

Preface

The 4th International Conference on Functional Materials Science 2018 (ICFMS 2018) was international conference for promoting collaborative research program on physical and chemical studies of functional materials under the collaboration between Indonesian researchers and some researchers from institutions/universities in Asia and Europe, held in Bali, Indonesia, November 13-15, 2018. It was jointly organized by Institut Teknologi Bandung, Universitas Padjadjaran, Institut Teknologi Sepuluh November, Universitas Gadjah Mada, Universitas Indonesia, and RIKEN Nishina Center, Japan.

Our first conference held in Bali on April 27-28, 2011, successfully gathered researchers from 14 universities in Indonesia and 10 institutions/universities in Asia and Europe. Our second conference held in Lombok on November 12-13, 2014, also successfully gathered researchers from more universities and institutions in Asia and Europe. The third conference held in Bali on October 19-20, 2016, also successfully gathered researchers from more universities and institutions in Asia and Europe.

For the 4th ICFMS 2018, more than 120 papers were presented in both oral and poster presentation in various scopes including (1) Advanced and Functional Materials, (2) Materials and Devices, (3) New Materials for Energy and Energy Conversion (4) Biomaterials, (5) Theoretical/Modeling/Computer Simulations of Functional Materials, (6) Spectroscopy for Advanced Materials, (7) Hybrid and Composite Materials, and (8) Magnetic Materials. Each published paper was peer-reviewed by two reviewers for quality ensuring.

In conjunction with 4th ICFMS 2018, we also hosted the 2nd RIKEN Symposium, which was a continuation of the successfully previous 1st event in the frame of “International Workshop on Organic Molecule Systems” held in Penang, Malaysia, 2017, in collaboration between RIKEN Nishina Center and Universiti Sains Malaysia (USM). This symposium was intended to provide a platform for the exchange of research knowledge on organic molecular systems achieved by using muons as well as expanding the RIKEN’s worldwide networks and linkages in collaborative research endeavors. Additionally, this activity also aims to encourage young students and researchers to work in the muon field in the future.

As an additional activity preceding the 4th ICFMS 2018, the organizing committee also offered a paper writing clinics for participants, especially for young scientists and students.

We believed great participation from all participants, organizing committees, and all reviewers made our conference successful.

Editor

Risdiana

Darminto

Budhy Kurniawan

A.A. Nugroho

Isao Watanabe

Organizer ICFMS 2018

Advisory Board

Prof. Yoji Koike (Tohoku Univ-Japan)

Dr. Isao Watanabe (RIKEN-Japan)

Prof. Shukri Sulaiman (University Sains Malaysia)

Prof. Andrivo Rusydi (National University of Singapore)

Dr. A. Agung Nugroho (Institut Teknologi Bandung)

Prof. Suminar Pratapa (Institut Teknologi Sepuluh Nopember)

Dr. Kuwat Triyana (Universitas Gadjah Mada)

Dr. Budhi Kurniawan (Universitas Indonesia)

Chairman

Prof. Darminto (Institut Teknologi Sepuluh Nopember)

Co-Chairman

Prof. Risdiana (Universitas Padjadjaran)

Secretary

Dr. Malik Anjelh Baqiya (Institut Teknologi Sepuluh Nopember)

Treasure

Dr. Lusi Safriani (Universitas Padjadjaran)

Organizing Committee

Dr. Togar Saragi (Universitas Padjadjaran)

Dr. Ayi Bahtiar (Universitas Padjadjaran)

Dr. Mochamad Zainuri (Institut Teknologi Sepuluh Nopember)

Dr. Yoyok Cahyono (Institut Teknologi Sepuluh Nopember)

Dr. Zaenal Arifin (Institut Teknologi Sepuluh Nopember)

CO. Website Builders: Ali Mufid, M.Si (Institut Teknologi Sepuluh Nopember)

