Graphene Oxide Modified Dye: Preparation and its Application in the Dyeing of Biomass-Derived Aldehyde-Tanned Chrome-Free Leather

by

Song Guo,[1,3] Wei Ding,[1,3*] Xiaoyan Pang[1,2] and Zhiwen Ding [1,2*]
[1]*China Leather and Footwear Research Institute Co. Ltd.*, Beijing 100015, P.R. China
[2]*Key Laboratory of Leather and Footwear Green Manufacturing Technology of China Light Industry*, Beijing100015, China
[3]*China-Ethiopia Leather Technology 'One Belt and One Road' Joint Laboratory*, Beijing 100015, China

Abstract

In this work, a graphene oxide (GO) modified small molecule reactive dye was prepared and further applied in the dyeing of the biomass-derived aldehyde tanning agent (BAT) tanned chrome-free leather for clarifying its application properties. The modified dye (GORD) was prepared by introducing Reactive Red180 (RRD-180) onto the surface of GO using the dehydration condensation method. GORD was characterized using FTIR spectroscopy, UV-Vis spectroscopy, and thermogravimetric analysis. The uptake ratios and the color fastness to sunlight of the GORDs were tested. FTIR and amino group consumption tests showed that RRD-180 was successfully grafted onto the GO lamellar structure, and the color rendering feature of the GORD was similar to that of RRD-180. The introduction of GO reduced the initial degradation temperature of GORD in the second stage (from 170°C to 150°C), but this did not affect the shrinkage temperature of the dyed leather. The uptake ratios of RRD-180 and GORDs were both higher than 90%, indicating that GO modification did not affect the reactive dye's uptake by leather. Importantly, the coloring fastness to sunlight of the grain and flesh sides of the dyed leather was improved, indicating that the GORD endowed the dyed leather with a certain UV-shielding performance. This work provides new ideas for promoting the industrial applications of GO and GO-based functional materials in chrome-free leather manufacturing.

Introduction

Reactive dyes contain groups that can react with cellulose and protein fibers under suitable conditions to form covalent bonds, thus achieving good fastness properties.[1] However, the light fastness of the products dyed with reactive dyes is relatively poor, especially for light-colored fabrics, which are difficult to meet the requirements of use.[2] Graphene has an ultraviolet absorption peak at approximately 281 nm, so it can absorb ultraviolet light in the wavelength range of 100 nm to 281 nm. For wavelengths greater than 281 nm, the two-dimensional planar structure of graphene can act as an impedance through reflection, thus enhancing the UV aging resistance.[3] Therefore, graphene and its derivatives have been extensively used in the coating of textile materials to obtain functional fabrics with UV-shielding properties. However, graphene is hydrophobic and easy to agglomerate due to strong van der Waals forces, which limits its wide application.[4]

Graphene oxide (GO) is a derivative of graphene, which has good dispersion stability in water and most polar organic solvents.[5] Compared with graphene, GO has excellent properties, which not only includes good wettability and surface activity, but also can be exfoliated by small molecules or polymers after intercalation, and play a very important role in improving the comprehensive performance of materials such as thermal, electrical and mechanical properties.[6,7] Xie et al. reported a facile strategy to prepare functional Poly (vinyl alcohol) (PVA) hybrid film with good ultraviolet (UV) shielding property and visible light transmittance using GO nanosheets as UV-absorbers.[8] The absorbance of ultraviolet light at 300 nm could be up to 97.5%, while the transmittance of visible light at 500 nm remained 40% plus. This hybrid film could protect proteins from UVA light induced photosensitive damage, remarkably. R. Miraftab et al. prepared GO-AZO composites by grafting amino groups on azo dyes with epoxy groups on GO.[9] The GO-AZO/PU composites were blended into a polyurethane matrix under optimal conditions and the GO-AZO/PU composites significantly improved its durability and resistance against degradation when exposed to UV irradiation.

In our previous work, GO was incorporated into waterborne polyurethane-based polymeric dyes to prepare GO modified polymeric dyes.[10] It was found that the introduction of GO into polymer dye systems can improve the heat resistance and sunlight fastness properties of the material. The GO modified waterborne polyurethane-based dye had the potential to be used in high performance leather finishing. Based on this, in this work, a GO modified reactive dye (GORD) was prepared using the carboxyl and epoxy groups on GO and the amino group on Reactive Red-180 through a dehydration condensation reaction. This composite dye was then applied to the dyeing of BAT-tanned chrome-free leather to improve the UV shielding performance of the dyed leather and provide a new idea for industrial applications of GO.

