Nanostructure, Band Gap, and Antibacterial Activity of Spinel Fe$_2$MO$_4$/OO Magnetic Fluids

Nur Millaty Abadiah$^1$, Defi Yuliantika$^2$, Yuanita Amalia Hariyanto$^2$, Rosy Eko Saputro$^2$, Masruroh$^1$, Ahmad Taufiq$^2$,*, Siriwat Soontaranoon$^3$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Brawijaya, Jl. Veteran, Malang 65145, Indonesia
$^2$Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
$^3$Synchrotron Light Research Institute, 111 University Venue, Nakhon Ratchasima 30000, Thailand

*Corresponding author: ahmad.taufiq.fmipa@um.ac.id

Abstract. This research aimed at investigating Fe$_2$MO$_4$ ferrofluids nanostructure, with M was Fe, Ti and Cr. Fe$_2$MO$_4$ nanoparticles were synthesized through coprecipitation method, and the phase and crystallinity were analyzed using XRD instrument. The obtained results showed the Fe$_3$O$_4$ phase, but there was a shift in diffraction peak position contributed by the doping of Ti$^{2+}$ and Cr$^{3+}$ ions. Furthermore, a similar change occurred in the lattice parameter, crystal volume, and particle size. The particle sizes of Fe$_3$O$_4$, Fe$_2$TiO$_4$, and Fe$_2$CrO$_4$ particles were 10.2, 13.4, and 6.9 nm, respectively. The functional groups of the Fe$_2$MO$_4$/OO ferrofluids were characterized using FTIR and obtained the Fe-O stretching band shift due to the modification of structure. Furthermore, FTIR analysis was used as a reference to confirm functional groups of the ferrofluids. The absorbance data collection was performed through the characterization using UV-Vis instrument, and there was intervalence charge transfer at a wavelength near infra-red indicating there was Fe element and nanoparticle interface which raised an optimum absorption at the interval of 400-550 nm. Furthermore, through the obtained absorbance data, there was an energy gap of 2.2-2.24 eV. Interestingly, the results of antibacterial testing results through the dilution method showed a modification of structure could increase the antibacterial activity of the Fe$_2$MO$_4$/OO ferrofluids by minimizing the percentage of surviving colony number.

Keywords: MFe$_2$O$_4$, spinel, doping, nanostructure, antibacterial activity

1. Introduction
Magnetite (Fe$_3$O$_4$) is one of the types of abundant magnetic material in nature in the form of iron sand. Generally, Fe$_3$O$_4$ has an inverse spinel structure, (Fe$^{3+}$)$_6$(Fe$^{2+}$Fe$^{3+}$)$_2$O$_4$ with A and B refer to the tetrahedral and octahedral atom positions respectively [1]. Studies related to magnetite significantly vary in the last five years, for example, related to composite preparation [2], synthesis in various dimensions [3,4], as well as the substitution of metal ion other than Fe through doping process.
Related to doping, to obtain a better physical property, a substitution of Fe cation on sub-lattice A or B can be performed using both magnetic and non-magnetic transition metal [5], such as Cu [6,7], Mn [8,9], Ni [10], Zn [11,12], Cr [13], Ti, and so forth.

The substitution of Fe cation with Ti and Cr into MFe$_2$O$_4$ system becomes an interesting innovation within the last five years. The studies regarding Fe$_{3-x}$Ti$_4$O$_4$ have been broadly applied to identify geomagnetic evolution [14], advanced and biomedical technologies. Meanwhile, Fe$_{3-x}$Cr$_4$O$_4$ have been widely applied to technologies prioritizing a better performance of electronic properties [15,16]. Moreover, the application of MFe$_2$O$_4$ in the biomedical field provides an excellent prospect, even more as an antibacterial agent due to the presence of reactive oxygen species (ROS) it contains. The presence of ROS can destroy the defense of bacteria as well as the DNA and protein inside [17].

Related to the antibacterial activity of MFe$_2$O$_4$, optimization needs to be conducted by using it as a filler in the magnetic fluids (ferrofluids) system coated with oleic acid (OA) and dispersed in olive oil (OO). However, in-depth research related to the structure is crucial to be conducted moreover in the correlation on both physical parameters and its potential of the application. In this research, we observed in-depth the MFe$_2$O$_4$ nanostructure with M as a substituted dopant namely Fe, Cr, and Ti, and then correlated with the antibacterial activity. Hence, information from the physical point of view and biological contribution can be conveyed when the MFe$_2$O$_4$/OO ferrofluids are applied as an antibacterial agent.