Table of Contents

Preface

Chapter 1: Advanced and Functional Materials

| | |
|--|-----|
| The Study on Tuning Photoluminescence of Colloidal Graphene Quantum Dots Synthesized through Laser Ablation F.H. Murdaka, A.A. Nugroho, A. Kusumaatmaja, Isnaeni and I. Santoso | 3 |
| Crystal Structure and Electrical Properties of (1-x) (Ba_{0.85}Sr_{0.15})TiO₃ - x(K_{0.5}Na_{0.5})NbO₃ System U. Nuraini, Y.N. Kaukaba, Mashuri and Suasmoro | 8 |
| Precipitated Silica from Sodium Silicate by CO₂ on Fixed Bed Column R. Dewati, Suprihatin, K. Sumada and S. Muljani | 14 |
| The Morphology of Si-K-HAs Composite Prepared by Spray Drying S. Muljani, H. Setyawan and K. Sumada | 19 |
| Mechanical Exfoliation of Reduced Graphene Oxide From Old Coconut Shell as Radar Absorber in X-Band A.F. Kurniawan, M.S. Anwar, K. Nadiyyah, Mashuri, Triwikantoro and Darminto | 25 |
| Characterization of TiN Oxide Doping Antimony Thin Layer with Sol- Gel Spin Coating Method for Electronic Device A. Doyan, Susilawati, A. Harjono, S. Azzahra and M. Taufik | 30 |
| The Effects of Layer Thickness of Radar Absorbing Materials Prepared by Double Layer Method on X-Band Wavelength Frequency M. Zainuri, R.F. Puspitasari, D. Ristiani and Triwikantoro | 35 |
| Geopolymer Concrete for Radiation Shielding Application Nurhasmi, D. Tahir, B. Abdullah, A. Ansar, S. Ilyas, I. Mutmainna and W.I. Madda | 41 |
| Effects of Spin-Orbit Coupling on the Electronic and Excitonic Structures of Monolayer WS₂ B.E. Dharma, A. Syahroni and M.A. Majidi | 48 |
| Characterization of BaM and PaNi-Based Radar Absorbency (RAM) Behavior with Multilayer Geometry Structure for X-Band Absorption M. Zainuri and D. Andryani | 54 |
| Preparation and Characterization of Electrospun Composite Fiber of Polymer-TiO₂ G. Yudoyono, Sudarsono and D. Anggoro | 60 |
| Structural Analysis and Electrical Properties of Amorphous Carbon Thin Films D.I. Pamungkas, Mukarromah, B. Priyanto, H. Nakajima, S. Tunmee and Darminto | 66 |
| Optical Transmission of p-Type a-Si:H Thin Film Deposited by PECVD on ITO-Coated Glass S. Prayogi, M.A. Baqiya, Y. Cahyono and Darminto | 72 |
| Synthesis of Silica-Potassium-Nitrogen from Carbamide and Potassium Silicate by CO₂ Precipitator K. Sumada, S. Muljani and C. Pujiastuti | 77 |
| Effect of Modified SiO₂ on the Hydrophobic Properties as Self-Cleaning Materials L. Silvia, A.H. Wardani, Y. Dwihapsari and M. Zainuri | 83 |
| Particle Size Analysis of the Synthesised ZrO₂ from Natural Zircon Sand with Variation of pH Deposition Using Alkali Fusion-Coprecipitation Method C.F.K. Murti, H. Aldila, Endarko and Triwikantoro | 89 |
| Fabrication of Amorphous Carbon Thin Film from CH₄ Using PEVCD B. Priyanto, M. Saleh, S. Tunmee, C. Euaruksakul, Y. Cahyono, Triwikantoro and Darminto | 95 |
| Low Temperature Graphene Growth Effort on Corning Glass Substrate by Using VHF-IP HWC-PECVD M.A. Yusuf, A. Rosikhin, J.D. Malago, F.A. Noor and T. Winata | 100 |
| Electrochemical Deposition of Polyaniline on Carbon Steel for Corrosion Study in Geothermal Solution G.A. Aristia, L.Q. Hoa and R. Baessler | 107 |