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*Corresponding author email: dingwei1368@outlook.com; ding-zhiwen@163.com
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Experimental

Materials

Graphite powder (2000 mesh) was purchased from Hanhui Graphite Co., Ltd (Shenzhen, China). Sulfuric acid (98 wt%), potassium permanganate, sodium nitrate, hydrogen peroxide, and hydrochloric acid (37 wt%) were bought from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Pickled sheepskin was purchased from Xinji Lingjue Leather Co., Ltd (Xinji, Hebei, China). Reactive Red-180 (RRD-180), Potassium iodide starch test paper, were bought from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). N,N'-dicyclohexylcarbodiimide (DCC) was bought from Woogood Dongfang Co., Ltd (Beijing, China). Hydrochloric acid (37%), potassium bromide, sodium nitrite, N-N-Dimethylacetamide (DMAC) were bought from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Biomass-derived aldehyde tanning agent was prepared according to the method described by Ding et al.[11,12]

Preparation of GORD

GO was prepared using a modified Hummers' method, which was reported in our recent work.[10] Firstly, 1.0 g of graphite, 0.5 g of sodium nitrate, and 8.0 g of potassium permanganate were added to a three-necked flask. Then, 40 mL of concentrated sulfuric acid was slowly added, and the reaction was carried out at a low temperature of 0°C for 5.5 h, followed by a medium-temperature reaction at 35°C for 3.0 h. The reaction temperature was then raised to 95°C, and 40 mL of distilled water was slowly added drop by drop into the three-necked flask and kept warm for another 30 min. Finally, 100 mL of distilled water was added, and hydrogen peroxide was added dropwise until the solution turned bright yellow. The liquid was filtered, and the filtrate was washed with a 5% dilute hydrochloric acid solution, followed by multiple washes with distilled water until the pH of the liquid was neutralized to 6.5~7. The product was then dried at 60°C to obtain graphite oxide.

As the preparation scheme of GO modified Reactive Red-180 (GORD) shown in Figure 1, graphite oxide was firstly added into 100 g of DMAC and dispersed with an ultrasonic disperser (below 20°C, 800 W, 24 min) to obtain a GO dispersion. Then, 20 g of RRD-180 and 5 g of DCC were added to a three-necked flask containing the dispersed GO solution, the mixture was mechanically stirred at 60°C in a thermostatic oil bath for 6 h and stood overnight. It was important to note that the mass of GO used was 0%, 0.1%, 0.4%, 0.7%, and 1.0% of the mass of RRD-180, respectively. The upper clear layer was poured into a glass evaporation vessel and dried in a constant temperature blast oven at 60°C for 24 h. The dried crude product was ground into powdery product using an agate mortar and collected for further use. The products with different GO dosages were defined as GORD-0.1%, GORD-0.4%, GORD-0.7%, and GORD-1.0%, respectively.

Dyeing of leather using GORD

Firstly, the pickled sheepskin was weighed, and the dosage of experimental materials was calculated as 200% of the weight of the pickled sheepskin. The tanning process was carried out in a drum. Pickled sheepskin, 100% of water, and 6% of sodium chloride were added into the drum and rotated for 30 min. After that, 2% of BAT was added to the drum and rotated at room temperature for 4 h. The pH of the tanning liquor was then slowly adjusted to 8.0 using sodium bicarbonate, and the tanning liquor was heated to 40°C. After running for another 4 h, the drum was stopped overnight. Finally, the tanned leather was washed using 400% of water at room temperature for 10 min and then horsed up for 24 h to obtain the BAT-tanned leather.[13,14]

Next, BAT-tanned chrome-free leather was shaved to a thickness of 1.0 mm and weighed. Twice the weight was used as the weight benchmark of the subsequent chemicals. Shaved BAT-tanned leather and 200% of water were added to the drum and ran for 20 min. The pH of the treatment liquor was measured and adjusted to 5.0~5.5 by adding the appropriate amount of formic acid. After running for 40 min, the liquor was drained. Next, 2.0% of GORD and 200% of water were added into the drum, which was then kept running for 2 h at 50°C. Finally, 1.5% of formic acid was added to adjust the pH of the dyeing liquor to 3.8~4.0. After running for 20 min, the dyeing