2. Methods

In this study, the materials used were Fe element source supplied from natural iron sand from Sine Beach materials, Indonesia, titanium dichloride (TiCl$_4$), chloride acid (HCl), ammonium hydroxide (NH$_4$OH), OA, OO, distilled water, and alcohol. The synthesis of MFe$_2$O$_4$ (M = Fe, Cr dan Ti) nanoparticles was initiated with the process of preparing 20-gram natural iron sand prepared by washing and drying for 20 hours. The iron sand was reacted with HCl using a magnetic stirrer at a speed of 650 rpm at room temperature for 30 minutes. After this process was completed, FeCl$_3$ and FeCl$_2$ solutions were obtained, and then reacted with TiCl$_4$ or CrCl$_3$.6H$_2$O through magnetic stirrer at a speed of 550 rpm at room temperature. In this process, the doping was performed after 15 minutes, the spinning speed was lowered to 450 rpm, and titration was performed with 23 mL NH$_4$OH. After titration was accomplished, the spinning speed of magnetic stirrer was increased to 600 rpm and held for 25 minutes. The ongoing reaction in the stage above is formulated in Equations 1 and 2. The result of the process was the presence of black-colored precipitate. The obtained precipitate was washed using distilled water until normal pH was reached.

\[
\begin{align*}
2\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Ti}^{2+} + 8\text{OH}^- & \rightarrow \text{Fe}_2\text{TiO}_4 + 4\text{H}_2\text{O} \\
2\text{FeCl}_3 + \text{FeCl}_2 + \text{H}_2\text{O} + x\text{CrCl}_3.6\text{H}_2\text{O} + 8\text{NH}_4\text{OH} & \rightarrow \text{Cr}x\text{Fe}_{3-x}\text{O}_4 + 8\text{NH}_3\text{Cl} + 5\text{H}_2\text{O}
\end{align*}
\]

The synthesis of MFe$_2$O$_4$/OO ferrofluids (M = Fe, Cr dan Ti) proceeded from the reaction process of 2-gram MFe$_2$O$_4$ precipitate mixed with distilled water then heated while being stirred in hotplate magnetic stirrer with a spinning speed of 500 rpm at a temperature of 100 °C until the water content evaporated thoroughly. Also, the stirring was stopped and mixed with oleic acid using the rough stirring method until the mixture was homogeneous. Further, the sample was cooled until reaching room temperature. After that, the mixture was dispersed in OO using the rough stirring method. Illustration of MFe$_2$O$_4$/OO ferrofluids synthesis is shown in Figure 1.

The characterization of the crystal structure was done using XRD with Cu-K$\alpha$ radiation operating at 40 kV and 35 mA, in the range of 20°-90°. The XRD data were evaluated using the Rietveld refinement approach to gather the crystalline structure, lattice parameters, crystalline phase, and crystallite size of the samples, while the functional groups of the samples were characterized via FTIR. The band gap energy and nanostructure characters were evaluated by means of UV-Vis spectrometer and synchrotron SAXS respectively. Finally, the antibacterial activity was evaluated by means of the dilution method.
3. Results and Discussion

Based on the X-ray diffraction data as shown in Figure 2. The samples have the same phase namely Fe₃O₄; however, they have a difference in diffraction peak heights. The difference in peak heights is caused by the doping process which was successfully performed. The resulted samples of doping with Ti and Cr have different structural characteristics referring to Fe₃O₄ diffraction pattern. The first difference is Fe₂TiO₄ experiencing a peak shift towards a smaller angle; on the contrary, Fe₂CrO₄ has a peak shift towards a bigger angle. Theoretically, this is caused by Ti²⁺ and Cr³⁺ in interpolating to Fe³⁺ octahedral atom position having a different ionic radius, namely, 86 pm [18] and 62 pm [19]. When compared to Fe³⁺ ionic radius with the score of 64 pm, a bigger Ti²⁺ ionic radius creates a diffraction peak shift towards a smaller angle, and a smaller Cr³⁺ ionic radius makes a smaller diffraction peak shift towards a bigger angle. Furthermore, the three samples were refined using different crystal models, namely Fe₃O₄ data refined with model data of database code ICSD 36314, Fe₂TiO₄ data refined with model data of database code AMCS 0000953 and Fe₂CrO₄ data refined with model data of database code 0000945. The detailed crystal structure obtained from the refinement process is shown in Table 1.