Chapter 2: Bio- and Food Technologies, Materials in Biomedicine

| | |
|--|-----|
| Relationship between the Structure and Electrical Conductivity of 12-Mer Single-Stranded Polyadenine Studied by Scanning Tunnelling Microscope H. Rozak, W.N. Zaharim, I. Miyazaki, N.E. Ismail, S.N. Abu Bakar, D. Kernain, R. Samian, K. Ichimura, M.I. Mohamed-Ibrahim, S. Sulaiman and I. Watanabe | 119 |
| Study of Carbonated Calcium Phosphate Precipitation on Collagen R. Tasomara, S. Julia, Y.W. Sari, Nurlily and D.S. Soejoko | 126 |
| Physicochemical and Cytotoxicity Characterization of Injectable Bone Substitute Based on Hydroxyapatite - Chitosan - Streptomycin for Spinal Tuberculosis Cases S.A. Rachmawati, D. Hikmawati, A.S. Budiadin and A.P. Putra | 133 |
| Quality Improvement of Biomaterial of <i>Lemna</i> Sp Y. Andriani, Iskandar, I. Zidni and Risdiana | 139 |
| Hydroxyapatite-Collagen Composite Made from Coral and Chicken Claws for Bone Implant Application Siswanto, D. Hikmawati, Aminatun and M. Zamawi Ichsan | 145 |
| Study on Formalization of Oil Palm Trunk Modified by Melamine Formaldehyde T.N. Manik, Mashuri and Darminto | 151 |
| The Role of Relative Humidity on Physical Characteristics of Poly Vinyl Alcohol-<i>Aloe vera</i> Fiber Membrane by Using Electrospinning Methods D. Hikmawati, E.F. Adiputri, A.P. Putra and J. Ady | 157 |
| Synthesis of Carbon Nanosphere at Low Temperatures Based on Bamboo Fiber Y.K. Lahsmin, D. Tahir, B. Abdullah, S. Ilyas and I. Mutmainna | 163 |
| Irradiation Effect on the Structural Properties of <i>Ipomoea batatas</i> L as a Function of Temperature and Time S. Fatimah, M. Nur, S.D.A. Ilyas and D. Tahir | 169 |
| Sorption Efficiency in Dye Removal and Thermal Stability of Sorghum Stem Aerogel E.L. Septiani, O.P. Prastuti, Y. Kurniati, M. Fauziyah, Widiyastuti, H. Setyawan, Wahyudiono, H. Kanda and M. Goto | 175 |
| Investigation of Structural and Antifungal Behaviors of Nano-Sized Anatase Titanium Dioxide Synthesized by Co-Precipitation Route A. Taufiq, D. Arista, Sunaryono, R.E. Saputro, N. Hidayat, S. Soontaranon, E. Handoko and Darminto | 181 |
| Optimization of Polydimethylsiloxane Synthesized Parameters as Vitreous Humour Substitutes S. Setiadji, Fitrilawati, A.N. Fauza, A. Ardi, R.M. Novianti, N. Syakir, Waslaluiddin, I. Rahayu, A.S. Kartasasmita and Risdiana | 189 |
| Physical Characteristics of Soft Tissue Phantom from Silicone Rubber Based Vulcanization System A. Ansar, D. Tahir, B. Abdullah, Nurhasmi, S. Fatimah and Jusmawang | 194 |
| Synthesis of Precipitate Calcium Carbonate with Variation Morphology from Limestone by Using Solution Mixing Method Z. Arifin, Triwikantoro, B.A. Subagyo, M. Zainuri and Darminto | 200 |
| Banana Peel Activated Carbon in Removal of Dyes and Metals Ion in Textile Industrial Waste O.P. Prastuti, E.L. Septiani, Y. Kurniati, Widiyastuti and H. Setyawan | 204 |
| The Analysis of Composite Particle Board Based on Mushroom Growing Media Waste T.P. Harmi, Sutarman, W. Edi, A. Faldy, A. Syamsul and G.A.N. Fitri | 210 |
| Solvent Effect on Bond Dissociation Enthalpy (BDE) of Tetrahydrocurcumin: A Theoretical Study L.S.P. Boli, N.D. Aisyah, V. Khoirunisa, H. Rachmawati, H.K. Dipojono and F. Rusydi | 215 |
| The Effects of Split Valence Basis Sets on Muon Hyperfine Interaction in Guanine Nucleobase and Nucleotide Structures W.N. Zaharim, S. Sulaiman, S.N. Abu Bakar, N.E. Ismail, H. Rozak and I. Watanabe | 222 |
| Predicting Notable Radical Scavenging Sites of Gnetin C Using Density Functional Theory V. Khoirunisa, L.S.P. Boli, R. Nur Fadilla, A.G. Saputro, H. Rachmawati, H.K. Dipojono and F. Rusydi | 229 |

