

Preparation and characterisation of carbon-coated Magnéli phase Ti_4O_7 by modified carbon-thermal reduction route

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A carbon-coated Magnéli phase Ti_4O_7 composite has been successfully synthesised, via modified carbonthermal reduction of amorphous TiO_2 , which was prepared from hydrolysis of titanium sulphate and polyvinyl alcohol, at a relatively low temperature and fast reaction rate. Moreover, the effect of heat treatment temperature and time on the reduced phases is revealed. Despite removal of oxide ions, scanning electron microscopic images clearly show the obtained carbon-coated Ti_4O_7 composite retains well the spherical morphology of the precursor, and the high-pressure pelleted treatment effectively inhibits the growth of the final product during the heat treatment process. In addition, the prepared composite with mesopore structure exhibits a Brunauer, Emmett, and Teller (BET) surface area as high as $84.495 \text{ m}^2 \text{ g}^{-1}$ and good electrochemical stability in alkaline electrolyte, as well as some oxygen reduction reaction catalytic activity. The results presented in this work open an avenue for its potential electrochemical applications.

1. Introduction: Magnéli phase Ti_4O_7 has received great interests as a promising candidate for electrochemical applications owing to its high conductivity and chemical inertness even under highly aggressive conditions [1–4]. Numerous works have been performed from various points of view. Thus, urgent demand on electrode additives for batteries [2], catalyst supports for fuel cells [5] and electrodes for waste water remediation [6, 7] has strongly promoted research on this material. There are many conventional approaches available to synthesise the Ti_4O_7 materials under controlled reducing conditions at relatively high temperature using different reducers such as metals [8], carbon [9–12], carbonaceous organic materials [13] and reducing atmosphere (H_2 and NH_3) [1, 14–16]. However, most of the production methods are energy and time consuming. Moreover, the use of high processing temperatures over 1000°C not only inevitably leads to morphology deformation but also results in particle aggregation and dense low surface area materials, which limit its practical applications as electrode materials, where high surface area, a large number of active sites, as well as a porous structure are all-important for performance [17]. In our previous work [1], we successfully synthesised Ti_4O_7 powders containing small amounts of impurities by reducing rutile phase TiO_2 in an instantaneously decomposed ammonia atmosphere at 1050°C for 3 h. However, such high temperature and long reaction time result in Ti_4O_7 products with small specific surface area ($1.99 \text{ m}^2 \text{ g}^{-1}$) due to agglomeration, which limits their application in electro catalysis.

Therefore, it is of significance in developing a low-cost, environmentally sound and sustainable, as well as high efficient route to synthesise high purity Ti_4O_7 with high phase purity, small particle size and uniform distribution. Most recently, a low-temperature and low-cost begin technique, known as ‘green synthesis approach’, which makes use of plant sources for the preparation of metal or metallic oxide nanoparticles, has been developed and reported [18–20]. The increase in the number of published articles using plant extracts to synthesise nanoparticles witnesses the significance of this method [18]. However, to our best knowledge, this method using the plant extracts as both capping and reducing agent is currently confined to the laboratory and has not been reported for industrial application. On the other hand, the formation of Ti_4O_7 by a simple heat treatment of the powder mixture of

TiO_2 and carbon precursor has been carried out for practical applications [21].

Herein, in the present work, we focus on a feasible modified carbonthermal reduction route for synthesis of carbon coated Magnéli phase Ti_4O_7 composite at low temperature and fast reaction rate. The effect of heat-treated temperature and holding time on the preparation method is evaluated, as well as the physical characteristics and electrochemical properties of the products.