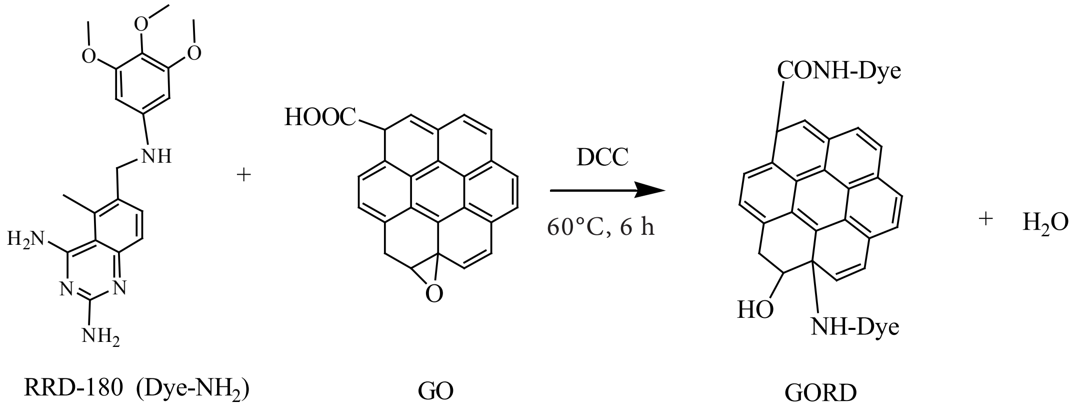

Figure 1. The schematic diagram for the modification reaction between GO and RRD-180.

liquor was drained, and the dyed leather samples were naturally dried for further analyses. The sample dyed with 2.0% of RRD-180 was used as a control group for comparison.

Characterizations

The Fourier transform infrared spectroscopy spectra of dyes were recorded by Tensor 27 infrared spectrometer (Bruker Inc., Billerica, Massachusetts, USA) with the scanning range in the spectrum of 600~4000 cm^{-1}. The UV-vis spectra of the GO, RRD-180, and GORD solutions were recorded by the TU-1810 ultraviolet-visible spectrophotometer (PERSEE, Beijing, China). Thermogravimetric measurements of dyes were performed in a nitrogen atmosphere using a TGA Q500 thermogravimetric analyzer (TA Instruments of America). The samples ranging from 7 mg to 8 mg in weight were heated from 25°C to 800°C at a heating rate of 20°C/min and under a nitrogen flow of 10 mL/min. Shrinkage temperature (T_s) is the most common index used to characterize the hydrothermal stability of leather.[15] Thus, the dyed samples were sampled to test their T_s using a digital leather shrinkage temperature instrument (MSW-YD4, Sunshine Electronic Research Institute of Shaanxi University of Science and Technology, Xi'an, Shanxi, China).

The coloring fastness to sunlight was used to assess the UV-shielding effect of the dyed leather via employing the LY-605A yellowing resistance tester (Dongguan Liyi Experiment Instrument Co., Ltd., Dongguan, Guangdong, China). The testing was conducted according to the GB/T 30669 standard method (340 nm, energy of 0.77 $W/(m^2 \cdot nm)$) at a chamber temperature of 60°C for 24 h. The color change of the leather sample was evaluated using an automatic color difference meter SC-80C (Beijing Kangguang Optical Instrument Co., Ltd., Beijing, China) for the measurement of L* a* b* values both before and after 24 h of irradiation. The color difference ΔE was calculated according to Equation 1.[16]

$$\Delta E = \sqrt{(L_{0h} - L_{24h})^2 + (a_{0h} - a_{24h})^2 + (b_{0h} - b_{24h})^2} \quad (1)$$

The amino group content of GORD was determined by titration using sodium nitrite solution.[14,17] GORD (2.0 g) was added into a volume-metric flask and diluted to 100 mL using distilled water. After that, 10 mL of the aforementioned diluted solution, 100 mL of distilled water, 5 mL of hydrochloric acid, and 5 mL of KBr solution (100 g/L) were added into a beaker. Under constant stirring, sodium nitrite standard solution (1.20×10^{-2} mol/L) was used to titrate the sample at 0~5°C, and a blank sample was tested at the same time. The amino group content (AC wt%) was calculated according to Equation 2.