Chapter 3: Investigation of Magnetic and Superconducting Properties

| | |
|--|-----|
| Synthesis and Characterization of Magnetic Rubidium Superoxide, RbO₂ F. Astuti, M. Miyajima, T. Fukuda, M. Kodani, T. Nakano, T. Kambe and I. Watanabe | 237 |
| Electrical Transport Properties of Perovskite La_{0.7}Sr_{0.2}Ba_{0.1}Mn_{1-x}Ni_xO₃ (x = 0 and 0.1) Manganite D.R. Munazat, B. Kurniawan and A. Imaduddin | 243 |
| The Doping Effects of SiC and Carbon Nanotubes on the Manufacture of Superconducting Monofilament MgB₂ Wires A. Imaduddin, Samsulludin, M.R. Wicaksono, I. Saefuloh, S. Herbirowo, S.D. Yudanto, Hendrik, H. Nugraha, Lusiana, E. Mabururi, N. Darsono and A.W. Pramono | 249 |
| Magnetic Properties of YBa₂Cu₃O₆ Studied by Density Functional Theory Calculations I. Ramli, S.S. Mohd-Tajudin, M.R. Ramadhan, D.P. Sari, S. Sulaiman, M.I. Mohamed-Ibrahim, B. Kurniawan and I. Watanabe | 257 |
| Enhanced Room-Temperature Ferromagnetism in Superconducting Pr_{2-x}Ce_xCuO₄ Nanoparticles M.A. Baqiya, P.E.D. Putra, R. Irfanita, Suasmoro, Darminto, T. Kawamata, T. Noji, H. Sato, M. Kato and Y. Koike | 263 |
| Magnetic Properties of Hole-Doped Pyrochlore Iridate (Y_{1-x-y}Cu_xCa_y)₂Ir₂O₇ J. Angel, R. Asih, H. Nomura, T. Taniguchi, K. Matsuhira, M.R. Ramadhan, I. Ramli, M. Wakeshima, Y. Hinatsu, M.I. Mohamed-Ibrahim, S. Sulaiman and I. Watanabe | 269 |
| Physical Properties of Encapsulated Iron Oxide T. Saragi, B. Permana, A. Therigan, S. Hidayat, N. Syakir and Risdiana | 277 |
| Characterization of Barium M-Hexaferrite with Doping Zn and Mn for Microwaves Absorbent Susilawati, A. Doyan, M. Taufik, Wahyudi, E.R. Gunawan, A. Fitriani and Nazarudin | 282 |
| Comparative Study on Magnetism of Reduced Graphene Oxide (rGO) Prepared from Coconut Shells and the Commercial Product R. Asih, E.B. Yutomo, D. Ristiani, M.A. Baqiya, T. Kawamata, M. Kato, I. Watanabe, Y. Koike and Darminto | 290 |
| Magnetic Study of the Lower Critical Field of Organic Superconductor λ-(BETS)₂GaCl₄ D.P. Sari, K. Hiraki, T. Nakano, M. Hagiwara, Y. Nozue, T. Kusakawa, A. Hori, A. Yamamoto, I. Watanabe and Y. Ishii | 296 |
| Complex Permittivity, Permeability and Microwave Absorption Studies of Double Layer Magnetic Absorbers Based on BaFe₁₂O₁₉ and BaFe₁₀CoZnO₁₉ E. Handoko, I. Sugihartono, M.A. Marpaung, U. Cahyana, S. Aritonang, Z. Jalil, Rusmono, A. Taufiq, Sunaryono, M. Randa and M. Alaydrus | 302 |
| Preparation of Local Raw Material for α-Fe₂O₃ Nanoparticles Powder from Mineral Extraction of Iron Sand M.P. Izaak, H. Sitompul, W.A. Adi and Y.E. Gunanto | 308 |
| Study of Magnetic Properties in Electron Doped Superconductor Eu_{2-x}Ce_xCuO_{4+α} Y. Maryati, N. Nafisah, D.G. Auliya, E. Nurwati, T. Amalia, Y.R. Tayubi, T. Saragi and Risdiana | 314 |
| Crystal Structure and Magnetic Properties of Non-Stoichiometric Co₂MnGa Heusler Alloy M.Y. Pandu Akbar, R.R. Sihombing, A. Sakai, A.A. Nugroho and S. Nakatsuji | 319 |
| Analysis of Physical Properties, Crystal Structure and Magnetic Properties of Barium Hexaferrite Doped with 2 % wt. of SrO and Prepared by Coprecipitation Method Suprapedi, Muljadi, Djuhana and Ramlan | 325 |
| Effect of Copper Substitution on the Electrical Transport Properties of La_{0.7}Ba_{0.1}Sr_{0.2}Mn_{1-x}Cu_xO₃ (X = 0 and 0.05) Manganites B. Kurniawan, D.S. Razaq and A. Imaduddin | 331 |
| Enhanced Microwave Absorbing Capabilities of Multilayer Absorbers Based on BaFe₁₂O₁₉ and Fe₃O₄ E. Handoko, I. Sugihartono, M.A. Marpaung, U. Cahyana, S. Aritonang, Z. Jalil, Rusmono, A. Taufiq, Sunaryono and M. Alaydrus | 338 |
| The Effect of Freezing-Thawing Route Number on Magnetic Properties and Nanostructural of Fe₃O₄/ Carboxymethyl Cellulose/Polyvinyl Alcohol Magnetic Hydrogel Sunaryono, M.N. Kholifah, A. Taufiq and E. Handoko | 344 |

