, P. (2010). Voltammetric microsensor using PEDOT-modified gold electrode for the simultaneous assay of ascorbic and uric acids. *Journal of Electroanalytical Chemistry*, 647(2): 159-168.
26. Wang, C., Du, J. and Wang, H. (2014). A facile electrochemical sensor based on reduced graphene oxide and Au nanoplates modified glassy carbon electrode for simultaneous detection of ascrobic acid, dopamine and uric acid. *Sensors & Actuators: B. Chemical*, 204: 302-309.
27. Tian, X., Cheng, C. and Yuan H. (2012). Simultaneous determination of L-ascorbic acid, dopamine and uric acid with gold nanoparticles-–β-cyclodextrin–graphene-modified electrode by

square wave voltammetry. *Talanta*, 93: 79-85.
28. Yu, X., Sheng, K. and Shi, G. (2014). A Three-dimensional interpenetrating electrode of reduced graphene oxide for selective detection of dopamine.*The Analyts*, 139: 4525-4531.
29. Hsu, M., Chen, Y., Lee, C., and Chiu, H. (2012). Gold nanostructures on flexible substrates as electrochemical dopamine sensors. *Applied Material and Interface*, 4(10): 5570-5575.

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SITE-SELECTIVE CARBOXYMETHYLATION OF CHITOSAN UNDER HETEROGENEOUS CONDITIONS

(Penentuan Tapak bagi Proses Pengkarboksimetil pada Kitosan dalam Keadaan Heterogen)

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Abstract

The substitution sites on chitosan are affected by the presence of a base. Herein, the effects of pH on the site-selective carboxymethylation of chitosan were investigated. Carboxymethyl chitosan was synthesized by reacting chitosan with monochloroacetic acid at different pH under heterogeneous conditions. Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy confirmed that carboxymethylation was successful, with the appearance of peaks around 1326-1320 cm^{-1} (C–N groups) and 1257-1253 cm^{-1} (C–O–C groups) and allowed differentiation between the carboxymethyl substitution sites on chitosan. Additionally, the peaks at approximately 3.28 and 4.12 ppm in the ^{1}H nuclear magnetic resonance (NMR) spectra confirmed that substitution occurred at amine and hydroxyl groups, respectively. Overall, the carboxymethylation of chitosan under heterogeneous conditions at pH 8.5-11 gave O-substitution, at pH 12-13 gave N,O-substitution, and at pH 14 gave N-substitution. This pH dependence of the site-selective substitution of chitosan is important for polymer electrolyte application.

Keywords: carboxymethyl chitosan, pH effect, substitution site, heterogeneous conditions

Abstrak

Tapak penggantian kitosan dipengaruhi oleh kehadiran bes. Dalam kajian ini, kesan pH terhadap tapak penggantian pengkarboksimetil kitosan telah dikaji. Karboksimetil kitosan disintesis melalui tindak balas

kitosan dengan asid monokloroasetik pada pH berbeza dalam keadaan heterogen. Spektroskopi inframerah transformasi Fourier (ATR-FTIR) mengesahkan bahawa karboksimetilasi telah berjaya dilakukan dengan kemunculan puncak sekitar 1326–1320 cm^{-1} (kumpulan C–N) dan 1257–1253 cm^{-1} (kumpulan C–O–C), yang menunjukkan perbezaan tapak penggantian karboksimetil pada kitosan. Selain itu, puncak sekitar 3.28 dan 4.12 ppm dalam spektrum resonans magnetik nukleus (^{1}H NMR) mengesahkan bahawa penggantian berlaku pada kumpulan amina dan hidroksil. Secara keseluruhan, karboksimetilasi kitosan dalam keadaan heterogen pada pH 8.5-11 memberikan penggantian pada tapak O, pH 12-13 memberikan penggantian pada tapak N dan O, dan pH 14 memberikan penggantian pada tapak N. Kebergantungan tapak pemilihan untuk penggantian kitosan dengan pH ini adalah penting untuk aplikasi elektrolit polimer.

