High Performance Leather based on in Situ Formation of Reduced Graphene Oxide in Chrome Tanning

by

Xinle Yang,[1] Yanchun Li,[1]* Mao Yang,[1] Xugang Dang,[2] and Shan Cao[1]

[1]*School of Light Industry and Engineering, Qilu University of Technology (Shandong Academy of Sciences),* No.3501 Daxue Rd, Changqing District, 250353, Jinan, Shandong Province, China.

[2]*Institute for Biomass and Function Materials & National Demonstration Centre for Experimental Light Chemistry Engineering Education, School of Bioresources Chemistry and Materials Engineering, Shaanxi University of Science and Technology,* Xi'an, 710021, China.

Abstract

A novel method of high performance leather prepared via in situ reduction of graphene oxide after tanning was proposed in this research. First, nano-graphene oxide (GO) was prepared by an improved Hummers method. Then, the prepared GO was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Finally, GO was added during the chrome tanning process, and GO was reduced by ascorbic acid after the chrome tanning was completed. Moreover, the shrinkage temperature, tensile strength, tear strength and thermal conductivity of the finished leather were investigated. The results showed that the absorption of chrome tanning agent was significantly improved by the addition of GO. The tensile strength, tear strength, and the thermal conductivity of the resulted leather obviously surpassed the leather tanned by chrome tanning agent. Specifically, the tensile strength and tear strength of the leather reached 21.25 MPa and 163.95 $N{\cdot}mm^{-1}$, respectively, when the amount of reducing agent was ten times the amount of GO. A combination of the tanning of leather and the in situ reduction of GO is expected to become a new processing method for preparation of high performance.

Introduction

Nanomaterial refers to the material in which at least one of the two phase microstructures has a one-dimensional scale up to the nanometer scale.[1] Nano-particle phase consists of a small number of atoms or molecules. Due to the small size and large specific surface area of nanoparticles, the quantum effect and surface effect endow nanomaterial with a variety of special properties.

With the rapid development of nanotechnology, the applications of nanomaterial in leather have been further studied.[2] Montmorillonite and SiO_2 as tanning agents significantly improve the mechanical properties of leather.[3,4] Nano-ZnO is used in retanning for improving the antibacterial properties of leather.[5] Nano-TiO_2 used in leather finishing endow leather with self - cleaning.[6,7]

Graphene is an ideal two-dimensional nanomaterial with perfect crystal structure and excellent mechanical, thermal, optical, electrical properties.[8] The Young's modulus and fracture strength of graphene can reach 1000 GPa and 130 GPa.[9,10] The thermal conductivity of graphene is approximately 5300 W/m•K, which exceeds carbon materials such as diamond.[11,12] Graphene has excellent properties but lacks reactive groups that can undergo chemical reactions. And graphene oxide (GO), a derivative of graphene, significantly ameliorates this drawback.[13] The aqueous dispersion of GO has good stability, and the surface and edges of GO nanosheet layers contain reactive groups such as hydroxyl, carboxyl and carbonyl groups. It provides the conditions for the binding of GO to leather fibers. Besides, there are many spaces of different sizes between the fibers that comprise the primitive skin. It provides the conditions for the penetration of GO into the leather. In addition, GO has nano size effect and small size effect, thereby nano GO has the potential to be used in the leather production process.[14] At present, graphene has been mainly used in leather production as a finishing agent and tanning agent to improve the physical properties of leather and reduce the use of other leather chemicals.[15-18]

Compared with GO, graphene has better mechanical and thermodynamic properties. If graphene is combined with leather, it will further improve the physical and mechanical properties of leather. Due to the lack of functional groups in graphene, it cannot bind to collagen fibers. If the GO combined with the leather fiber is used as an intermediate, and then the reduced graphene oxide (RGO) is obtained by reducing the GO, thus the combination of graphene and leather is realized.[19,20] In addition, during the reduction process, the functional groups in GO cannot be completely removed and the conjugated structures cannot be completely restored. The better the reduction effect, the closer the physical properties of the obtained RGO to those of graphene. Therefore, RGO has better mechanical and thermal properties than GO.[21,22] Ascorbic acid (vitamin C) is a green reducing agent that can efficiently reduce GO. After the

*Corresponding author email: qlulyc@126.com

Manuscript received November 1, 2021, accepted for publication December 28, 2021.

addition of ascorbic acid, the oxygenated group of GO was removed substantially, especially the content of C-O (epoxy and alkoxy groups), resulting in RGO.[21]

In this work, nano GO was added in the chrome tanning process, and ascorbic acid was used for situ reduction of GO after the tanning process. The positive effects of GO application for leather tanning were investigated by analyzing the physical properties of leather. It is expected that this work will improve the physical properties of the leather.