$$\text{AC (wt\%)} = c \times (V_1 - V_2) / m \times 16 \times 100\% \quad (2)$$

where 'c' is the concentration of sodium nitrite standard solution (mol/L), V_1 is the consumed volume of sodium nitrite standard solution for sample titration (L), V_2 is the consumed volume of sodium nitrite standard solution for sample blank titration (L), and 'm' is the dry weight of the sample to be tested (g). Similarly, the AC of RRD-180 was determined using the same method. The amino group consumption ratio was calculated according to Equation 3.

$$\text{Amino group consumption ratio (\%)} = 1 - AC_{GORD} / AC_{RRD\text{-}180} \times 100\% \quad (3)$$

Before and after the dyeing processing, the treatment liquor was collected to determine the total organic carbon (TOC) concentration (multi N/C 2100, Analytik Jena, Jena, Thuringia, Germany). The uptake ratio of dye was calculated according to Equation 4.

$$\text{Uptake ratio of dye (\%)} = (C_0 - C_1) / C_0 \times 100\% \quad (4)$$

C_0 is the TOC value of diluted raw filler-dye solution multiplied by the dilution multiple; C_1 is the TOC value of diluted filling-dyeing wastewater multiplied by the dilution multiple.

Statistical analysis

For all experimental analysis at least 3 samples were used. Data for each group were presented as the mean ± SD ($n \geq 3$). Statistical analysis was performed with the software GraphPad Prism 8.0.1 (GraphPad Software, USA) by using ordinary one-way ANOVA method without matching and correction for multiple comparisons. RRD-180 and its dyed leather sample were set as controls. The statistical significance was defined at $p < 0.05$.

Result and Discussion

Structure characterizations

The structures of GO, RRD-180, and GORD-1.0% were characterized by FTIR. As presented in Figure 2, for the spectrum of GO, the strong broad absorption peak at 3200~3700 cm^{-1} was generated by the hydroxyl stretching vibration.[18] The peak at 1730 cm^{-1} was the characteristic peak of carbonyl stretching vibration in the carboxyl group at the edge of graphene oxide,[19] and the peak intensity was weak because the carboxyl group is generally distributed at the edge of graphene oxide with less quantity. The peak at 1635 cm^{-1} was the C=C stretching vibration peak of the graphene oxide benzene ring-like skeleton structure.[20] The absorption peak at 1398 cm^{-1} was the characteristic peak of the stretching vibration of the carboxylic acid C-O at the edge of graphene oxide,[21] and the absorption peak near 1076 $cm^{-1}$was generated by the C-OH stretching vibration of alcohols.[22] Compared to the FTIR spectra of RRD-180, the FTIR spectra of GORD-1.0% showed a much weaker peak for the absorption vibration of $-NH_2$ at 3448 cm^{-1},[23] a wider and stronger absorption band for the stretching vibration of the C-N bond at 1415 cm^{-1}, and stronger absorption peaks for the amide II band at 1558 cm^{-1} and the amide III band at 1335~1200 cm^{-1}.[24,25] All the above indicated that new amide bonds were formed.

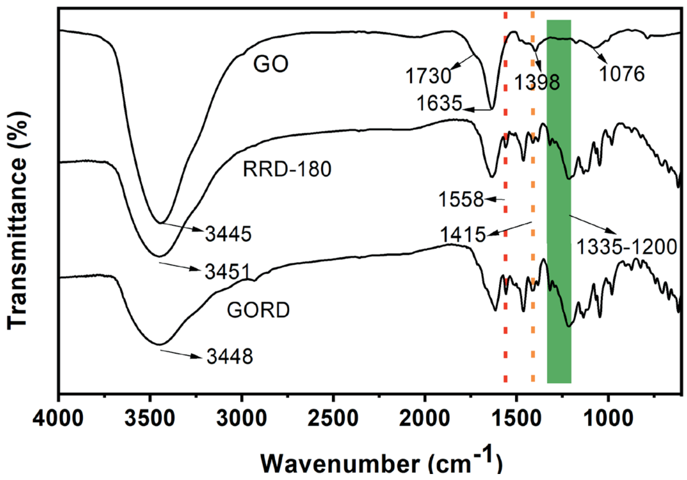

Figure 2. FT-IR spectra of GO, RRD-180, and GORD-1.0%.