| | |
|---|-----|
| Synthesis and Characterization of Nd₂Fe₁₄B Powder Prepared by Using Milling and Heat Treatment | |
| Ramlan, P. Sardjono, Muljadi, D. Setiabudidaya and F. Gulo | 352 |
| Growth of Free-Standing La_{2-x}Sr_xCuO₄ Nanoparticles | |
| S. Winarsih, F. Budiman, H. Tanaka, T. Adachi, T. Goto, B. Soegijono, B. Kurniawan and I. Watanabe | 357 |
| Study of Magnetoresistance Effect and Magnetic Properties of La_{0.67}Sr_{0.33}Mn_{1-x}Ni_xO₃ (x = 0 and 0.2) Material Prepared by Sol-Gel Method | |
| U. Widyaiswari, B. Kurniawan, A. Imaduddin and I. Watanabe | 363 |
| | |
| Chapter 4: Materials for Technologies of Energy Storage and Conversion | |
| | |
| Characteristics of Large Area Perovskite Solar Cells from Electrodes of Used Car Batteries | |
| A. Bahtiar, C. Agustin, E.S. Nurazizah, A. Aprilia and D. Hidayat | 373 |
| Study of Electrochemical Deposition Process of Graphene Oxide on DSSC TiO₂ Based Photoanode | |
| A. Aprilia, V. Marcelina, F. Yuliasari, Y.W. Hartati, Fitrilawati, L. Safriani and R.E. Siregar | 378 |
| The Effect of Reduced Graphene Oxide (rGO) Coating on Electrical Conductivity of Lithium Ferro Phosphate (LFP) as an Alternative Cathode for Li-Ion Battery | |
| E. Suarso, A.Z. Laila, F.A. Setyawan, M. Zainuri, Z. Arifin and Darminto | 386 |
| Preparation of Lithium Iron Phosphate-Carbon Composite as a Cathode for Lithium Ion Battery | |
| I. Rahayu, A.R. Noviyanti, D. Rakhmawaty, A. Anggraeni, H.H. Bahti, S. Hidayat and Risdiana | 392 |
| Analysis of Defects and Surface Roughness on the Hydrogenated Amorphous Silicon (a-Si:H) Intrinsic Thin Film for Solar Cells | |
| Y. Cahyono, N. Dwi Purnamasari, M. Zainuri, S. Pratapa and Darminto | 398 |
| μSR Study with Light Irradiation of P3HT:ZnO Nanoparticles as Active Material of Hybrid Solar Cells | |
| L. Safriani, Risdiana, Fitrilawati, A. Bahtiar, A. Aprilia, R.E. Siregar, M. Manawan, D. Puspitasari Sari, J. Angel and I. Watanabe | 404 |
| Band Gap Optimization of Thin Film a-Si:H Bifacial Solar Cells (BFSCs) Using AFORS-HET | |
| D. Hamdani, Y. Cahyono, G. Yudoyono and Darminto | 409 |
| Structure, Chemical Stability and Magnetic Properties of Lanthanum Silicate Oxide Apatite Synthesized by Hydrothermal Method | |
| Y.T. Malik, A.R. Noviyanti, N. Akbar, I. Hastiawan, T. Saragi and Risdiana | 415 |
| Effect of Electrical Resistance of TiO₂ Layer Characteristics of Dye Sensitized Solar Cell Using Chlorophyll as a Sensitizer | |
| N. Puspitasari, N.Y. Cahaya, G. Yudoyono, G. Prajitno and Darminto | 422 |
| Energy Storage Characteristics of Electrochemically Deposited Graphene Oxide on ITO and Cu Substrates | |
| Fitrilawati, V. Marcelina, D.U. Dzujah, A. Bahtiar, Y.W. Hartati and N. Syakir | 428 |
| Characteristics of CMC from Corncob and its Application as Electrode Binder in Lithium Ion Battery | |
| S. Hidayat, I. Mubarak, B. Adiperdana, B.J. Suroto, N. Riveli, Y.W. Hartati and I. Rahayu | 433 |
| Synthesis of n-Doped Reduced Graphene Oxide from Coconut Shell as Supercapacitors | |
| I. Khambali, I.S. Ardiani, A.R. Kurniawan, Triwikantoro, M. Zainuri and Darminto | 437 |
| Synthesis and Characterization of Supercapacitor Electrode from Fiber of <i>Borassus flabelifer</i> L by Activation Method | |
| F.A. Prasetya, U. Anggarini, Y. Zakaria and R.D.S. Putri | 444 |
| Bi Doping Effect on the Conductivity of Lanthanum Silicate Apatite | |
| A.R. Noviyanti, N. Akbar, I. Hastiawan, I. Rahayu, Haryono, Y.T. Malik and Risdiana | 451 |
| Effect of Ni Doping Variations on Microstructure and Conductivity of Cathode LiNi_xFe_{1-x}PO₄/C Materials | |
| M. Zainuri, B.A. Anang and E. Novialent | 456 |

Chapter 5: Modeling, Computational Procedures and Devices in Research of Functional Materials

| | |
|--|-----|
| Effects of the Supercell's Size on Muon Positions Calculations of La_2CuO_4 M.R. Ramadhan, I. Ramli, M.D. Umar, S. Winarsih, D.P. Sari, A. Manaf, B. Kurniawan, M.I. Mohamed-Ibrahim, S. Sulaiman and I. Watanabe | 465 |
| Study on the Diffusion Rate of the Charge Carrier Transport in Regio-Random P3HT N. Riveli, B. Adiperdana, L. Safriani, B.J. Suroto, A.R. Noviyanti, I.H. Mohammad, I. Rahayu, M. Manawan, T. Saragi and Risdiana | 471 |
| An Approach to the Intermediate State of the Distributed Internal Fields on Muon Site M.D. Umar and I. Watanabe | 476 |
| μSR Spectrum Reconstruction Using Monte Carlo Approach: A Preliminary Study B. Adiperdana and Risdiana | 483 |
| Optical Spectra of Bi_2Se_3: The Effects of Electron-Hole Interactions D.N. Asturo, A. Syahroni and M.A. Majidi | 489 |
| Effects of Polarization Function on the Spin Contamination and Distribution in β'-$\text{Me}_4\text{P}[\text{Pd}(\text{dmit})_2]_2$ S.N.A. Ahmad, S. Sulaiman, L.S. Ang and I. Watanabe | 494 |
| Numerical Simulation on Effects of TCO Work Function on Performance of a-Si:H Solar Cells A. Sholih, D. Hamdani, S.T. Wicaksono, M.I.P. Hidayat, Y. Cahyono and Darminto | 501 |
| A Potential Application of Photonic Jet in Observing Micro-Metric Materials A. Abdurrochman, M.O. Wahidullah, D. Naufal, D.S. Sofiati, A. Aprilia, L. Safriani, S. Perrin and S. Lecler | 507 |

Predicting Notable Radical Scavenging Sites of Gnetin C Using Density Functional Theory

Vera Khoirunisa^{1,2,a}, Lusia Silfia Pulo Boli^{1,3,b}, Rizka Nur Fadilla^{1,3,c},
Adhitya Gandaryus Saputro^{1,d}, Heni Rachmawati^{5,e},
Hermawan Kresno Dipojono^{1,f}, and Febdian Rusydi^{3,4,*}