Experimental

Materials and chemicals

Powdered graphite with an average particle size of about 1.3 μm was used (Qingdao Huatai Lubrication seal Technology Co., LTD, China). Pickled cattle hide from Dezhou xinglong leather Products Co., LTD (Dezhou, China). Potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), ascorbic acid, formic acid all were reagent grade (Sinopharm Chemical Reagents Co., LTD, China). Concentrated sulfuric acid (H_2SO_4, 98%) was reagent grade (Laiyang Economic and Technological Development Zone Fine Chemical Plant, China). Sodium formate (CHO_2Na) and sodium bicarbonate ($NaHCO_3$) were reagent grade (Tianjin Guangfu Technology Development Co., LTD., China). Sodium chloride was industrial grade (Feicheng Shengli Salt Co., LTD., China). Chromium powder was industrial grade (Brother Enterprises Holding Co., Ltd., China).

Preparation of GO

A 500 mL three-end flask was placed in an ice bath (<5°C). 3 g graphite and 75 mL H_2SO_4 were added and stirred to mix well. $KMnO_4$ (9 g) was slowly added to the flask under 5°C over 20 min, kept below 5°C for 2 h, and then at 35°C for 1 h. The contents of the flask were then diluted with deionized water (140 mL) and heated to 95°C for 30 min, and then H_2O_2 (12 g) was added dropwise over 20 min. The obtained graphene oxide was washed with deionized water by centrifugation until the pH of the washing water was 7.0. The GO suspension was ultrasonic treated for 2h and centrifuged to obtain nano GO, which was dispersed by deionized water and controlled to 0.15% mass fraction of GO.

Tanning process

Pickled cattle hide was symmetrically sampled from both sides of the backbone and numbered according to ISO 2418:2005, and the tanning experiment with GO and chrome tanning agent was carried out. The amount of GO was 0.15% of the pickled cattle hide quality (good experimental conditions obtained in the previous test), the amount of chrome tanning agent was 6% of the pickled cattle hide quality, and the amount of reducing agent was 0%, 0.75%, 1.50%, and 2.25% of the pickled cattle hide quality respectively. The experiment was carried out in a small test drum (QY-I drum, Xuzhou Dongyuan Leather Machinery Factory, China), and the weight of the pickled cattle hide increased by 30% as the basis of measurement.

Table I

Experimental scheme for in-situ reduction of GO.

Number	Tanning agent dosage	Reducing agent dosage
1	6%Cr	–
2	6%Cr+0.15%GO	–
3	6%Cr+0.15%GO	0.75% ascorbic acid
4	6%Cr+0.15%GO	1.50% ascorbic acid
5	6%Cr+0.15%GO	2.25% ascorbic acid

The pickled cowhide was treated with saline solution containing an equal weight of water and 7% NaCl in a rotating drum, and the diluted formic acid solution adjusts the pH of the float to 2.5-3.0. The drum temperature was adjusted to 25°C and rotated for 15 minutes. The GO aqueous dispersion was added, the drum was rotated for 1.5h. Then the temperature was increased to 33°C to add chrome tanning agent and the drum was rotated for 1.5 h. Then, 1% CHO_2Na was dissolved with 20 times of water and added to the drum and rotated for 30min. The 10% $NaHCO_3$ solution was added several times with 20 minutes interval each time until the pH of the float reached 3.8-4.0, then rotated for 40min and left overnight. The next day the drum was rotated for 30 min and then taken out and rested.

Reduction of GO

Wet blue and equal weight of water were put into the drum, heated to 50°C and added different dosage of ascorbic acid, then the drum was rotated for 3 h. Then the leather was dyed and fat liquored according to the traditional technological process. A control sample of chrome tanned leather was prepared by conventional chrome tanning method.