UV-vis absorption spectra of GO, RRD-180, and GORD samples in the wavelength range of 200~800 nm were presented in Figure 3. It illustrated that the characteristic absorption peaks of RRD-180 appeared at 515 nm and 540 nm in the visible range, respectively. It could be also observed that the absorption curves of GORD and RRD-180 were very similar. Besides, in the region of 200~400 nm, the absorption curves of GORD and RRD-180 were very similar. The peak of RRD-180 at 540 nm slightly shifted to 539 nm after the modification with GO. This indicated that the color rendering of the dye did not change before and after the modification.

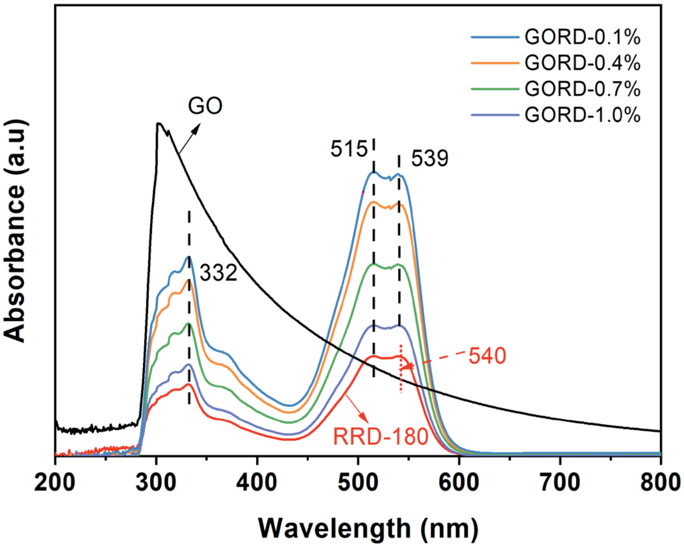

Figure 3. UV-vis spectra of GO, RRD-180, and GORD.

The amino group contents of RRD-180 and GORDs are shown in Table I. The amino group consumption ratio during the reaction can be calculated by detecting the amino group content in the solution before and after the reaction, and the consumption ratios of the amino group were presented in Figure 4. It could be observed that the consumption ratio of the amino group first decreased slightly with the increase of GO, and then increased with the increase of GO dosage after exceeding 0.7%. Overall, the consumption ratio of the amino group was around 50%, which might be due to the fact that there were two amino groups on the RRD-180, and there were fewer carboxyl groups on GO, thus it was more difficult for one amino group on RRD-180 to react with GO. Then, the other amino group was more difficult to contact with the carboxyl groups, so the amino group consumption ratio of the as-prepared GORD was around 50%. According to the significance analysis of the data shown in Table I, it can be determined that the amino group contents of GORDs were significantly different from that of RRD-180, further demonstrating the obvious consumption of amino group from RRD-180 during the preparation process of GORD.

Furthermore, the thermal stability of GORD was investigated via thermogravimetric analysis (TGA). It could be observed that the TGA curves of GO were mainly divided into three stages (Figure 5). The first stage was from 25°C to about 150°C and was mainly caused by the absorption of water by GO, accounting for about 8.9% of the total GO mass. The second stage occurred between 150°~240°C and was mainly caused by the cleavage of unstable oxygen-containing

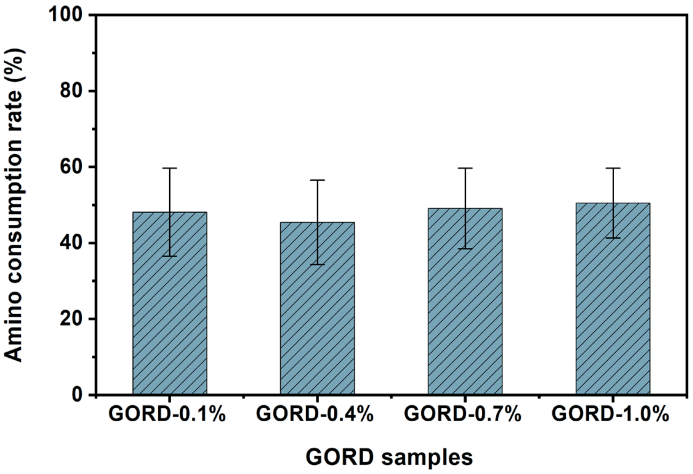

Figure 4. Consumption ratio of the amino group during the synthesis of GORD.

