Bio-Based Surface Modification of Wool Fibers by Chitosan-Graphene Quantum Dots Nanocomposites

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ABSTRACT: *Wool proteins have various chemical active groups which could create chemical reactions and bonds with functional groups existent in different substances. Hence, to have special features and competencies, one could perform surface modification of wool fibers using various chemical composites. This paper aims mainly to achieve surface modification of wool fibers by chitosan-nitrogen doped graphene quantum dots (Ch-NGQDs) as bio-based nanocomposites, and to investigate its consequent effects on the various properties of wool fibers such as color fastness, colorimetric parameters, and antibacterial activities. To do this, first, Ch-NGQDs nanocomposites were synthesized including certain weight percentages. Then, wool fibers were modified by prepared nanocomposites. In order to characterize and confirm the synthesis of NGQDs and Ch-NGQDs nanocomposites, FT-IR, XRD, HR-TEM, UV-Visible, and photoluminescence spectrometry were applied. Subsequently, surface modification of wool fibers by Ch-NGQDs nanocomposites was studied using FESEM spectrometry, analysis of fastness properties, colorimetric parameters, and Mueller-Hinton broth antibacterial test. Findings showed that surface modification of wool fibers by Ch-NGQDs nanocomposites led to partial improvement in their color fastness and colorimetric parameters. Additionally, surface modification of wool fibers resulted in the elimination of Staphylococcus aureus bacteria.*

KEYWORDS: *Graphene quantum dots, Chitosan, Wool fibers, Surface modification, Antibacterial properties.*

INTRODUCTION

Graphene quantum dots are formed of one or more layers. These particles are less than 20 nanometers in diameter that result from the oxidation process of carbon compounds. Because of the existence of various functional groups such as carboxyl and hydroxyl groups on the edges, these particles are soluble in water [1-2]. Using compounds like thiourea, urea, and amines in the synthesis of the graphene quantum dots, one could create nitrogen and sulfur, functional groups, on the GQDs edges [3-5]. GQDs could be prepared via pyrolysis and hydrothermal methods of carbon compounds such as citric acid, glucose, graphite, black carbon, pyrene, and so forth [6-7]. Carbon-based quantum dots along with the most important member of their chemical family, namely graphene quantum dots due to their unique features are used in various industries including semiconductors, diodes, solar cells, and bioimaging [8-10]. These nanoparticles are an appropriate candidate for biological applications owing to their solubility in water, ignorable toxicity, low cost, easy preparation, biocompatibility, and simple way of functionalizing GQDs.

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So, the use of these compounds in the pharmacology and production of antibiotic substances, drug carriers, and any related applications has drawn the attention of recent research [11-14]. Carbon Dots (CDs) and GQDs include antibacterial properties by reacting with bacteria and destroying their cell walls. According to reports, encountering various bacteria, GQDs show selective antibacterial effects [15-16].

Staphylococcus aureus (gram-positive) is regarded as an infective bacterium that leads the skin, nose, and respiratory system to be infectious. These bacteria can easily multiply on various textiles and cause kinds of diseases [17].

Chitosan is the second biopolymer after cellulose because of properties such as being non-poisonous, biodegradable, absorbability on surfaces, thermal and chemical resistance, also antibacterial and antifungal effects is a positive material for scientific processes and engineering applications [18-19].

The presence of hydroxyl and amino groups in the structure of chitosan allows it to be chemically modified in order to control the physical features. The formation of chemical bonds between chitosan and carbon substances such as graphene, graphite, and GQDs can create different nanocomposites which have better properties compared to pure polymer. To improve the feature of dye absorption, decrease the matting of wool fibers, and create an antimicrobial property in fibers, chitosan is used. The composition of chitosan with GQDs could produce a soluble polymer in water possessing a strong antimicrobial feature, and consequently eliminates kinds of bacteria [17-20].

Wool is a basic substance in the textile industry has been used by human beings to prepare clothes for a long time. Wool proteins are formed by different amino acids and their structure includes various chemical active groups like carboxyl and amino groups which could chemically react and bond with functional groups existent in various organic and inorganic materials [21-22]. Overall, there have been several ways to perform in the textile industry for surface chemical modification in order to have better efficiency and improved properties. Surface modification of wool fibers by organic compounds, polymers, biopolymers [23-24], nanoparticles, and nanocomposites could improve the chemical and physical features of fibers such as chromaticity mechanical properties, resistance against flames, color fastness, antibacterial activities and et cetera [25-26]. The textile industry is considered one of the industries concerned with individual health for every age and social group. Wool textile is a good place for microorganisms' accumulation and growth especially if they are in contact with the body under suitable temperature and humidity [27]. The purpose of giving the textiles an antibacterial feature is to protect them against the negative impacts of microbes and fungi. The usage of the right chemical compound can prevent microbes from accumulating and growing. In other words, it causes an antibacterial property in various textiles like wool fibers [20,28,29].