Characterization

Fourier transform infrared spectra (FTIR) of the GO were scanned by an IRAffinity-1S FTIR spectrometer (Shimadzu, Japan) using KBr pellets over the wavenumber of 500–4000 cm^{-1}.

A SmartLab SE X-ray diffractometer (SmartLab, Japan) was used to examine the XRD diffraction of GO with a scanning angle of 5-80°.

A Zeiss G500 SEM (Zeiss, Germany) was used to observe the surface morphology of graphene oxide and leather fibers.

The elemental content and electron binding energy of GO and graphite were analyzed by an EscaLabXi+ X-ray photoelectron spectrometer (Thermo Fisher, USA).

Physicochemical properties of leather

The leather was conditioned (T=20°C, Rh=65%) for 24 h and then tested for physical and mechanical properties. Determination of shrinkage temperature (T_s), tear strength, tensile strength and elongation at break of leather in accordance with industry standards ISO 3380:2002, ISO 3377-2:2002, ISO 3376:2002.

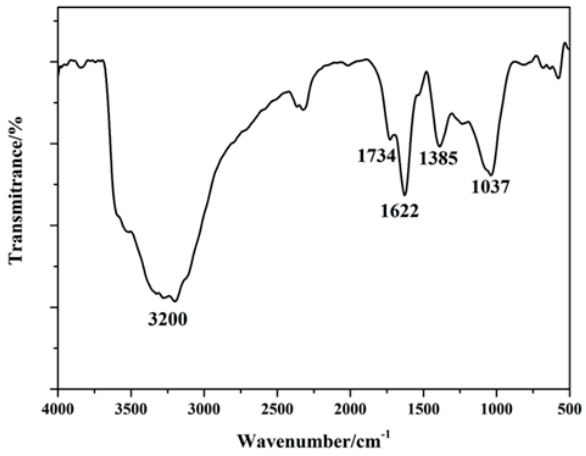

Figure 1. FTIR spectra of GO.

The Cr_2O_3 content of leather was determined using an ETHOS UP large microwave digestion instrument (Milestone, Italy) and an Avio 200 ICP-OES (PerkinElmer, USA) according to the industry standard QB/T 5315-2018.

The thermal conductivity of the leather was tested by using a Universal thermal conductivity meter TC3100 (XIATECH, China) in accordance with GB/T 10297-2015.

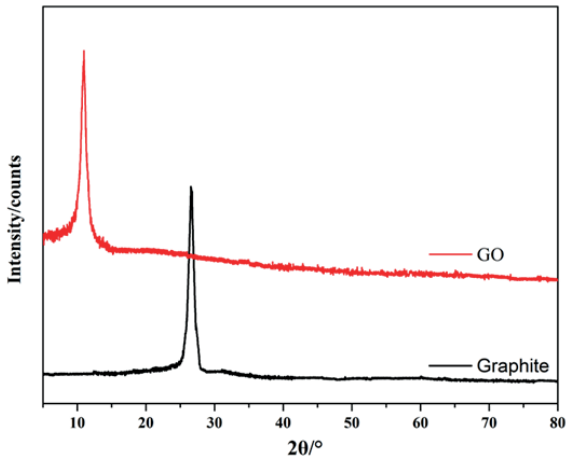

Figure 2. XRD patterns of GO and graphite.

Results and Discussion

Infrared analysis of GO

Prepared GO were analyzed by using FTIR (Figure 1). The infrared spectra showed absorption peaks of hydroxyl group (-OH) at 3200 cm^{-1}, carbonyl group (C=O) at 1734 cm^{-1}, double bond (C=C) at 1622 cm^{-1} and carboxyl group (-COOH) at 1385 cm^{-1} and epoxy bond (-C-O-C-) at 1034 cm^{-1}, indicating the successful preparation of GO containing -OH, C=O, -COOH and C-O-C groups.[23]

XRD analysis of GO

Figure 2 shows the XRD patterns of graphite and prepared GO. In Figure 2, the graphite has an obvious diffraction peak at $2\theta = 26.7°$. The sharp peak indicates that the graphite has high crystallinity. After oxidation, the characteristic diffraction peak of graphite disappears, and a new diffraction peak appears near $2\theta = 10.8°$. The layer spacing increases to 0.817 nm, which is larger than 0.335 nm of graphite. In the process of graphite oxidation, the carbon atom layer is connected to carboxyl, hydroxyl, epoxy and other oxygen-containing functional groups. The functional groups cause the carbon atom layer to fold, and water molecules are inserted between the layers, thereby increasing the distance between the carbon atom layers.[24]