Table I

The content of amino groups in RRD-180 and GORD

Samples	RRD-180	GORD-0.1%*	GORD-0.4%*	GORD-0.7%*	GORD-1.0%*
Content (%)	8.31±0.66	4.31±0.97	4.54±0.93	4.24±0.88	4.12±0.77

The values are represented as mean ± standard deviation. * represents the significant difference ($p < 0.05$), and the RRD-180 sample was used as the control.

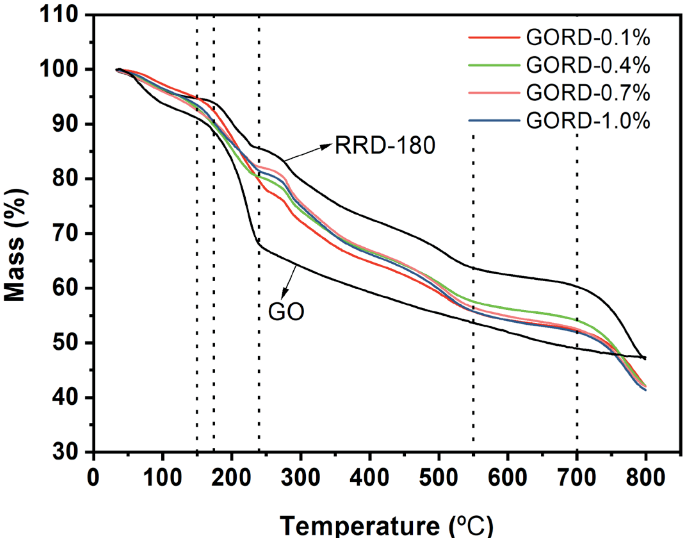

Figure 5. TGA curves of GO, RRD-180, and GORD.

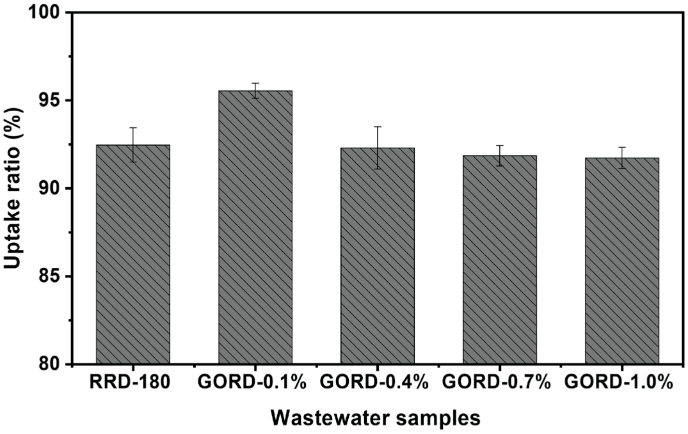

Figure 6. The uptake ratio of RRD-180 and GORD.

functional groups,[26] with a weight loss of about 23.1% at this stage. The third stage occurred after 300°C and was the degradation of more stable oxygen-containing functional groups on GO or the GO backbone.[27] The TGA curves of RRD-180 were mainly divided into four stages: 25°~170°C, 170°~550°C, 550°~700°C, and after 700°C. Impacted by the thermal weight loss of introduced GO, the second stage weight loss temperature of GORD was reduced to about 150°C. Meanwhile, the weight loss rate of GORD was higher in the interval of 170°~240°C compared with that of RRD-180. After 240°C, the thermal weight loss rate of GORD was the same as that of RRD-180.

Application performances of GORD in leather dyeing

The shrinking temperature (T_s) is used to characterize the hydrothermal stability of the leather. The T_s of the dyed leather samples ranged from 70°~71°C (Table II) with no major differences among different leather samples. This suggested that the GORD had no negative effect on the hydrothermal stability of the leather samples, which was probably due to a very small amount of GO used in the dyeing test, at most one part in ten thousand.

The uptake ratio of dye was calculated by measuring the total organic carbon concentration of the dye baths before and after dyeing. The maximum uptake ratio of the dye was achieved at 95.5% when the amount of GO/RRD-180 was 0.1%. Further increasing the dosage of GO, the uptake ratio of the GORD decreased slightly (Figure 6). Nevertheless, both RRD-180 and GORD showed an uptake ratio higher than 90%, indicating that the GORD had a good uptake ratio and the introduction of GO did not negatively affect the penetration and fixation of the modified dye. With the outstanding adsorption and penetrability of RRD-180 and GORDs, they had completely penetrated into the interior of the leather.