In the present study, first, Nitrogen-Doped Graphene Quantum Dots (NGQDs) were synthesized *via* the pyrolysis method of citric acid and triethanolamine. NGQDs reacted with chitosan (Ch) to give Ch-NGQDs nanocomposites. Then, these nanocomposites were employed for the surface modification of wool fibers. Afterward, the accuracy of formation and different features of Ch-NGQDs nanocomposites, characteristics of color fastness, and colorimetric parameters of modified wool fibers were evaluated. In the end, the antibacterial effects of the synthesized nanocomposites on wool fibers were studied on the *Staphylococcus aureus (S. aureus)*.

EXPERIMENTAL SECTION

Materials

Citric acid, triethanolamine, sodium hydroxide, and acetic acid were bought from Merck company. Medium molecular weight chitosan was prepared from sigma Aldrich Co. four-fold, 200 tex wool fibers were purchased from Azarbarf company and nonionic soap was bought from Nikfam company (Iran). Dyeing of wool fibers was done by C.I. Reactive Red 195, Yellow 160, and Black 5 from Daystar company.

Tools and devices

In order to characterize functional groups of NGQDs and Ch-NGQDs nanocomposites, FT-IR spectroscopy with the aid of Thermo Nicolet Avatar 360, made in USA was used. Evaluation of crystallinity for NGQDs particles and synthesized nanocomposites was conducted using Philips PW 1730 X-Ray Diffractometer (XRD). By HR-TEM model TEC9G20, the particle diameter was measured. Analysis of the morphology of the modified wool fibers was conducted by FESEM of TESCAN MIRA3 FESEM. The optical properties of the samples were examined using UV-Vis spectrophotometer Perkin Elmer Lambda 25,

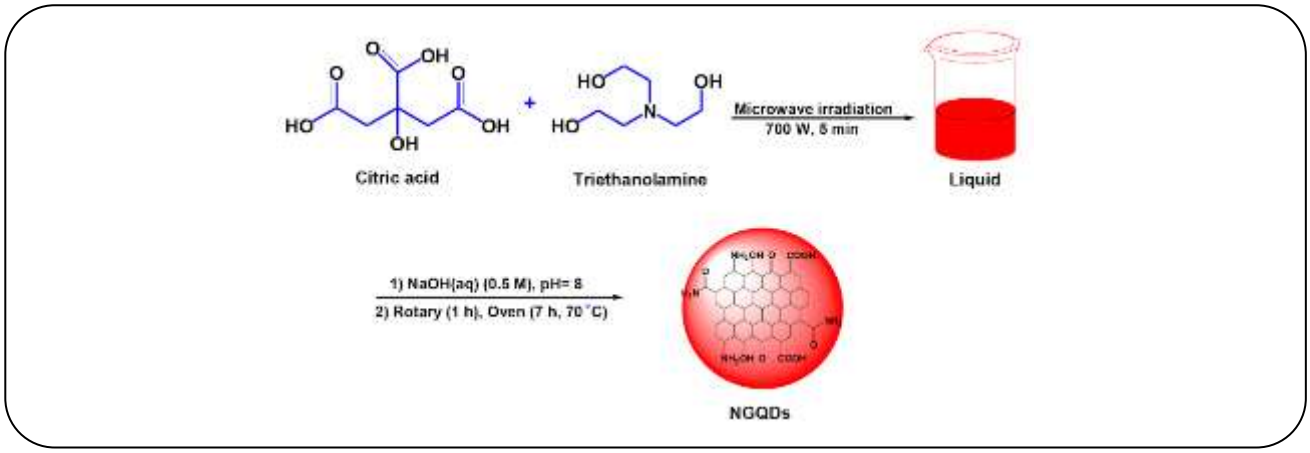

Fig. 1: Synthesis steps of NGQDs.

and photoluminescence was performed by fluorescence spectrometer Perkin Elmer LS 55.