Morphology analysis

The SEM of GO is shown in Figure 3 (a). GO is a sheet-layer structure full of wrinkles, indicating that GO was successfully prepared through oxidation and exfoliation processes. In Figure 3 (b), it shows that GO are uniformly distributed in the collagen fibers. Figure 3 (c) shows the thin GO sheet layers are wrapped around the collagen fiber bundle. The insertion of GO can increase the space between the fibers, which will facilitate the penetration of tanning agents and be beneficial to improve the performance of the leather.

XPS analysis of GO

The elemental composition and chemical functional groups of graphite and GO were tested using XPS, and the results are shown in Table II and Figure 4. It can be seen from Table II and Figure 4(a) that the oxygen content of GO increased significantly and the

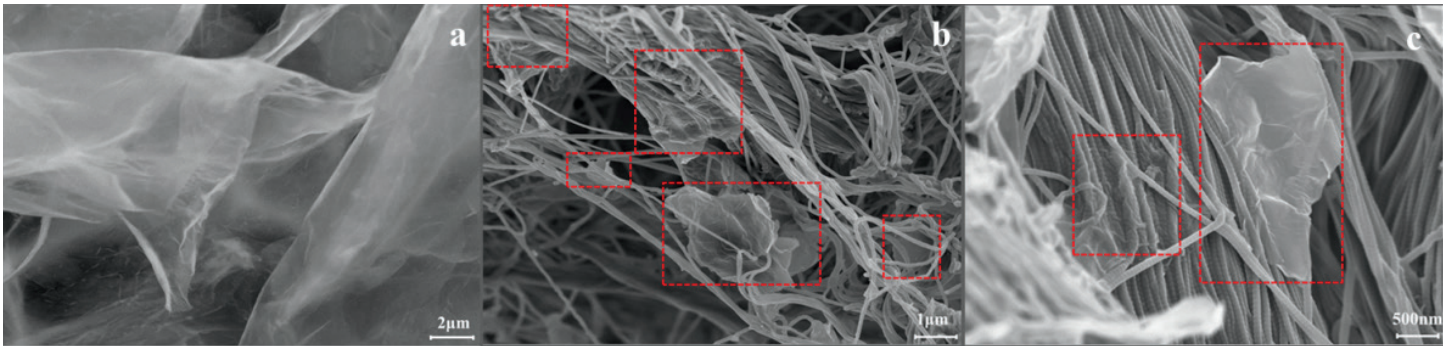

Figure 3. (a) SEM images of GO; **(b) (c)** SEM images of leather fibers.

Table II

Chemical composition of graphite and GO.

	Elemental content/%		
	C	O	C/O
Graphite	96.31	3.69	26.10
GO	70.52	29.48	2.39

ratio of C/O decreased from 26.10 to 2.39 compared to graphite. The decreased C/O ratio indicates the successful insertion of oxygen-containing functional groups into the graphite lamellar structure during the oxidation process.

Figure 4 (b) shows XPS spectra of C1s of GO. As shown in Figure 4 (b), the peaks of the four peaks are 287.4, 286.8, 285.3, and 284.6eV, corresponding to –COOH (26.62%), C=O (27.12%), C-O (27.52%), C-C/C=C (18.74%), respectively. This also indicates that after the graphite was oxidized, the carbon layer contained a large number of hydroxyl, carboxyl, carbonyl, and epoxy groups.[25]

Physical - mechanical properties testing of leather

Physical-mechanical properties of leather are shown in Table III. The application of GO can effectively improve the mechanical properties of leather. The tensile strength and tear strength of leather are increased from 14.30 MPa and 93.47 N•mm^{-1} to 17.58 MPa and 121.20 N•mm^{-1}, respectively.

After the addition of ascorbic acid, GO is reduced by removing a large number of epoxy and carboxyl groups. The large amount of RGO improves the performance of the leather. The tensile strength and tear strength of the leather are increased to 21.25 MPa and 163.95 N·mm^{-1}, respectively.