Kata kunci: karboksimetil kitosan, kesan pH, tapak penggantian, keadaan heterogen

References

1. Zhao, D., Yu, S., Sun, B., Gao, S., Guo, S. and Zhao, K. (2018). Biomedical applications of chitosan and its derivative nanoparticles. *Polymers*, 10(4): 462.
2. Wang, W., Meng, Q., Li, Q., Liu, J., Zhou, M., Jin, Z. and Zhao, K. (2020). Chitosan derivatives and their application in biomedicine. *International Journal of Molecular Sciences*, 21(2): 487.
3. Kalliola, S., Repo, E., Srivastava, V., Zhao, F., Heiskanen, J. P., Sirvio•, J. A., Liimatainen, H. and Sillanpa•a•, M. (2018). Carboxymethyl chitosan and its hydrophobically modified derivative as pH-switchable emulsifiers. *Langmuir*, 34(8): 2800-2806.
4. Rayung, M., Aung, M. M., Azhar, S. C., Abdullah, L. C., Su'ait, M. S., Ahmad, A., and Jamil, S. N. A. M. (2020). Bio-based polymer electrolytes for electrochemical devices: Insight into the ionic conductivity performance. *Materials*, 13(4): 838.
5. Zhang, E., Xing, R., Liu, S., Li, K., Qin, Y., Yu, H., and Li, P. (2017). Comparison in docetaxel-loaded nanoparticles based on three different carboxymethyl chitosans. *International Journal of Biological Macromolecules*, 101: 1012–1018.
6. Aranaz, I., Acosta, N., Civera, C., Elorza, B., Mingo, J., Castro, C., Gandía, M. D. L. L. and Caballero, A. H. (2018). Cosmetics and cosmeceutical applications of chitin, chitosan and their derivatives. *Polymers*, 10(2): 213.
7. Jimtaisong, A. and Saewan, N. (2014). Utilization of carboxymethyl chitosan in cosmetics. *International Journal of Cosmetic Science*, 36(1): 12–21.
8. Zhong, H., He, A., Lu, J., Sun, M., He, J. and Zhang, L. (2016). Carboxymethyl chitosan/ conducting polymer as water-soluble composite binder for $LiFePO_4$ cathode in lithium ion batteries. *Journal of Power Sources*, 336: 107-114.
9. Sun, S. and Wang, A. (2006). Adsorption kinetics of Cu(II) ions using N,O-carboxymethyl-chitosan. *Journal of Hazardous Materials*, 131(1–3): 103-111.
10. Mi, Y., Su, R., Fan, D., Zhu, X. and Zhang, W. (2013). Preparation of N,O-carboxymethyl chitosan coated alginate microcapsules and their application to *Bifidobacterium Longum* BIOMA 5920. *Materials Science and Engineering: C*, 33(5): 3047-3053.
11. Muzzarelli, R. A. A., Tanfani, F., Emanuelli, M. and Mariotti, S. (1982). N-(carboxymethylidene) chitosans and N-(carboxymethyl)chitosans: Novel chelating polyampholytes obtained from chitosan glyoxylate. *Carbohydrate Research*, 107(2): 199-214.
12. Nudga, L. A., Plisko, E. A. and Danilov, S. N. (1973). N-alkylation of chitosan. *Zhurnal Obshchei Khimii*, 43(12): 2756-2760.
13. An, N. T., Dung, P. L., Thien, D. T., Dong, N. T. and Nhi, T. T. Y. (2008). An improved method for synthesizing N,N′-dicarboxymethylchitosan. *Carbohydrate Polymers*, 73(2): 261-264.
14. An, N. T., Dung, P. L., Thien, D. T., Dong, N. T. and Nhi, T. T. Y. (2009). Water-soluble N-carboxymethylchitosan derivatives: preparation, characteristics and its application. *Carbohydrate Polymers*, 75(3): 489-497.
15. Nikmawahda, H. T., Sugita, P., and Arifin, B. (2015). Synthesis and characterization of n-