A dyeing apparatus with hot air flow made in India and a double beam spectrometer (model CECI 9200) made in England were prepared for the dying of wool fibers. In order to modify the surface of wool fibers by Ch-NGQDs nanocomposites, Incubator 1000 made by Heidolph Co. Germany was applied. Light fastness was measured for all the samples with and without Ch-NGQDs additives and various weight percentages according to ISO 105 B02:1988 (E) using a xenon lamp. The samples were exposed to the xenon lamp for 100 hours, and to analyze the samples, light fastness with a blue scale (1-8, 1: poor, 8: excellent) was used. Washing fastness of dyed wool fibers for all the samples was conducted according to ISO 105 C06 C25:1994 (E) method. Color change of the samples was studied on the grayscale (1-5 poor and excellent light fastness) for the dyed samples. Colorimetric values (L*, a*, b*, C*, h˚) were estimated under D65 illumination with 10˚ standard observer by Color-Eye XTH, X-Rite Inc., USA spectrophotometer in the wavelength range of 400-700 nm. Antibacterial activity against *S. aureus* bacteria was examined *via* the Mueller-Hinton broth method.

Synthesis of NGQDs

NGQDs were synthesized via pyrolysis of citric acid and triethanolamine exposed to microwave radiation. Initially, a mix of 21 g citric acid, 15 g triethanolamine, and 50 mL distilled water was prepared, then, was placed in a microwave with a power of 700 W for 8 min. The prepared brown liquid of the previous step reached pH 8 by 0.5M NaOH solution. Next, this mixture was set in a rotary evaporator at 100˚C for 1 h. In the end, NGQDs were dried at 70˚C for 7 h. Fig. 1 shows the synthesis steps of NGQDs.

Preparation of Ch-NGQDs nanocomposites

First, 100 mL of distilled water was poured into each of 5 prepared beakers. Then, various quantities of chitosan (0, 0.5, 1, 1.5, and 2 g) were added to the beakers, and to achieve better solubility of chitosan in water, 1 mL acetic acid was poured into each beaker. Next, these mixtures were stirred in a magnetic stirrer for 24 hours at ambient temperature, and a chitosan solution was prepared. In the next step, varying NGQDs weights (2, 1.5, 1, 0.5, 0 g) were added to the mixtures, according to Table 1. Each mixture was separately dispersed by ultrasonic device for 30 min and then was stirred in the magnetic stirrer for 12 h. Ultimately, the mixtures were dried at ambient temperature after 3 days, and Ch-NGQDs nanocomposites including various weight percentages were prepared. Fig. 2 shows the preparation steps of Ch-NGQDs nanocomposites.

RESULTS AND DISCUSSION

Characterization of NGQDs and Ch-NGQDs

To characterize the Ch-NGQDs nanocomposites, Ch-NGQDs3 (50% NGQDs+50% chitosan) was selected because of the similar results among Ch-NGQDs nanocomposites.

FT-IR spectroscopy

Fig. 3 represents FT-IR spectra related to the NGQDs and Ch-NGQDs nanocomposite. The main absorption bands of NGQDs are pertained to the –OH (3439 cm^{-1}), -NH (3206 cm^{-1}), C-H (2880 cm^{-1}), C=O (1720 cm^{-1}), C=C

Tables 1: Composition of Ch-NGQDs nanocomposites..

Samples	Chitosan (g)	Ch-NGQDs (g)
Ch-NGQDs1	0	2
Ch-NGQDs2	0.5	1.5
Ch-NGQDs3	1	1
Ch-NGQDs4	1.5	5
Ch-NGQDs5	2	0