The color fastness to sunlight irradiation is an important application performance of dyes and materials. The photofading mechanism of dyes is very complicated, but the main reason is that the dyes are excited after absorbing photons, and a series of photochemical reactions occur to destroy the structure, resulting in discoloration and fading.[28] As shown in Figure 7, the ΔE value of the grain side and flesh side of GORD dyed samples were lower than that of the RRD-180 dyed sample after being irradiated by sunlight under the same conditions. With increasing the additive amount of GO in the GORD, the ΔE value of the flesh side of GORD-dyed leather became lower, and the ΔE value of the grain side of GORD-dyed samples increased slightly, but it was still lower than that of RRD-180 dyed leather sample, indicating that the color change of GORD dyed leather samples under sunlight exposure was weaker. According to the significance analysis results, for the grain side, the color fastness of leather dyed with GORD-0.1% had no significant difference

Table II

The T_s of the dyed leather samples

Samples	RRD-180	GORD-0.1%	GORD-0.4%	GORD-0.7%	GORD-1.0%
T_s/°C	70.7±0.53	70.9±1.64	70.0±0.42	70.3±1.90	71.0±1.15

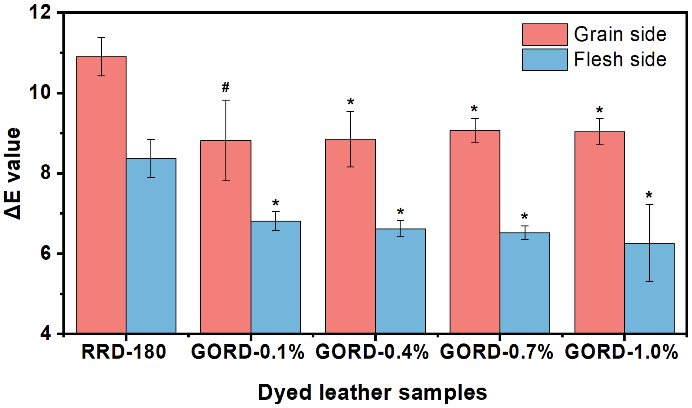

Figure 7. ΔE values of dyed leather samples after being exposed to sunlight for 24 h. The values are represented as mean ± standard deviation. $^{\#}$ represents that the data had no significant difference ($p > 0.05$), and * represents the significant difference ($p < 0.05$). RRD-180 dyed leather sample was used as the control.

compared with that of leather dyed with RRD-180. Whereas, the color fastness of leathers dyed with other GORDs had significant difference compared with that of leather dyed with RRD-180. For the flesh side, the color fastness of all the GORDs-dyed leathers had significant difference compared with that of leather dyed with RRD-180. This suggested that the GO, evenly dispersed on the surface of the samples, was capable of improving the color fastness to sunlight of the leather samples. This was because the GO fragments in the GORD had the potential to absorb and reflect some of the neutrons to lower the photons absorbed by dye molecules.[29] As a result, the dyed leather showed better fastness to sunlight. The above results illustrated the success of preparing a composite dye with UV-shielding ability, which improved the color fastness of dyed leather to sunlight.

Conclusions

Graphene oxide modified Reactive Red-180 (GORD) was prepared and used in the dyeing of biomass-derived aldehyde-tanned chrome-free leather in this work. The thermal properties, uptake ratio, shrinkage temperature, and sunlight fastness of GORD with different graphene oxide (GO) contents were investigated. The successful synthesis of GORD was demonstrated using IR analysis, UV analysis, and end-amino content testing. The introduction of GO was found to reduce the heat resistance of the GORD by TGA, due to the presence of more unstable functional groups on the GO. The application experiment suggested that the GO modification did not negatively affect the dye uptake ratio and the shrinkage temperature of dyed leather. Importantly, the sunlight fastness of the GORD-dyed leather was improved, which indicated that the GORD had UV-shielding ability and could improve the weathering performance of the dyed leather. This work further explores the application scope of GO, which is beneficial for the industrialization of GO and GO-based materials.

Acknowledgments

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