¹Department of Engineering Physics, Institut Teknologi Bandung, Bandung, Indonesia

²Engineering Physics Program, Institut Teknologi Sumatera, Lampung Selatan, Indonesia

³Theoretical Physics Research Group, Department of Physics, Universitas Airlangga, Surabaya, Indonesia

⁴Research Center for Quantum Engineering Design, Universitas Airlangga, Surabaya, Indonesia

⁵School of Pharmacy, Institut Teknologi Bandung, Bandung, Indonesia

^akhoirunisa.vera@gmail.com, ^blusia_silfia@yahoo.co.id, ^cfadillarizkanur@gmail.com,
^dganda@tf.itb.ac.id, ^eh_rachmawati@fa.itb.ac.id, ^fdipojono@gmail.com, *rusydi@fst.unair.ac.id

Keywords: bond dissociation energy, density functional theory, gnetin C, radical scavenging activity.

Abstract. We have been investigating the scavenging activity of gnetin C theoretically in the molecular level. In this work, we perform density functional based calculations to predict the possible site of gnetin C for free radical scavenging activity. The water solvent effect is considered as polarizable continuum model. All possible scavenging sites have been evaluated by obtaining the bond dissociation enthalpy (BDE) for one hydrogen atom abstraction. The results demonstrate that O-H bonds generally have lower BDE relative to C-H bonds of gnetin C. We also find that C-H bonds in 5-membered heterocyclic ring have exceptionally lower BDE. This could be additional possible sites for gnetin C to scavenge more free radicals in addition to hydroxyl groups.

Introduction

The unbalance numbers of reactive oxygen species (ROS) in the body can cause a disturbance called oxidative stress. The oxidative stress causes three main oxidative damages namely protein oxidation, lipid peroxidation, and oxidative damage to DNA. The combination of these three oxidative damages contributes to aging process [1-3] and development of several chronic diseases such as cancer, diabetes, and neurological disease [4].

To overcome the oxidative stress, a substance which has an ability to inhibit, prevent, or eliminate the oxidative damage to the target molecule is needed. This substance is known as antioxidant [5]. A class of phenolic compounds is a type of antioxidant which could stabilize free radicals by transferring electrons, so electrons in an outermost orbital of free radical are paired [6]. Moreover, phenolic compounds can also be a radical scavenger by donating a hydrogen atom to radicals [7].

Resveratrol has been extensively studied for its role as an antioxidant in the biological system [8-13]. Numerous studies also show that resveratrol is a potential drug candidate for multi-purpose treatment because of its potent antioxidant properties [14]. Due to its promising application, we extend the study of antioxidant activity to its dimer, gnetin C. An experimental study shows that dimer resveratrol from melinjo has a good activity to scavenge 2,2-diphenyl-1-picryl-hydrazyl (DPPH) [15]. However, the theoretical study of antioxidant activity of dimer resveratrol is still limited.

This work is an initial study to understand the antioxidant behavior of dimer resveratrol in water environment using density functional theory (DFT). Therefore, in this study, we examine the possible site of gnetin C to interact with radical as the first step. The possible site is evaluated by determining

bond dissociation enthalpy (BDE) of hydrogen abstraction. This work will be the base for further study of the reaction between radical and gnetin C.

Computational Detail

The hydrogen donation process is simplified into a reaction model as shown in Eq. 1.



$\text{Res}_{(\text{H})}$ represents gnetin C as a neutral molecule. Gnetin C radical (Res^{\bullet}) is modeled by eliminating one hydrogen atom (H) from each different sites, including O-H and C-H sites.

All electronic calculations are performed based on DFT as implemented in Gaussian 09 software package [16]. In the calculations, we employ B3LYP as exchange correlation and 6-31++G(d,p) as basis set. We choose B3LYP because it gives a good prediction in our previous molecular study [17, 18]. We consider aqueous solvation using polarizable continuum model (PCM). The ground state geometry of gnetin C is performed by full geometry optimization. All of possible radical structures are optimized using unrestricted calculation. Frequency calculation is also carried out to ensure that ground state structure has no imaginary frequency, and to give thermal correction at 298.15 K. Finally, bond dissociation enthalpy (BDE) is obtained by the following equation:

$$\text{BDE} = (\text{H}_{\text{Res}} + \text{H}_{\text{H}}) - \text{H}_{\text{Res}^{\bullet}} \quad (2)$$

H_{Res} , $\text{H}_{\text{Res}^{\bullet}}$, and H_{H} denote the enthalpies of gnetin C, gnetin C radical, and a hydrogen atom, respectively.

Results and Discussions

The optimized structure of gnetin C and site numbering of hydrogen abstraction are shown in Fig. 1. The ground state of gnetin C is found to have a singlet spin multiplicity, while the gnetin C radical is in a doublet spin multiplicity. The geometric structure of gnetin C does not change when it becomes radical after donating a hydrogen atom. O-H bond length is predicted to be around 0.970 Å, and the C-H bonds vary from 1.086 to 1.090 Å.