Referring to Table 1, the influence of dopant’s ionic radius contributes to the change in lattice parameter which eventually influenced the volume and particle size. In the research report by Pearce et al., a study on Fe₃ₓTiₓO₄, stated that the higher the Ti molar fraction added, the more significant the value of lattice parameter, volume, particle size. They asserted that this increase was caused by the structural substitution in Fe³⁺ octahedral cationic sub-lattice and corresponded to Fe³⁺ reduction into Fe²⁺ to maintain load stability [20]. Similar results are conveyed by Riaz et al. who performed Fe₃ₓCrₓO₄ synthesis, and a similar mechanism was performed due to the substitution of dopant ion interpolating in Fe³⁺ octahedral atom position [21].

Table 1. Lattice parameter, crystal volume and particle size of Fe₂MO₄ nanoparticles

| Sample   | Lattice parameter (Å) | Crystal volume (Å³) | Particle size (nm) |
|----------|-----------------------|---------------------|--------------------|
| Fe₃O₄    | 8.355                 | 583.4               | 10.2               |
| Fe₂TiO₄  | 8.362                 | 584.7               | 13.4               |
| Fe₂CrO₄  | 8.361                 | 568.3               | 6.9                |
Figure 2. X-ray diffraction patterns of Fe₂MO₄ nanoparticles

In this work, an in-depth nanostructure characterization was performed using SAXS instrument with the results presented in Figure 3. The figure shows a theoretical calculation model corresponding well on the data for all q scores. On the data above, the log-normal mathematical approach of the spherical model was conducted. Further, the data obtained showed polydispersity correspond with the report by Taufiq et al. [22]. The results of the SAXS data analysis is presented in Table 2.

Figure 3. SAXS profiles of Fe₂MO₄/0O ferrofluids
Table 2. Results of SAXS data analysis of Fe₂MO₄/OO ferrofluids

| Sample     | Primary particle size (nm) | \( \chi_i \) | \( D \) |
|------------|---------------------------|--------------|--------|
| Fe₃O₄     | 3.17                      | 86.12        | 3.09   |
| Fe₂TiO₄   | 3.69                      | 50.92        | 2.98   |
| Fe₂CrO₄   | 3.72                      | 117.59       | 3.15   |

The discussion of SAXS data analysis results is limited to the discussion of primary particle size parameter, \( \chi_i \) which represents the aggregation size, and \( D \) represents the fractal dimension. Referring to Table 2, the size of the primary particle on each sample has relatively same scores which ranged between 3.17 - 3.72 nm. This is because SAXS was able to analyze the particle size at a small angle which cannot be performed using XRD. Next, the identified highest aggregation size was found in Fe₂CrO₄ sample, and this is because Cr³⁺ doping has a smaller ionic radius than Fe³⁺ causing a shrink in the particle size which makes a tendency of greater aggregation. When compared to Fe₂TiO₄ samples where Ti⁴⁺ has a bigger ionic radius makes the particle size expand and lessen the tendency of aggregation [23]. A similar influence occurred in the final parameter namely fractal dimension which increases along with the size of the dopant radius used. This represents the growth of one dimension to three dimensions in a denser construction [22].

![Figure 4. FTIR spectrum of Fe₂MO₄/OO ferrofluids](image)

The FTIR spectrum of all samples is shown in Figure 4. The FTIR analysis was used as the primary reference to investigate the functional group representing the substances contained in the ferrofluid. It can be observed that the samples have identical results. Interestingly, the Fe-O bond appeared in the area of 590 cm⁻¹ for Fe₃O₄ samples experienced a shift towards a smaller area for Fe₂TiO₄ sample namely 588 cm⁻¹. On the contrary, for Fe₂CrO₄ sample experienced a shift towards a wider area namely 599 cm⁻¹ [23,24]. This shift is caused by Ti²⁺ and Cr³⁺ have successfully interpolated into Fe³⁺ octahedral atom position. The stretching band of the oleic acid functional group acts as a surfactant is detected in several areas, namely C=C in the area of 1377 cm⁻¹, COO⁻ (carboxyl bond) in the area of 1452 cm⁻¹, and CH₂ in the areas of 2856 and 2927 cm⁻¹ [25]. Lastly, there is a stretching band of olive
oil functional group, namely C-H in the area of 1087 cm\(^{-1}\), an ester bond (CO) in 1168 and 1226 cm\(^{-1}\), carbonyl ester in 1705 and 1727 cm\(^{-1}\). Furthermore, there were CH\(_2\) symmetrical and asymmetrical bonds in the areas of 2856 and 2927 cm\(^{-1}\), these bonds are also present in the oleic acid because olive oil has a high content of oleic acid. Finally, a typical bond which is only owned by olive oil is the unsaturated bond emerged in the area of 3011 cm\(^{-1}\) [26].