2. Experimental: First, a spherical TiO_2 precursor having an amorphous structure was synthesised [22]. Specifically, 400 ml of 1-propanol was dissolved in 400 ml of deionised water under stirring, followed by addition of 4 g of polyvinylpyrrolidone (PVP). Then, 15 g of titanium sulphate ($\text{Ti}(\text{SO}_4)_2$) was added into the above solution under vigorous stirring. The resulting white suspensions were harvested by centrifugation after 1 h of reaction. For the synthesis of the carbon-coated Ti_4O_7 composite, the as-prepared TiO_2 spheres were homogeneously mixed with polyvinyl alcohol (PVA) powders in an equal mass ratio. The mixed powders were then pressed in a uniaxial hydraulic machine by applying 30 MPa of pressure for 6 min to form pellets with a mass of 2.0–3.0 g, 28 mm in diameter and 3.0–4.0 mm in thickness. Finally, these pellets were put into a quartz tube electric furnace ($\Phi 30 \times 1000 \text{ mm}$) and were heat-treated for different time periods at various temperatures in N_2 at a flow rate of 40 ml min^{-1} .

The reduced compacts were mechanically ground into fine powder, and the phase structure of the samples was identified by X-ray diffraction using $\text{Cu K}\alpha$ radiation (XRD; D8, Rigaku 2500, Japan) at 40 kV with a scan rate of 8° min^{-1} . The surface morphology of the obtained samples was observed using a scanning electron microscope (SEM; S-4800, Hitachi, Japan) equipped with field emission guns. The Brunauer, Emmett, and Teller (BET) surface area was determined from the adsorption isotherm of N_2 (ASAP 2020, Micromeritics Corporation, USA). The electrochemical properties were studied using an electrochemical workstation (CHI760E, Shanghai, China).

3. Results and discussions: Pellets having equal mass ratio of spherical TiO_2 precursor and PVA were heat-treated for 1 h at various temperatures ranging from 900 to 1100°C in a flow of

nitrogen atmosphere. The XRD patterns shown in Fig. 1 clearly reveal the structural evolution of titanium-based oxides under different heat-treated temperatures. First, a large amount of Ti_4O_7 phase accompanied by a small amount of Ti_5O_9 appeared when the sample was heat-treated at 900°C . Only minor signals attributable to rutile TiO_2 having relevant diffraction peaks were observed. As the temperature increased to 950°C , a large number of rutile phase TiO_2 diffraction peaks appeared, and only weak diffraction peaks assigned to Ti_4O_7 were detected. Upon raising the temperature from 1000 to 1100°C , the peaks corresponding to the Ti_4O_7 phase disappeared in favour of those attributed to rutile phase TiO_2 and even TiN phase (from 1050 to 1100°C).

Besides temperature, reduction time was also found to be a crucial parameter for obtaining Magnéli phase Ti_4O_7 . Fig. 2 illustrates the

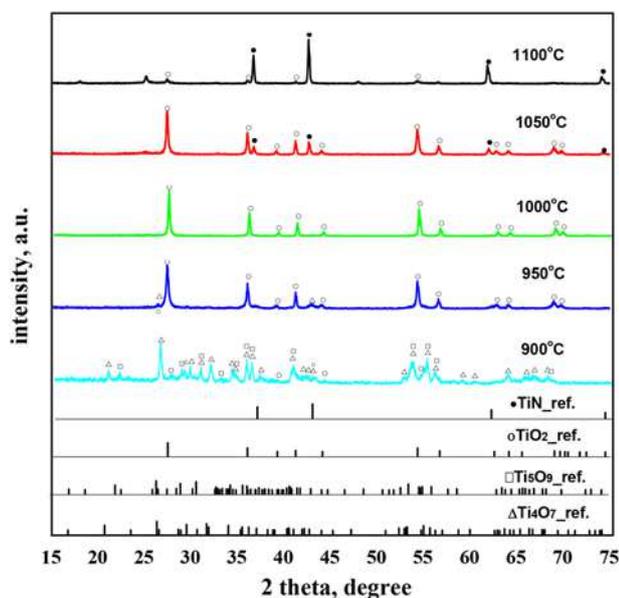


Fig. 1 X-ray diffraction patterns of the samples heat-treated for 1 h at various temperatures