Bond dissociation enthalpy (BDE) is an important parameter that has been used to evaluate the antioxidant activity of polyphenols [19]. BDE describes the stability of hydroxyl bond. The lower the values of BDE, the more stable phenoxy radical formed after donating a hydrogen atom to free radical. Based on BDE value, we evaluate the possible sites of gnetin C to react with free radical. However, in this study, we do not limit the determination of BDE for hydroxyl bond only but also consider the possibility of C-H as hydrogen atom donor.

All the 22 sites of gnetin C has been examined. The 22 sites consist of five O-H bonds and 17 C-H bonds. The details of BDE value are listed in Table 1. In most of the cases, BDE values of O-H bonds are less than that of C-H bonds. It ranges from 74.85 to 82.71 kcal/mol. The experimental BDE for gnetin C has not been reported yet. However, the reported experimental BDE for structurally related to resveratrol is within this range, 78.9 kcal/mol [20]. These BDE values are also close to the average values for experimental BDE of polyphenols [21]. These point out that most of the antioxidant activities of gnetin C are mainly related to its hydroxyl groups.

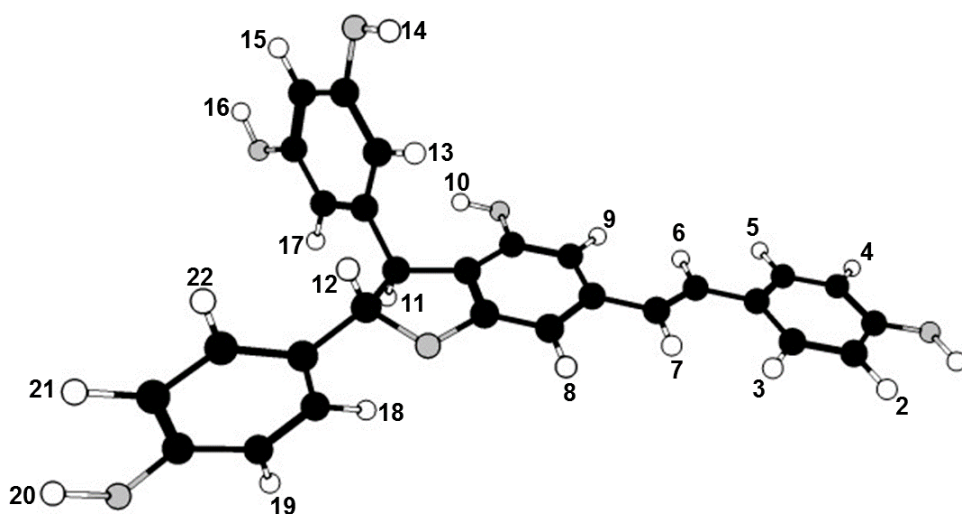


Fig. 1: The geometric structure of Gnetin C. The black, grey, and white atoms represent C, O, and H atoms.

Table 1: Bond dissociation enthalpies of O-H and C-H bond in gnetin C, at T=298.15 K.

| Site number | BDE (Kcal/mol) | Site number | BDE (Kcal/mol) |
|-------------|----------------|-------------|----------------|
| 1-OH | 74.85 | 8-CH | 113.81 |
| 10-OH | 81.90 | 9-CH | 112.13 |
| 14-OH | 82.71 | 11-CH | 75.74 |
| 16-OH | 82.44 | 12-CH | 79.68 |
| 20-OH | 81.54 | 13-CH | 112.59 |
| 2-CH | 113.81 | 15-CH | 110.34 |
| 3-CH | 109.70 | 17-CH | 113.58 |
| 4-CH | 112.41 | 18-CH | 110.34 |
| 5-CH | 110.71 | 19-CH | 112.36 |
| 6-CH | 100.33 | 21-CH | 111.84 |
| 7-CH | 100.76 | 22-CH | 110.78 |

In contrast to most of C-H bond sites, the C-H bonds which located in the conjugation chain connecting two phenyl rings have lower BDE. Site 11 and 12 even have a low BDE as O-H site does. The absence of double bond in this conjugation chain significantly lessens BDE of C-H bond. This exception may contribute to the antioxidant activity of dimer resveratrol in addition to hydroxyl group. Therefore, these sites are also important to be considered for scavenging site.

Conclusion

Bond dissociation enthalpies of gnetin C to donate one hydrogen atom have been determined. Our results suggest that O-H sites are important sites for scavenging free radical. As dimer resveratrol, the C-H bond in conjugation chain between two phenyl rings in its dimer may also be considered as additional scavenging sites. Nevertheless, the BDE value is not enough to explain the antioxidant activity of dimer resveratrol since the reactivity also depends on the type of radical. The thermodynamic and kinetic study of the reaction between gnetin C and hydroperoxyl radical should be performed. At this point, unnecessary interacting site for further study has been eliminated. The further study is underway and will be reported in somewhere else.

Acknowledgment

We thank to Institut Teknologi Bandung (ITB) and Research Center for Nanosciences and Nanotechnology (RCNN) for computer facilities support. VK also thanks to Lembaga Pengelola Dana Pendidikan (LPDP) for the doctoral scholarship. We also thank "Hibah Mandat grant 2018 of Airlangga University" that has funded this research.