The absorbance data obtained through UV-Vis measurement is presented in Figure 5. Based on Figure 5, it can be identified that the absorbance of the samples has a similarity in the wavelength area near infra-red. This can be explained physically by the presence of Fe\(^{2+}/Fe^{3+}\) intervalence charge transfer transition [27]. The obtained graphic experienced an increase in the wavelength areas of 400-550 nm, and there was splitting which represented the increase of optimum absorbance by the presence of magnetic particle interface, where the smaller the magnetic particle, the bigger the absorbance value [28]. When related to the structure and particle size, Fe\(_2\)CrO\(_4\) sample shows the highest maximum absorbance because its particle size is the smallest, followed by Fe\(_3\)O\(_4\) sample and finally Fe\(_2\)TiO\(_4\) sample with the biggest particle size. Furthermore, the structure of the samples also influences the acquisition of each band gap energy as shown in Figure 6.

![Figure 5. The absorbance results of Fe\(_2\)MO\(_4\)/OO ferrofluids](image)

Based on Figure 6, the highest energy gap was obtained for Fe\(_2\)TiO\(_4\) sample and then followed by Fe\(_3\)O\(_4\) and Fe\(_2\)CrO\(_4\). The increase of this band gap energy is due to the presence of valence electron shell addition to Fe\(_2\)TiO\(_4\) sample [23]; therefore, higher energy was necessary to perform electron transfer from valence band to conduction band. Theoretically, it can also be described by the natural property of Ti element which is a semiconductor implying that it has a relatively significant gap between its valence and conduction bands [29] compared to Fe and Cr.
Figure 6. Band gap energy of (a) Fe$_3$O$_4$, (b) Fe$_2$TiO$_4$ and (c) Fe$_2$CrO$_4$ ferrofluids

Figure 7. Antibacterial activity results of Fe$_2$MO$_4$/OO ferrofluids

The antibacterial activity of the samples was observed through dilution method by reviewing the surviving bacterial colony percentage after the sample treatment. The results of the antibacterial activity of the samples are shown in Figure 7. Overall, the samples have antibacterial potential as proven by the decrease in the leftover bacterial colony percentage. This also confirms that the modification of structure through doping technique has successfully increased the antibacterial activity [30]. This claim is based on the comparison of surviving bacterial colony percentages for the samples.
Fe₃CrO₄ sample showed excellent bacterial viability with the least surviving leftover colony followed by Fe₃TiO₄ sample and the last Fe₃O₄. The ability of Cr³⁺ in oxidizing reactive oxygen species significantly contributes to the increase in its antibacterial activity [31]. Accordingly, the samples can be suggested as antibacterial agent candidates.

4. Conclusion
This work has successfully produced the Fe₃MO₄/OO ferrofluids through coprecipitation method with M namely Fe, Ti, and Cr sequentially. Based on the XRD characterization results, there was a shift in Fe₃TiO₄ sample towards a smaller angle and Fe₃CrO₄ sample towards a bigger angle due to the influence of dopant metal ionic radius. This impacted on the increase and decrease in the score of lattice parameter, crystal volume, and particle size. The calculation of particle size generated between 6.9 and 13.4 nm. The functional group of the samples showed the presence of Fe-O stretching band shift towards a small wavelength area for Fe₃TiO₄ and Fe₃CrO₄ towards a big wavelength area. The FTIR data also confirmed the stretching band of ferrofluids component. The absorbance data stated that the existence of intervalence charge transfer indicated the presence of Fe element at the wavelength near infra-red. Furthermore, the band gap energy was also obtained for the three samples with the score ranged between 2.20 up to 2.24 eV. The observation of antibacterial activity showed that the samples had possessed antibacterial potential. However, it has a bacterial viability difference in which the best one is possessed by Fe₃CrO₄ ferrofluids.