During the infiltration process, part of GO was present in the middle of collagen fibers and on the surface of bare skin in the form of physical adsorption. The GO between collagen fibers has no real binding to collagen but has a filling effect.

GO can also form chemical bonds with collagen fibers. The hydroxyl group (-OH) of GO is hydrogen bonded to the peptide bond (-CO-NH-) of collagen fibers; while the amino group (-NH_2) and carboxyl group (-COOH) of collagen fibers are hydrogen bonded to the oxygen atom of GO. The chemical combination and the nanometer effect of GO and their synergies lead to preliminary tanning of the leather, and also increases the space between the leather fibers, which facilitates the penetration of the chrome tanning agent.[26] In addition, the chrome tanning agent forms complexes with GO, which increases the molecular weight of the chrome complex and improves the absorption rate of the tanning agent.

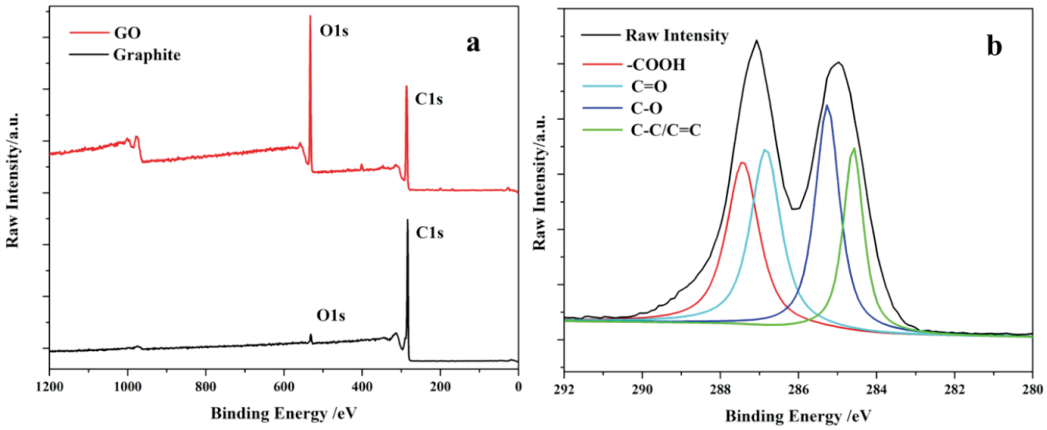

Figure 4. (a) XPS spectra of GO and graphite, **(b)** XPS spectra of C1s of GO.

Table III

Physical - mechanical properties of leather.

Number	Ts/°C	Tensile strength/MPa	Tear strength/N·mm^{-1}	Content of Cr_2O_3/%	Elongation at break/%
1	96.8	14.30	93.47	1.92	30.0
2	97.3	17.58	121.20	2.15	32.5
3	97.5	20.37	148.37	2.20	35.5
4	97.8	21.25	163.95	2.21	36.0
5	97.8	17.45	149.27	2.16	34.5

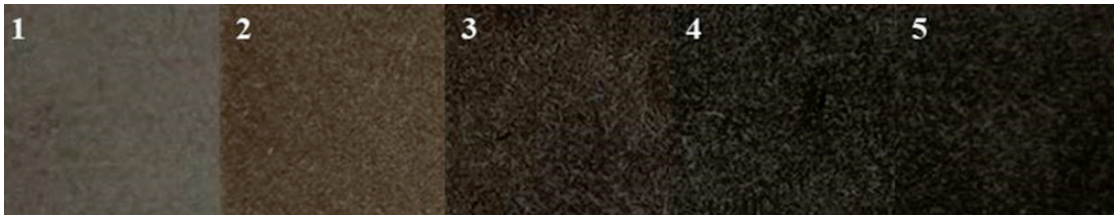

Figure 5. Pictures of leather surfaces

After adding the reducing agent, the unreacted oxygen-containing functional groups of GO are substantially removed and reduced to RGO with better physical properties. At the same time, the functional group of GO combined with collagen fiber will fix RGO and prevent it from agglomeration, so that RGO can keep uniform dispersion in the fiber, thus improving the physical and mechanical properties of leather. However, excess reducing agent will remove the oxygen-containing functional groups of GO bound to collagen fibers, resulting in RGO easily agglomerated and physical and mechanical properties reduced. In summary, the physical-mechanical properties of the leather can be effectively improved by using a reducing agent that is ten times the amount of GO.