References

- [1] D. Harman, Aging: A Theory based on free radical and radiation chemistry, *J. Gerontol.* 11 (1956) 298-300.
- [2] D. Harman, The aging process, *Proc. Natl. Acad. USA* . 78 (1981) 7124-28.
- [3] V. Lobo, A. Patil, A. Phatak, and N. Chandra, Free radicals, antioxidants and functional foods: impact on human health, *Pharmacogn. Rev.* 4 (2010) 118-26.
- [4] A. Shinde, J. Ganu, and P. Naik, Effect of Free Radicals & Antioxidants on Oxidative stress: A review, *Journal of Dental & Allied Sciences* 1 (2012) 63-66.
- [5] B. Halliwell, Biochemistry of oxidative stress, *Biochem. Soc. Trans.* 35 (2007) 1147-50.
- [6] T.A. Barhé and G.R. Tchouya, Comparative study of the anti-oxidant activity of the total polyphenols extracted from *Hibiscus Sabdariffa L.*, *Glycine max L. Merr.*, yellow tea and red wine through reaction with DPPH free radicals, *Arabian Journal of Chemistry* 9 (2016) 1-8.
- [7] C.G. Fraga, Plant polyphenols: how to translate their in vitro antioxidant actions to in vivo conditions, *IUBMB Life* 51 (2007) 308-315.
- [8] M.J. Burkitt and J. Duncan, Effects of trans-resveratrol on copper-dependent hydroxyl-radical formation and DNA damage: evidence for hydroxyl-radical scavenging and a novel, glutathione-sparing mechanism of action, *Arch. Biochem. Biophys.* 381 (2000) 253-263.
- [9] K. Sinha, G. Chaudhary, Y.K. Gupta, Protective effect of resveratrol against oxidative stress in middle cerebral artery occlusion model of stroke in rats, *Life Sci.* 71 (2002) 655-665.
- [10] K.T. Howitz, K.J. Bitterman, H.Y. Cohen, D.W. Lamming, S. Lavu, J.G. Wood, R.E. Zipkin, P. Chung, A. Kisielewski, L. Zhang, B. Scherer, D.A. Sinclair, Small molecule activators of sirtuins extend *Saccharomyces cerevisiae* lifespan, *Nature* 425: 191-196, 2003.
- [11] S.S. Leonard, C. Xia, B.H. Jiang, B. Stinefelt, H. Klandorf, G.K. Harris, X. Shi. Resveratrol scavenges reactive oxygen species and effects radical-induced cellular responses, *Biochem. Biophys. Res. Commun.* 309 (2003) 1017-1026.
- [12] S. Bradamante, L. Barenghi, A. Villa, Cardiovascular protective effects of resveratrol, *Cardiovasc. Drug Rev.* 22 (2004) 169-188.
- [13] D.R. Valenzano, E. Terzibasi, T. Genade, A. Cattaneo, L. Domenici, A. Cellerino, Resveratrol prolongs lifespan and retards the onset of age-related markers in a short-lived vertebrate, *Curr. Biol.* 16 (2006) 296-300.
- [14] R. Pangeni, J.K. Sahni, J. Ali, S. Sharma, and S. Baboota, Resveratrol: review on therapeutic potential and recent advances in drug delivery, *Expert Opinion on Drug Delivery*, 11 (2014) 1285-1298.

-
- [15] E. Kato, Y. Tokunaga, and F. Sakan, Stilbenoids isolated from the seeds of melinjo (*Gnetum gnemon* L.) and their biological activity, *Journal of Agricultural and Food Chemistry* 57 (2009) 2544-2549.
- [16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Jr. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, (2010): Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT.
- [17] F. Rusydi, A.G. Saputro, and H. Kasai, A density-functional study on the change of Q/B-band intensity ratio of zinc tetraphenyl porphyrin in solvents, *Journal of Physical Society of Japan* 83 (2014) 084802.
- [18] F. Rusydi, G. Shukri, A.G. Saputro, M.K. Agusta, H.K. Dipojono and S. Suprijadi, Dipole strength calculation based on two-level system approximation to study Q/B-band intensity ratio of ZNTBP in solvent, *Journal of Physical Society of Japan* 86 (2017) 044706.
- [19] J.S. Wright, E.R. Johnson, G.A. Dilabo, Predicting the activity of phenolic antioxidants: theoretical method, analysis of substituent effects, and application to major families of antioxidants, *Journal of American Chemical Society* 123 (2001) 1173-83.
- [20] G. Brigatti, M. Lucarini, V. Mugnaini, and G.F. Pedulli, Determination of the substituent effect on the O-H bond dissociation enthalpies of phenolic antioxidants by the EPR radical equilibration technique, *J. Org. Chem.* 67 (2002) 4828-4832.
- [21] M. Lucarini, P. Pedrielli, G.F. Pedulli, Bond dissociation energies of O-H bonds in substituted phenols from equilibration studies, *J. Org. Chem.*, 61 (1996) 9259-9263.