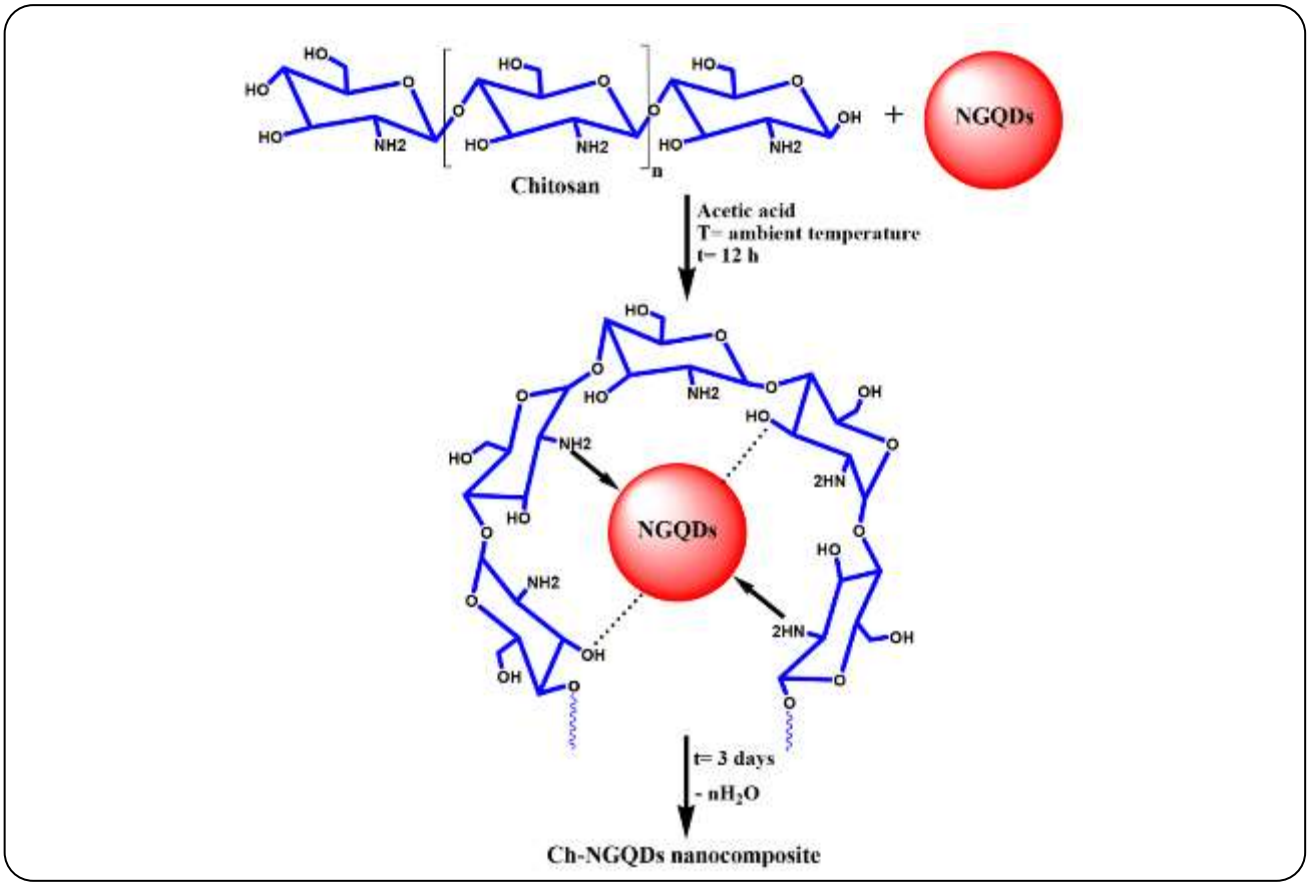

Fig. 2: Preparation steps of Ch-NGQDs nanocomposites.

stretching vibrations (1666 cm^{-1}) and -NH bending vibrations (1589 cm^{-1}) [30]. Important absorption bands of chitosan are correlated with the hydrogen bonds (3431 cm^{-1}) and C-H stretching vibrations (2890 and 2875 cm^{-1}). The observed peaks in the range of 1420-1605 cm^{-1} indicate the stretching vibrations of amide groups (amide I and amide II). C-O-C peak appeared at 1092 cm^{-1} [31]. With Ch-NGQDs nanocomposite formation, some transformations were created on the absorption bands in comparison with chitosan and NGQDs. The main absorption peaks of Ch-NGQDs nanocomposite indicates the stretching vibrations of -OH (3400 cm^{-1}), -NH (3043 cm^{-1}), C-H (2678-2900 cm^{-1}), C=O of new carbonyl, amide, and carboxyl groups (1703 and 1773 cm^{-1}) and C=C (1605 cm^{-1}) [32].

XRD analysis

The crystallinity of the structures of NGQDs and Ch-NGQDs nanocomposites was evaluated by XRD analysis. XRD spectra of NGQDs and Ch-NGQDs are represented in Fig. 4. According to Fig. 4, XRD pattern of NGQDs

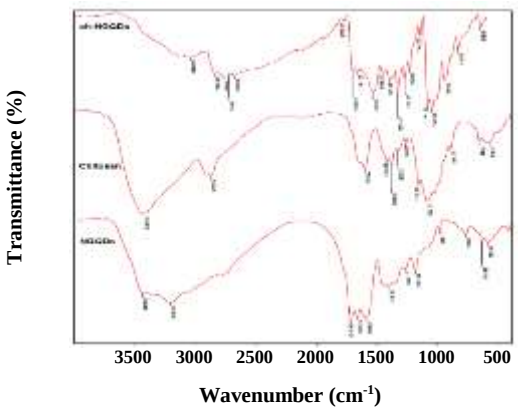

Fig. 3: FT-IR spectra of NGQDs, chitosan and Ch-NGQDs.