Thermal conductivity testing of leather

As can be seen in Figure 5 and Figure 6, the color of the leather changed from blue to brown and the thermal conductivity decreased from 0.1064 W/m•K to 0.1052 W/m•K after the addition of GO. The GO combined with collagen fibers in turn reduces the thermal conductivity of the leather. Because after the graphite is oxidized, its oxygen atom content is increased as well as improving the space between the carbon atom layers, leading to the decrease of GO thermal conductivity.[27] After adding ascorbic acid, the thermal conductivity of the leather increased to 0.1127 W/m•K while the color of the leather changed from brown to black. It indicates that the ascorbic acid successfully reduced the brown GO to black RGO, the π-π conjugated structure was restored thereby improving the thermal conductivity.[20]

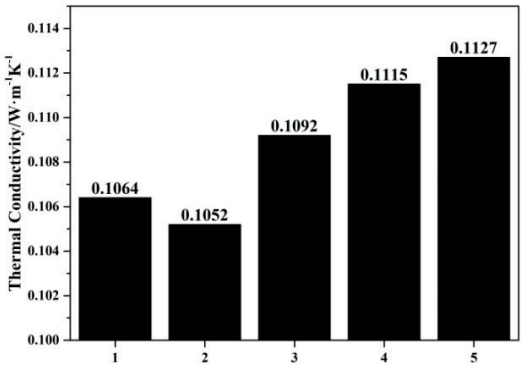

Figure 6. Thermal conductivity of leather.

Conclusions

In this work, GO was prepared by improved Hummers method and characterized by FT-IR, XRD, SEM, and XPS. It finds that hydroxyl, carboxyl and epoxy groups exist in GO. GO dispersion is used in the chrome tanning process, and ascorbic acid is used for situ reduction when the tanning is completed. GO is reduced by the addition of ascorbic acid, consequently improving the physical properties of the leather. The tensile and tear strengths of the leather increased to 21.25 MPa and 163.95 $N{\cdot}mm^{-1}$, the thermal conductivity increased to 0.1127 W/m·K, and the tanning agent utilization increased compared to the chrome tanned leather. The results show that the reduction of graphene oxide within the leather improved the tensile and tear strengths and thermal conductivity of the leather. Therefore, this paper provides a new idea of GO application to prepare high physical properties of thermally conductive leather.

Acknowledgments

The authors wish to thank the project ZR2020MB127 supported by Shandong Provincial Natural Science Foundation.

References

1. Wu, Q., Miao, W. S., Zhang, Y. D., et al.; Mechanical properties of nanomaterials: A review. *Nanotechnol. Rev* **9**, 259-273, 2020
2. Chen,Y., Fan, H. J., Shi, B.; Nanotechnologies for leather manufacturing: A review. *JALCA* **106**, 260-273, 2011.
3. Hu, J., Ma, J., Deng, W.; Properties of acrylic resin/nano-SiO_2 leather finishing agent prepared via emulsifier-free emulsion polymerization. *Materials Letters* **62**, 2931-2934, 2008
4. Bao, Y., Ma, J, Z.; Preparation of nanocomposites containing montmorillonite and SiO^2 particle for leather tanning agent. *JALCA* **107**. 429-434, 2012
5. Yorgancioglu, A., Bayramoglu, E, E., Renner, M.; Preparation of Antibacterial Fatliquoring Agents Containing Zinc Oxide Nanoparticles for Leather Industry. *JALCA* **114**, 171-179, 2019
6. Gaidau, C., Petica, A., Dragomir, T., et al.; Ag and Ag/TiO_2 nano-dispersed systems for treatment of leathers with strong antifungal properties. *JALCA* **106**, 102-109, 2011