References
[1] Jin C, Mi W B, Li P and Bai H L 2011 Experimental and first-principles study on the magnetic and transport properties of Ti-doped Fe₃O₄ epitaxial films Journal of Applied Physics 110 083905.
[2] Padhi D K, Panigrahi T K, Parida K, Singh S K and Mishra P M 2017 Green synthesis of Fe₃O₄/RGO nanocomposite with enhanced photocatalytic performance for Cr (VI) reduction, phenol degradation, and antibacterial activity ACS Sustainable Chemistry & Engineering 5 10551–62.
[3] Ma S, Zhan S, Jia Y and Zhou Q 2015 Superior antibacterial activity of Fe₃O₄-TiO₂ nanosheets under solar light ACS applied materials & interfaces 7 21875–83.
[4] Badawy S M and Abd El-Latif A A 2017 Synthesis and charaterizations of magnetite nanocomposite films for radiation shielding Polymer Composites 38 974–80.
[5] Xu Z J, Zeng L, Yu L, Bedzyk M J, Baisariyev M, Huang Y, Wei C, Wu T, Zhao H and Feng Z 2016 Valence Change Ability and Geometrical Occupation of Substitution Cations Determine the Pseudocapacitance of Spinel Ferrite XFe₂O₄ (X = Mn, Co, Ni, Fe).
[6] Zhou C, Sun L, Zhang A, Wu X, Ma C, Su S, Hu S and Xiang J 2015 Fe₃₋₋Cu₂O₄ as highly active heterogeneous Fenton-like catalysts toward elemental mercury removal Chemosphere 125 16–24
[7] Barros W R, Steter J R, Lanza M R and Tavares A C 2016 Catalytic activity of Fe₃₋₋Cu₂O₄ (0≤ x≤ 0.25) nanoparticles for the degradation of Amaranth food dye by heterogeneous electro-Fenton process Applied Catalysis B: Environmental 180 434–41.
[8] Malek T J, Chaki S H, Chaudhary M D, Tailor J P and Deshpande M P 2018 Effect of Mn Doping on Fe₃O₄ Nanoparticles Synthesized by Wet chemical Reduction Technique Iranica Journal of Energy and Environment 9 121–9.
[9] Asfaram A, Ghaedi M, Hajati S, Goudarzi A and Dil E A 2017 Screening and optimization of highly effective ultrasound-assisted simultaneous adsorption of cationic dyes onto Mn-doped Fe₃O₄-nanoparticle-loaded activated carbon Ultrasonecs sonochemistry 34 1–12.
[10] Zhang A, Zhu L and Nan Z 2019 Ni-doped Fe₃O₄ nanoparticles coupled with SnS₂ nanosheets as 0D/2D heterogeneous catalyst for photo-Fenton reaction Materials Chemistry and Physics 224 156–68.
[11] Bindhu M R, Rakhi R B, Umadevi M and Anjana P M 2018 Antimicrobial, electrochemical and
photo catalytic activities of Zn doped Fe₃O₄ nanoparticles.

[12] Pal M, Lee S, Kwon D, Hwang J, Lee H, Hwang S and Jeon S 2017 Direct immobilization of antibodies on Zn-doped Fe₃O₄ nanoclusters for detection of pathogenic bacteria Analytica chimica acta 952 81–7.

[13] Liu Y, Xing J, Li Y, Tan J, Sun L and Yan J 2016 Mechanical properties and anisotropy of thermal conductivity of Feₓ₃₋ₓCrₓO₄ (x= 0–3) Journal of Materials Research 31 3805–13.

[14] Schoenthal W, Liu X, Cox T, Mesa J L, Maicas M, Diaz-Michelena M, Laughlin D E and McHenry M E 2014 Synthesis and magnetic properties of single phase titanomagnettes Journal of applied physics 115 17A934.

[15] Chen C-L, Dong C-L, Asokan K, Chern G and Chang C L 2018 Electronic structure of Cr doped Fe₃O₄ thin films by X-ray absorption near-edge structure spectroscopy Solid State Communications 272 48–52.

[16] Akbar A, Riaz S, Atiq S, Kayani Z N and Naseem S 2016 Effect of 3d-Metal doping on ferromagnetic and dielectric properties of magnetite thin films World Congress on Advances in Civil, Environmental and Materials Research (ACEM’16).

[17] Prabhu Y T, Rao K V, Kumari B S, Kumar V S S and Pavani T 2015 Synthesis of Fe₃O₄ nanoparticles and its antibacterial application International Nano Letters 5 85–92.