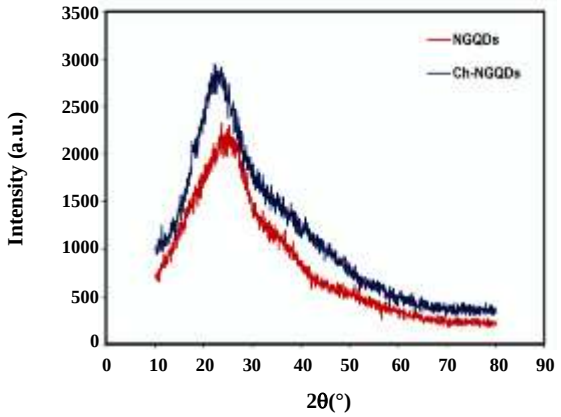

Fig. 4: XRD spectra of NGQDs and Ch-NGQDs.

shows a diffraction peak at 2θ=25.10˚, and for Ch-NGQDs, the diffraction peak is seen at 2θ=23.06˚. Additionally, the interlayer spacing of NGQDs and Ch-NGQDs are respectively 0.354 nm and 0.385 nm. The formation of strong chemical bonds between NGQDs and functional groups existent in chitosan chains leads the regular chains to be arranged together producing a crystal structure. These findings correspond to FT-IR analysis results that confirms the formation of Ch-NGQDs resulting of the chemical reaction between chitosan and NGQDs.

HR-TEM analysis

To measure the particle size of NGQDs and Ch-NGQDs soluble in water, HR-TEM was applied. HR-TEM images of NGQDs and Ch-NGQDs are represented in Fig. 5. Homogenous dispersion of NGQDs particles in water is clearly observed. Because of a surface negative charge, NGQDs are colloidal in water of which particle size is 10 to 15 nm. According to HR-TEM image 7(b), NGQDs seem to be hexagonal and similar to graphite.

Optical properties

The optical properties of NGQDs and Ch-NGQDs solutions were analyzed by UV-Visible and photoluminescence (PL) spectroscopy. Fig. 6 indicates UV-vis absorption bands. Two absorption bands are seen at about 200 and 340 nm related to NGQDs and Ch-NGQDs, these appeared peaks correspond to $\pi\rightarrow\pi^*$ transfer of C=C bonds (sp^2) and $n\rightarrow\pi^*$ transfer of C-N bonds. The intensity of this absorption in NGQDs is significantly higher than that of Ch-NGQDs relating to electron transfer and positive interactions between functional groups in NGQDs [33-34].

Photoluminescence spectra are shown in Fig. 7. Photoluminescence curves of NGQDs and Ch-NGQDs indicate excitation at 350 nm and emission peak around 455-490 nm. Intense visible radiations are caused by electron excitement of functional groups on the edges of these particles. Emission intensity is correlated with the concentration of NGQDs in the sample, so that in the Ch-NGQDs, the height of the appeared emission peak is lower than the peak of NGQDs. This approves the establishment of chemical bonds between functional groups existent in chitosan and NGQDs [35].

Surface modification of wool fibers

First, 30 g wool fibers were divided into 6 equal-weight portions and set in 6 containers. One of the portions was selected as blank (sample1) and into each of the other 5 containers, 50 mL water, 2% wf citric acid, and 5% wf Ch-NGQDs nanocomposites were added. The 5 mixtures were agitated by the magnetic stirrer for 3 hours, then shaken in Incubator for 12 hours at 50˚C. Washing and drying of the samples were performed at 60˚C. Table 2 displays the composition of each sample. Some chemical interactions between wool fibers and Ch-NGQDs nanocomposites are indicated in Fig. 8.

Dyeing

To have a uniform dyeing, first, impurities of wool fibers such as grease and wastes should be removed. In order to do this, wool fibers were washed with a nonionic soap (5% on weight fiber: owf) and sodium carbonate (3% owf) with L.R