7. Bitlisli, B, O., Yumurtas, A.; Self-cleaning leathers - the effect of nano TiO_2. *J Soc Leath Tech Ch* **92**, 183-186, 2008
8. Choi, W., Lahiri, I., Seelaboyina, R., et al.; Synthesis of Graphene and Its Applications: A Review. *Crit Rev Solid State* **35**, 52-71, 2010
9. Bizao, R, A., Botari, T., Perim, E., et al.; Mechanical properties and fracture patterns of graphene (graphitic) nanowiggles. *Carbon* **119**, 431-437, 2017
10. Lee, C., Wei, X, D., Kysar, J, W., et al.; Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* **321**, 385-388, 2008
11. Han, H., Zhang, Y., Wang, N., et al.; Functionalization mediates heat transport in graphene nanoflakes. *Nat Commun* **7**, 1-9, 2016
12. Balandin, A, A., Ghosh, S., Bao, W., et al.; Superior thermal conductivity of single-layer graphene. *Nano letters* **8**, 902-907, 2008
13. Dimiev, A. M., Tour, J, M.; Mechanism of graphene oxide formation. *ACS nano* **8**, 3060-3068, 2014
14. Lv, S., Zhou, Q, Li, Y., et al.; Tanning performance and environmental effects of nanosized graphene oxide tanning agent. *Clean Technol Envir* **18**, 1997-2006, 2016
15. Wei, L., Ma, J., Zhang, W., et al.; The tribological behaviors of polyacrylate/ graphene oxide and polyacrylate/surfactant-modified reduced graphene oxide composite coatings on flexible leather substrates. *Prog Org Coat* **122**, 64-71, 2018
16. Kale, M. B., Luo, Z., Zhang, X., et al.; Waterborne polyurethane/ graphene oxide-silica nanocomposites with improved mechanical and thermal properties for leather coatings using screen printing. *Polymer* **170**, 43-53, 2019
17. He, Y. Z., Zhang, Z. Y., Fan, et al.; Graphene Oxide Grafted Maleic Anhydride Vinyl Acetate Co-polymer and its Enhancement of Flame Retardant and UV-resistance of Retanned Leather. *JALCA* **114**, 216-227, 2019
18. Zhang, P., Xu, P., Fan, H., et al.; Phosphorus-nitrogen Flame Retardant Waterborne Polyurethane/Graphene Nanocomposite for Leather Retanning. *JALCA* **113**, 142-150, 2018
19. Wang, F., Jia, Z., Su, W., et al.; Adsorption of phenanthrene and 1-naphthol to graphene oxide and L-ascorbic-acid-reduced graphene oxide: effects of pH and surfactants. *Environ Sci Pollut Res Int* **26**, 11062-11073, 2019
20. Gao, J., Liu, F., Liu, Y., et al.; Environment-Friendly Method To Produce Graphene That Employs Vitamin C and Amino Acid. *Chem Mater* **22**, 2213-2218, 2010
21. Zhang, J., Yang, H., Shen, G., et al.; Reduction of graphene oxide via L-ascorbic acid. *Chem Commun* **46**, 1112-1114, 2010
22. Hajjar, Z., Rashidi, A. M., Ghozatloo, A.; Enhanced thermal conductivities of graphene oxide nanofluids. *Int Commun Heat Mass* **57**, 128-131, 2014
23. Manoratne, C. H., Rosa, S. R. D., Kottegoda, I. R. M.; XRD-HTA, UV Visible, FTIR and SEM Interpretation of Reduced Graphene Oxide Synthesized from High Purity Vein Graphite. *MSRI* **14**, 19-30, 2017
24. Sharma, R., Chadha, N., Saini, P.; Determination of defect density, crystallite size and number of graphene layers in graphene analogues using X-ray diffraction and Raman spectroscopy. *Indian J Pure Ap Phy* **55**, 625-629, 2017
25. Al, Gaashani, R., Najjar, A., Zakaria, Y., et al.; XPS and structural studies of high quality graphene oxide and reduced graphene oxide prepared by different chemical oxidation methods. *Ceram Int* **45**, 14439-14448, 2019
26. Zhou, Q, F., Lv, S, H., He, Y, Y., et al.; Preparation of graphene oxide and application in leather tanning process. *China Leather* **45**, 17-20+26, 2016
27. Mahanta, N, K., Abramson, A, R.; Thermal Conductivity of Graphene and Graphene Oxide Nanoplatelets. 13th InterSociety conference on thermal and thermomechanical phenomena in electronic systems, pp. 1-6, 2012