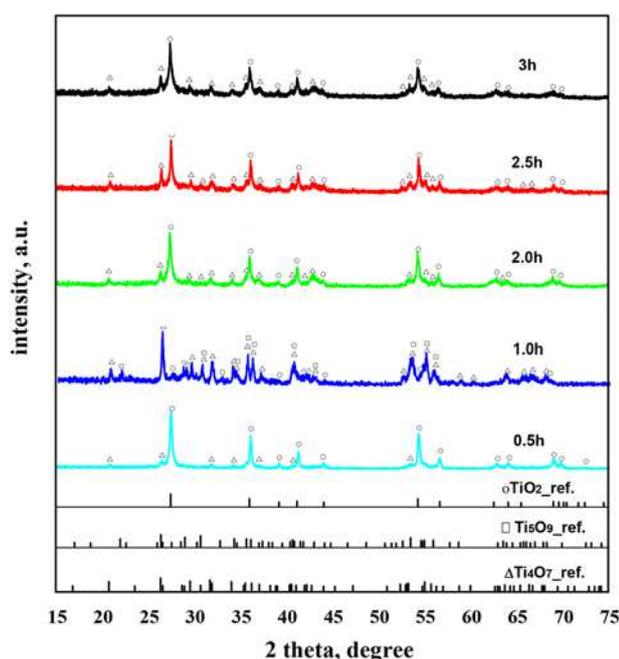


Fig. 2 X-ray diffraction patterns of the samples heat-treated for different time periods at 900°C

XRD patterns of the samples prepared at 900°C for 0.5 to 3 h. The phases found in the sample heat-treated for 0.5 h mainly contained TiO_2 and a small amount of Ti_4O_7 . The desired Ti_4O_7 phase was obtained after 1 h of reduction, being most of the XRD peaks in good agreement with the Ti_4O_7 reference (JCPDS Card no. 50–0787). After further treatment, a rutile phase TiO_2 was obtained, though a small amount of Magnéli phase Ti_4O_7 was still present. Therefore, the optimised reduction condition for the preparation of Ti_4O_7 was determined to be heating at 900°C for 1 h.

To the best of our knowledge, most existing studies focus on preparing the Ti_4O_7 phase under controlled reducing conditions at relatively high temperature. For example, Ti_4O_7 was obtained at 1000°C using carbon as reductant by a molten salt synthesis process [11]. Ti_4O_7 powders containing small amounts of impurities were synthesised by carbothermal reduction of TiO_2 in vacuum at 1025°C [9]. Carbon-coated Ti_4O_7 nanorods were synthesised by a microwave-assisted carbothermal reduction reaction at 975°C using PVP as reductant [23]. Our work differs from these studies in the pre-treatment process that involves pressing the composite into compact pellets. Predictably, the process of pressing into pellets effectively expands the contact area between TiO_2 and carbonaceous organic materials, which greatly accelerates the carbothermal reduction reaction. The target product Magnéli phase Ti_4O_7 can be thereby obtained after only 1 h of heating at relatively low temperature.

The crystallite size of the synthesised composite was determined and compared by using the Scherer's equation [21, 24]

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where $K=0.9$ is the constant shape factor, $\lambda=0.15418$ nm is the wavelength of $\text{CuK}\alpha$, the Bragg diffraction angle is θ and β is full width at half maximum in radians. The crystal size calculations were done to the most intense dominating peak and the values are summed up in Table 1.

As shown in Table 1, with the increase of heat-treated temperature and the extension of roasting time, the crystal size increases correspondingly. Specifically, the final product carbon coated Ti_4O_7 composite obtained at 900°C for 1 h has an average particle size of 33.3 nm.