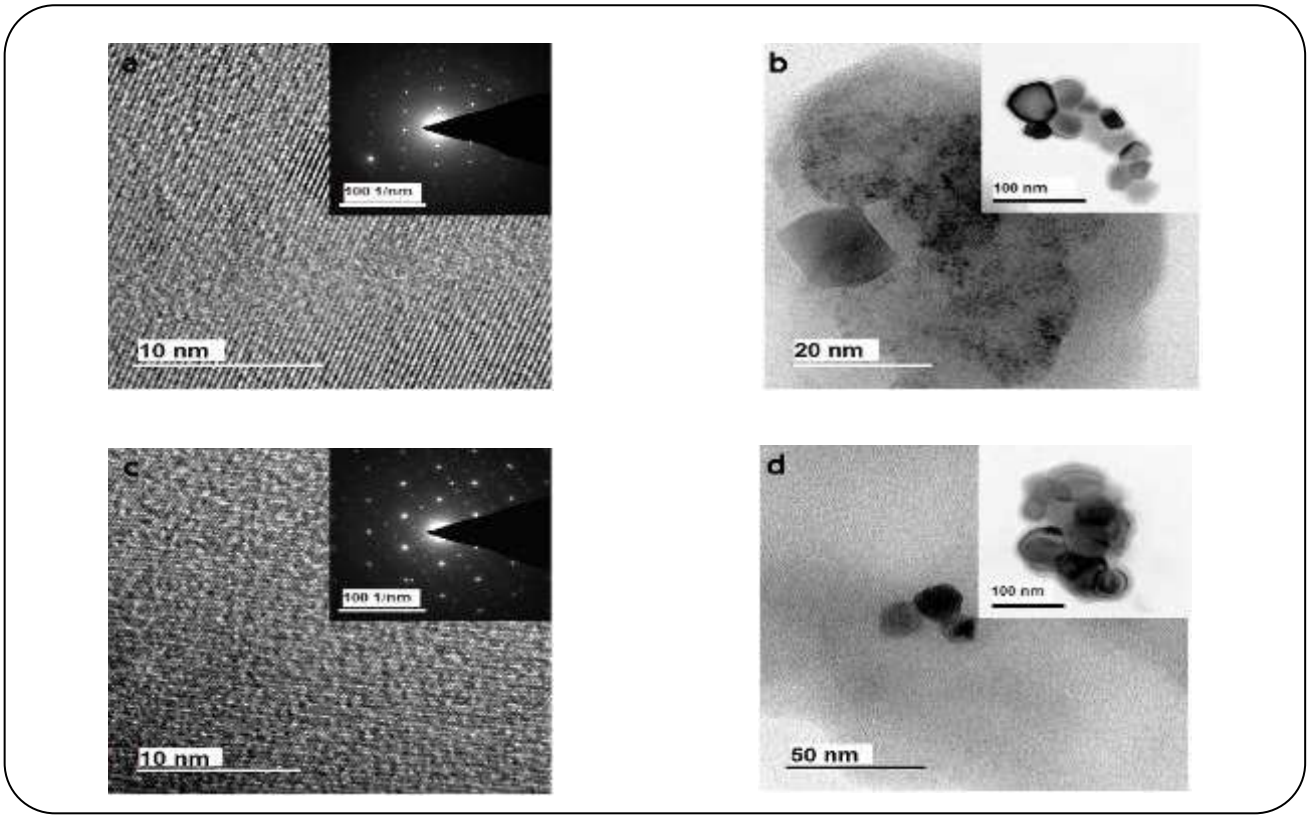

Fig. 5: HR-TEM images of: (a, b) NGQDs and (c, d) Ch-NGQDs.

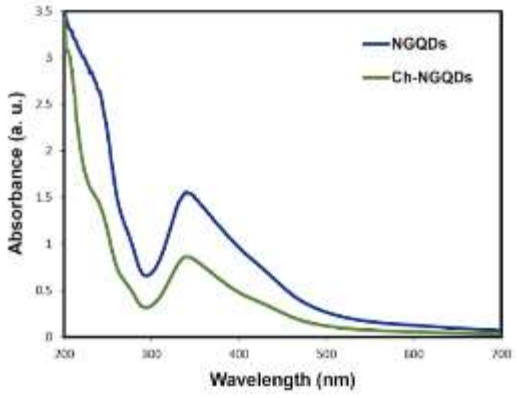

Fig. 6: UV-vis spectra of NGQDs and Ch-NGQDs.

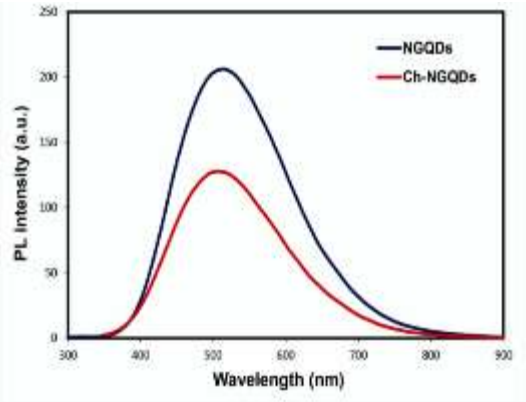

Fig. 7: PL spectra of NGQDs and Ch-NGQDs.

(liquor ratio) 50:1 at 50˚C for 40 min, then rinsed and dried. Next, 2% wf reactive dyes (C.I. Reactive Red 195, Yellow 160, and Black 5) were used to dye the blank and modified wool fibers at pH 4 with L.R 1:20. By a laboratory dyeing machine, at 95˚C the samples were dyed for 45 min. In the end, wool fibers were taken out of the machine, then rinsed and dried at ambient temperature.