[18] Kitamika Y, Shingu H, Tanigawa S and Hasegawa H 2018 Impact of Tungsten Content on the Surface Properties of TiN Films Journal of The Surface Finishing Society of Japan 69 123–5.

[19] Qian D, Gu Y, Chen Y, Liu H, Wang J and Zhou H 2019 Ultra-high specific capacity of Cr³⁺ doped Li₄Ti₅O₁₂ at 1.55 V as anode material for lithium-ion batteries Materials Letters 238 102–6.

[20] Pearce C I, Qafoku O, Liu J, Arenholz E, Heald S M, Kukkadapu R K, Gorski C A, Henderson C M B and Rosso K M 2012 Synthesis and properties of titanomagnetite (Feₓ₋₃, Ti₃O₄) nanoparticles: A tunable solid-state Fe (II/III) redox system Journal of colloid and interface science 387 24–38.

[21] Riaz S, Akbar A and Naseem S 2014 Ferromagnetic effects in Cr-doped Fe₂O₃ thin films IEEE Transactions on Magnetics 50 1–4.

[22] Taufiq A, Sunaryono, Hidayat N, Hidayat A, Putra E G R, Okazawa A, Watanabe I, Kojima N, Pratapa S and Darmiento 2017 Studies on Nanostructure and Magnetic Behaviors of Mn-Doped Black Iron Oxide Magnetic Fluids Synthesized from Iron Sand Nano 12 1750110.

[23] Du Y N, Xu J, Li Z Z, Tang G D, Qian J J, Chen M Y and Qi W H 2018 Valence of Ti cations and its effect on magnetic properties of spinel ferrites TiₓM₁₋ₓFe₂O₄ (M= Co, Mn) RSC Advances 8 302–10.

[24] Wu X R, Chen C, Lü H H and Li L S 2015 Synthesis, structure characterization and magnetic property of (Mg₁₋ₓFeₓ)(Al0.4CrₓFe₁₋ₓ)O₄ spinel solid solution Material Science and Environmental Engineering: Proceedings of the 3rd Annual 2015 International Conference on Material Science and Environmental Engineering (ICMSEE2015, Wuhan, Hubei, China, 5-6 June 2015) (CRC Press) p 109.

[25] Taufiq A, Saputro R E, Hariyanto Y A, Hidayat N, Hidayat A, Mufti N and Susanto H 2018 Functional Group and Magnetic Properties of Fe₃O₄ Ferrofluids: The Impact of Dispersion Agent Composition Journal of Physics: Conference Series vol 1093 (IOP Publishing) p 012010.

[26] Taufiq A, Saputro R E, Hidayat N, Hidayat A, Mufti N, Diantoro M, Patriati A, Putra E G R and Nur H 2017 Fabrication of magnetite nanoparticles dispersed in olive oil and their structural and magnetic investigations IOP Conference Series: Materials Science and Engineering vol 202 (IOP Publishing) p 012008.

[27] Chen J, Hsu H-S, Huang Y-H and Huang D-J 2018 Spin-dependent optical charge transfer in magnetite from transmitting optical magnetic circular dichroism Physical Review B 98 085141.
[28] German S V, Navolokin N A, Kuznetsova N R, Zuev V V, Inozemtseva O A, Anis’kov A A, Volkova E K, Bucharskaya A B, Maslyakova G N and Fakhruullin R F 2015 Liposomes loaded with hydrophilic magnetite nanoparticles: preparation and application as contrast agents for magnetic resonance imaging Colloids and Surfaces B: Biointerfaces 135 109–15.

[29] Li X, Dai Y, Ma Y, Liu Q and Huang B 2015 Intriguing electronic properties of two-dimensional MoS₂/TM₂CO₂ (TM = Ti, Zr, or Hf) hetero-bilayers: type-II semiconductors with tunable band gaps Nanotechnology 26 135703.

[30] Abdullaeva Z, Kelgenbaeva Z, Nagaoka S, Matsuda M, Masayuki T, Koinuma M and Nishiyama T 2017 Solvothermal Synthesis of Surface-Modified Graphene/C and Au-Fe₃O₄ Nanomaterials for Antibacterial Applications Materials Today: Proceedings 4 7044–52.

[31] Zhang Y, Chen Y, Zhao Y W and Xiang N 2018 Photocatalytic activity and microstructure of micro-arc oxidized TiO₂:Cr³⁺ composite coatings Materials Technology 33 592–602.