Figs. 3a and b show the surface morphology of the TiO_2 and Ti_4O_7 materials obtained after heating at 900°C for 1 h. As shown in Fig. 3a, the as-synthesised TiO_2 coated with PVP consisted of spherical particles homogeneously distributed with diameters in the range of 200–500 nm. Interestingly, after heat treatment with PVA at 900°C for 1 h, the spherical morphology of the TiO_2 precursor was well retained and sintering of TiO_2 grains was markedly suppressed, despite substantial removal of oxide ions and non-topochemical transformation of lattice frameworks after carbothermal reduction. Fig. 3b clearly shows that the produced Ti_4O_7 particles kept nearly the same particle size as the original TiO_2 precursor, even after heat treatment. The EDS analysis of the carbon-coated Ti_4O_7 composite, as portrayed in Fig. 3c, exhibits the element-wise profile of the sample. Two strong peaks were clearly noted for the element titanium at 4.5 keV and for the oxygen at 0.5 keV. The spectra data placed the elemental break-up composition of titanium and oxygen at 59.25 and 40.75%, respectively.

Table 1 Calculated crystallite 'D' predicted using Scherer's equation

Sample	D (nm) by XRD	Sample	D (nm) by XRD
C-Ti-O-900°C-1.0 h	33.3 nm	C-Ti-O-900°C-0.5 h	26.8 nm
C-Ti-O-950°C-1.0 h	41.0 nm	C-Ti-O-900°C-1.0 h	41.0 nm
C-Ti-O-1000°C-1.0 h	43.6 nm	C-Ti-O-900°C-2.0 h	44.0 nm
C-Ti-O-1050°C-1.0 h	55.3 nm	C-Ti-O-900°C-2.5 h	44.5 nm
C-Ti-O-1100°C-1.0 h	55.9 nm	C-Ti-O-900°C-3.0 h	45.2 nm

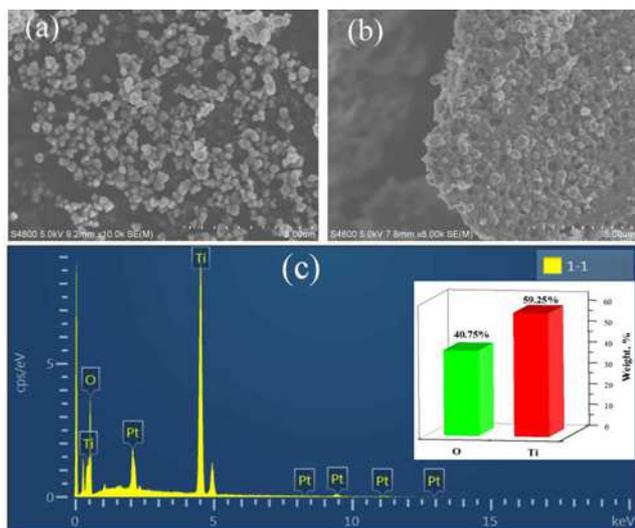


Fig. 3 SEM images and EDS spectrum of the synthesized samples
a SEM for TiO_2
b SEM for the carbon-coated Ti_4O_7
c EDS spectrum for the carbon coated Ti_4O_7

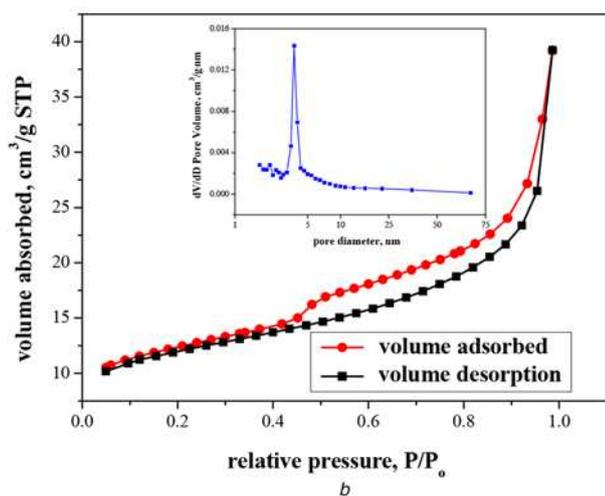
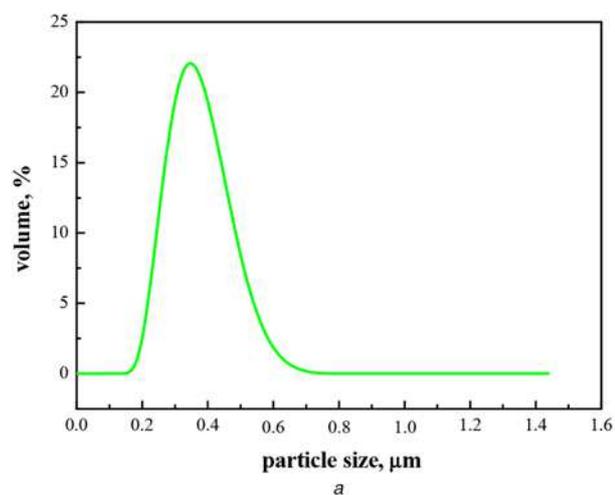