FESEM analysis

To confirm the distribution and linkage of Ch-NGQDs onto the modified wool fibers, FESEM analysis was used. Fig. 9 represents FESEM images of unmodified (blank) and modified wool fibers containing Ch-NGQDs nanocomposites. The difference between the morphology of the blank and modified wool fibers is clearly observable in Fig. 9. The blank

Tables 2: Composition of blank (unmodified) and modified samples.

Samples	Wool fibers (g)	Ch-NGQDs (g)	Ch-NGQDs nanocomposites
1	5	0	-
2	5	0.25	Ch-NGQDs1
3	5	0.25	Ch-NGQDs2
4	5	0.25	Ch-NGQDs3
5	5	0.25	Ch-NGQDs4
6	5	0.25	Ch-NGQDs5

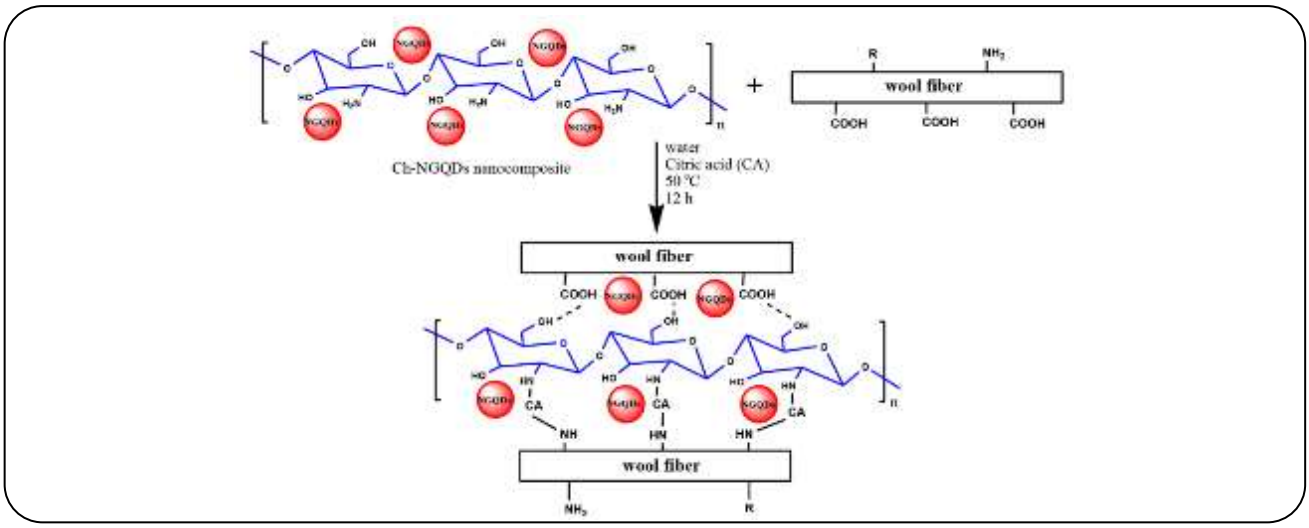

Fig. 8: Chemical interactions between wool fibers and Ch-NGQDs nanocomposites.

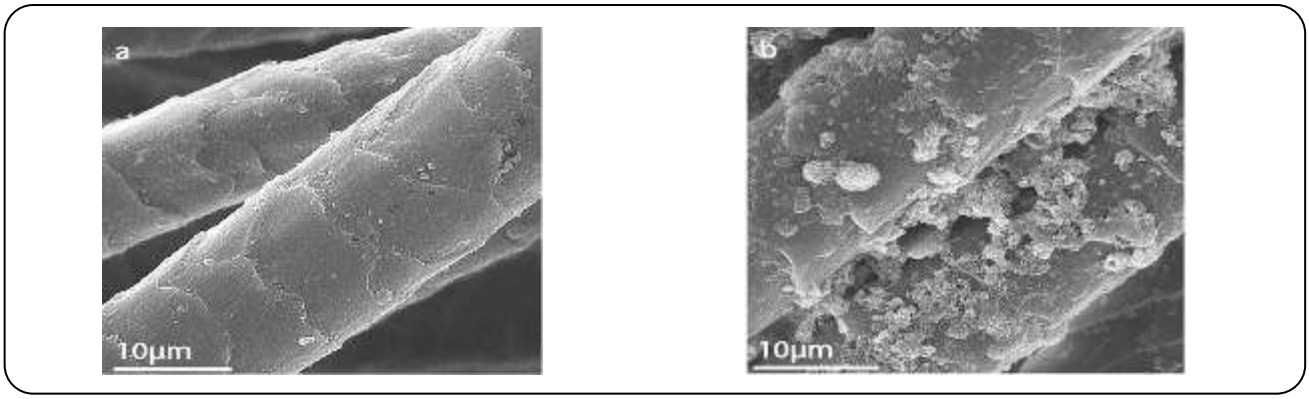

Fig. 9: FESEM images of (a) blank and (b) modified wool fibers.