alkylchitosan as well as its potency as a paper coating material. *Advances in Applied Science Research*, 6(2): 141-149.
16. Sashiwa, H., Shigemasa, Y., and René, R. (2000). Novel N-alkylation of chitosan via michael type reaction. *Chemistry Letters*, 29(8): 862-863.
17. Sun, G., Chen, X., Li, Y., Zheng, B., Gong, Z., Sun, J., Chen, H., Li, J. and Lin, W. (2008). Preparation of H-oleoyl-carboxymethyl-chitosan and the function as a coagulation agent for residual oil in aqueous system. *Frontiers of Materials Science in China*, 2(1): 105-112.
18. Leong, K. H., Chung, L. Y., Noordin, M. I., Mohamad, K., Nishikawa, M., Onuki, Y., Morishita, M., and Takayama, K. (2011). Carboxymethylation of kappa-carrageenan for intestinal-targeted delivery of bioactive macromolecules. *Carbohydrate Polymers*, 83(4): 1507-1515.
19. Singh, R. K. and Khatri, O. P. (2012). A scanning electron microscope based new method for determining degree of substitution of sodium carboxymethyl cellulose. *Journal of Microscopy*, 246(1): 43-52.
20. Elomaa, M., Asplund, T., Soininen, P., Laatikainen, R., Peltonen, S., Hyvärinen, S. and Urtti, A. (2004). Determination of the degree of substitution of acetylated starch by hydrolysis, ^{1}H NMR and TGA/IR. *Carbohydrate Polymers*, 57(3): 261-267.
21. Aggeryd, I., and Olin, Å. (1985). Determination of the degree of substitution of sodium carboxymethylcellulose by potentiometric titration and use of the extended henderson-hasselbalch equation and the simplex method for the evaluation. *Talanta*, 32(8A): 645-649.
22. Liu, J., Zhang, X., Kennedy, J. F., Jiang, M., Cai, Q. and Wu, X. (2019). Chitosan induces resistance to tuber rot in stored potato caused by *Alternaria tenuissima*. *International Journal of Biological Macromolecules*, 140: 851-857.
23. Mobarak, N. N., Ahmad, A., Abdullah, M. P., Ramli, N. and Rahman, M. Y. A. (2013). Conductivity enhancement via chemical modification of chitosan based green polymer electrolyte. *Electrochimica Acta*, 92: 161-167.
24. Lusiana, R. A., Siswanta, D. and Mudasir, M. (2014). Modifying surface charge of chitosan membrane by N,O-carboxymethyl chitosan blended with poly(vinyl alcohol). *International Journal of Advances in Chemical Engineering and Biological Sciences*, 1(1): 16-20.
25. Hirai, A., Odani, H. and Nakajima, A. (1991). Determination of degree of deacetylation of chitosan by ^{1}H NMR spectroscopy. *Polymer Bulletin*, 26(1): 87-94.
26. Muzzarelli, R. A. A., Ilari, P., and Petrarulo, M. (1994). Solubility and structure of N-carboxymethylchitosan. *International Journal of Biological Macromolecules*, 16(4): 177-180.
27. Prabaharan, M. and Gong, S. (2008). Novel thiolated carboxymethyl chitosan-g-β-cyclodextrin as mucoadhesive hydrophobic drug delivery carriers. *Carbohydrate Polymers*, 73 (1): 117-125.
28. Chen, X. G. and Park, H. J. (2003). Chemical characteristics of o-carboxymethyl chitosans related to the preparation conditions. *Carbohydrate Polymers*, 53(4): 355-359.
29. Bukzem, A. L., Signini, R., Dos Santos, D. M., Lião, L. M. and Ascheri, D. P. R. (2016). Optimization of carboxymethyl chitosan synthesis using response surface methodology and desirability function. *International Journal of Biological Macromolecules*, 85: 615-624.
30. Mourya, V. ., Inamdar, N. N. and Tiwari, A. (2010). Carboxymethyl chitosan and its applications. *Advanced Materials Letters*, 1(1): 11-33.
31. Pranowo, H. D., Mulya, F., Aziz, H. A, and Santoso, G. A. (2018). Study of substituent effect on properties of platinum(II) porphyrin semiconductor using density functional theory. *Indonesian Journal of Chemistry*, 18(4): 742-748.
32. Lu, X., Xue, J. Q., Wang, Y. J., Mao, W. B., Wu, M. and Li, J. X. (2010). Theoretical studies on the chemical structure of carboxymethyl chitosan. *Advanced Materials Research*, 160-162: 1822-1827.