Fig. 4 The particle size distribution and pore size distribution and N_2 adsorption-desorption isotherms of the obtained samples
a The particle size distribution for the synthesized TiO_2
b The pore size distribution and N_2 adsorption-desorption isotherms of the carbon coated Ti_4O_7

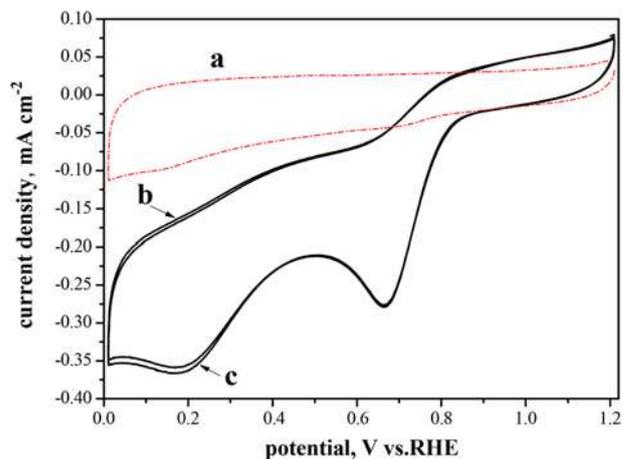


Fig. 5 CV curves of Ti_4O_7 in O_2 - and N_2 -saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1}

Fig. 4*a* shows the particle size distribution of the spherical morphology of the TiO_2 precursor. The volume fraction of particles with the particle size of 350 nm is relatively large, and the particles are evenly distributed between 200 and 600 nm. Clearly, after heat treatment, the produced carbon coated Ti_4O_7 will keep nearly the same particle size, which is confirmed by the results of SEM analysis in Figs. 3*a* and *b*. Furthermore, the BET surface area and pore size distribution of the carbon-coated Ti_4O_7 composite are presented in Fig. 4*b*, showing that the adsorption and desorption curves of the composite and corresponding BET specific surface area is determined to be $84.495 \text{ m}^2 \text{ g}^{-1}$, which is much higher than that reported by Masahiro Toyoda and coworkers [25]. The inset of Fig. 3*e* shows that the composite mainly contains mesopores with pore size between 2 and 10 nm. To be mentioned, the carbon coated Ti_4O_7 composite with mesopore structure and high BET specific surface will be beneficial for potential catalytic applications of this material in electrochemistry.

To evaluate the oxygen reduction reaction (ORR) activity and electrochemical stability of the synthesised materials, the obtained composite was coated on a glass carbon electrode, and its electrochemical properties were tested in O_2 - and N_2 -saturated 0.1 M KOH solution using cyclic voltammetry (CV) at a scan rate of 10 mV s^{-1} . The results shown in Fig. 5 demonstrate that the composite was active for ORR. As can be seen in Fig. 4*a*, no obvious oxygen reduction peak was detected in argon-saturated electrolyte. Interestingly, two cathodic peaks occurred at 0.174 V/RHE and 0.666 V/RHE in oxygen-saturated electrolyte, which may be caused by desorption of oxygen molecules and OH^- ions during the anodic process. Moreover, as shown in Figs. 4*b* and *c*, the similarities between the first and the 100th CV scans initiated from 0.01 V indicate that the obtained carbon coated Ti_4O_7 composite has good electrochemical stability, which renders it a promising candidate for applications in electrochemical systems.

4. Conclusion: Carbon-coated Ti_4O_7 composite was prepared by a modified carbonthermal reduction route. SEM images clearly show the obtained carbon-coated Magnéli phase Ti_4O_7 composite retains well the spherical morphology of the precursor, and the high-pressure pelleted treatment effectively inhibits the growth of the final product during the heat treatment process. The reduction temperature and time should be carefully controlled because shorter or longer time and higher or lower temperature would generate more impurities in the resultant of carbon coated Ti_4O_7 composite. In electrochemical characterisations, the obtained carbon-coated Ti_4O_7 composite with mesopore structure and high BET specific surface exhibits ORR catalytic activity and good

electrochemical stability, suggesting its potential application in the field of electron-catalysis

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6 References

- [1] Tang C., Zhou D.B., Zhang Q.: 'Synthesis and characterization of Magnéli phases: reduction of TiO_2 in a decomposed NH_3 atmosphere', *Mater. Lett.*, 2012, **79**, pp. 42–44
- [2] Walsh F.C., Wills R.G.A.: 'The continuing development of magnéli phase titanium sub-oxides and Ebonex® electrodes', *Electrochim. Acta.*, 2010, **55**, pp. 6342–6351
- [3] Bartholomew R.F., Frankl D.R.: 'Electrical properties of some titanium oxides', *Phys. Rev.*, 1969, **187**, pp. 828–833
- [4] Gusev A. A., Avvakumov E.G., Vinokurova O.B.: 'Synthesis of Ti_4O_7 magnéli phase using mechanical activation', *Sci. Sinter.*, 2003, **35**, pp. 141–145
- [5] Senevirathne K., Hui R., Campbell S., *ET AL.*: 'Electrocatalytic activity and durability of Pt/NbO₂ and Pt/ Ti_4O_7 nanofibers for PEM fuel cell oxygen reduction reaction', *Electrochim. Acta.*, 2012, **59**, pp. 538–547
- [6] Wang G.R., Liu Y., Ye J.W., *ET AL.*: 'Electrochemical oxidation of methyl orange by a Magnéli phase Ti_4O_7 anode', *Chemosphere*, 2020, **241**, p. 125804
- [7] Bejan D., Guinea E., Bunce N.J.: 'On the nature of the hydroxyl radicals produced at boron-doped diamond and ebonex® anodes', *Electrochim. Acta.*, 2012, **69**, pp. 275–281
- [8] Kitada A., Hasegawa G., Kobayashi Y., *ET AL.*: 'Selective preparation of macroporous monoliths of conductive titanium oxides $\text{Ti}_n\text{O}_{2n-1}$ (n=2, 3, 4, 6)', *J. Am. Chem. Soc.*, 2012, **134**, pp. 10894–10898
- [9] Zhang X., Liu Y., Ye J.W., *ET AL.*: 'Fabrication of Ti_4O_7 electrodes by spark plasma sintering', *Mater. Lett.*, 2014, **114**, pp. 34–36
- [10] Tsumura T., Hattori Y., Kaneko K., *ET AL.*: 'Formation of the Ti_4O_7 phase through interaction between coated carbon and TiO_2 ', *Desalination*, 2004, **169**, pp. 269–275
- [11] Wang G.R., Liu Y., Ye J.W., *ET AL.*: 'Fabrication of rod-like Ti_4O_7 with high conductivity by molten salt synthesis', *Mater. Lett.*, 2017, **186**, pp. 361–363
- [12] Ganiyu S.O., Oturan N., Raffy S., *ET AL.*: 'Sub-stoichiometric titanium oxide (Ti_4O_7) as a suitable ceramic anode for electrooxidation of organic pollutants: A case study of kinetics, mineralization and toxicity assessment of amoxicillin', *Water Res.*, 2016, **106**, pp. 171–182
- [13] Guo Y., Li J., Pitcheri R., *ET AL.*: 'Electrospun $\text{Ti}_4\text{O}_7/\text{C}$ conductive nanofibers as interlayer for lithium-sulfur batteries with ultra long cycle life and high-rate capability', *Chem. Eng. J.*, 2019, **355**, pp. 390–398
- [14] Li X., Zhu A.L., Qu W., *ET AL.*: 'Magnéli phase Ti_4O_7 electrode for oxygen reduction reaction and its implication for zinc-air rechargeable batteries', *Electrochim. Acta.*, 2010, **55**, pp. 5891–5898
- [15] Zhang L., Kim J., Zhang J., *ET AL.*: ' Ti_4O_7 supported Ru@Pt core-shell catalyst for CO-tolerance in PEM fuel cell hydrogen oxidation reaction', *Appl. Energy*, 2013, **103**, pp. 507–513
- [16] Lin H., Niu J.F., Liang S.T., *ET AL.*: 'Development of macroporous Magnéli phase Ti_4O_7 ceramic materials: as an efficient anode for mineralization of poly-and perfluoroalkyl substances', *Chem. Eng. J.*, 2018, **54**, pp. 1058–1067
- [17] Kundu D., Black R., Berg E.E., *ET AL.*: 'A highly active nanostructure metallic oxide cathode for aprotic Li-O₂ batteries', *Energy Environ. Sci.*, 2015, **8**, pp. 1292–1298
- [18] Anchan S., Pai S., Sridevi H., *ET AL.*: 'Biogenic synthesis of ferric oxide nanoparticles using the leaf extract of *Peltophorum pterocarpum* and their catalytic dye degradation potential', *Biocatalysis Agric. Biotechnol.*, 2019, **20**, p. 101251
- [19] Varadavenkatesan T., Lyubchik E., Pai S., *ET AL.*: 'Photocatalytic degradation of Rhodamine B by zinc oxide nanoparticles synthesized using the leaf extract of *Cyanometra ramiflora*', *J. Photoch. Photobio B.*, 2019, **199**, p. 11621
- [20] Vinayagam R., Selvaraj R., Arivalagan P., *ET AL.*: 'Synthesis, characterization and photocatalytic dye degradation capability of calliandra haematocephala-mediated zinc oxide nanoflowers', *J. Photoch. Photobio B.*, 2020, **203**, p. 111760
- [21] Varadavenkatesan T., Selvaraj R., Vinayagam R.: 'Dye degradation and antibacterial activity of green synthesized silver nanoparticles using *Ipomoea digitata* Linn. Fower extract', *Int. J. Environ. Sci. Technol.*, 2019, **16**, pp. 2395–2404
- [22] Hu M.L., Bai C.G., Xu S.M., *ET AL.*: 'Preparation of the size-controlled TiO_2 with spherical morphology', *Acta Phys.-Chim. Sin.*, 2008, **24**, pp. 2287–2292
- [23] Fukushima J., Takeuchi T., Hayashi Y., *ET AL.*: 'Microwave synthesis of carbon-coated Ti_4O_7 nanorods by rapid carbothermal reduction processing', *Chem. Eng. Process.*, 2018, **125**, pp. 27–33
- [24] Fouad D.E., Zhang C.H., Mekuria T.D., *ET AL.*: 'Effects of sono-assisted modified precipitation on the crystallinity, size, morphology, and catalytic applications of hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles: A comparative study', *Ultrason. Sonochem.*, 2019, **59**, p. 104713
- [25] Masahiro T., Takashi Y., Beata T., *ET AL.*: 'Preparation of carbon-coated Magnéli phases $\text{Ti}_n\text{O}_{2n-1}$ and their photocatalytic activity under visible light', *Appl. Catal. B-Environ.*, 2009, **88**, pp. 160–164