shows a surface with no extra particles, whereas the surface of the modified samples includes extra particles connected to the wool fibers. The white and prominent points seen on the modified fibers are indicative of Ch-NGQDs nanocomposites distribution on the wool fibers and creation of chemical bonds between functional groups of these particles and wool fibers.

Colorfastness

Table 3 represents color fastness values for the dyed wool fibers. The findings of the washing fastness test proved that modification of wool fibers using Ch-NGQDs nanocomposites had no negative impact on dye change of fibers and the recorded numeral values for the samples are acceptable (4), additionally, the washing fastness

Table 3: Color fastness of dyed wool fibers (blank and modified fibers).

Fastness	Ch-NGQDs1	Ch-NGQDs2	Ch-NGQDs3	Ch-NGQDs4	Ch-NGQDs5	Ch-NGQDs6
Lightfastness	6	6	6-7	6	6-7	6
Washing fastness	4	4	4-5	4	4-5	4

Table 4: Colorimetric data of dyed wool fibers (blank and modified fibers).

Samples	L*	a*	b*	C*	h°	K/S	ΔE
1	18.45	9.32	8.24	12.44	41.48	29.12	2.10
2	18.24	9.11	7.66	11.90	40.06	28.94	2.51
3	18.42	9.16	8.97	12.82	44.40	31.02	1.66
4	18.86	10.07	9.34	13,73	42.84	30.34	3.45
5	19.48	9.21	8.00	12.20	40.97	25.74	0.47
6	18.87	9.50	9.06	13.12	43.63	29.35	1.37

for the samples 3 and 5 are 4 to 5 which is considered a very good result.

Results from light fastness for the samples indicated that modification of dyed wool fibers by Ch-NGQDs nanocomposites led to proper light fastness against radiative lights. The recorded light fastness values are in the range of "good" to "very good" (6-7). Accordingly, one could conclude that modification of dyed wool fibers by NGQDs-based nanocomposites not only had no negative impact on light and washing fastness but also caused a partial improvement of fastness in some samples.

The reason behind this is an increase in the creation of chemical bonds between active groups existent in protein chains of wool fibers and Ch-NGQDs nanocomposites. It is worth mentioning that through suitable additives, environmental conditions, and tools such as microwave radiation, acceptable color fastness could be achieved [36-37]. Modification of wool fibers using Ch-NGQDs nanocomposites, in addition to the change of physical properties of fibers, causes a higher color depth and improved color fastness of the substance at the same time. It is worth mentioning that chromophores are protected from photolysis by adding nanocomposites that lead to the light fastness increase.

Colorimetric data

Color specifications of the dyed samples (L*, a*, b*, C*, h°) are reported in CIELAB color system. L* is variable in the range of 0-100 indicating the lightness grade of the samples. A lower L* value is a sign of dark-dyed samples. a* indicates a point across the green-to-red axis, and b* shows a change from blue to yellow colors. C* stands for the color chroma of the samples, h° represents the hue angle, and K/S values pertain to the color strength of the samples. Table 4 indicates colorimetric data for the blank and modified wool fibers by Ch-NGQDs nanocomposites. Adding Ch-NGQDs nanocomposites to the wool fibers, compared to sample 1, led to a little alteration in colorimetric values and no considerable differences in lightness, redness, and yellowness of the samples, according to Table 3. In some samples, L* (lightness), a* (redness), and b* (yellowness) values are partially changed. These changes vary depending on the chitosan and NGQDs concentration. Furthermore, a difference in ΔE values for modified samples is acceptable in comparison with unmodified samples [38]. These data correspond to K/S values. The acceptable and relatively low color difference between modified and unmodified wool fibers approves that there is no significant change in the color shade of the modified fibers following the modification of them by Ch-NGQDs nanocomposites. In other words, the modification of wool fibers has no negative impact on the dyed fibers. Hence, not only does wool fibers modification by Ch-NGQDs nanocomposites doesn't change the color of wool fibers remarkably, but leads to a partial improvement in some colorimetric features.

Antibacterial properties of wool fibers

To perform an antibacterial test against *S. aureus* bacteria, the Mueller-Hinton broth method was used. Accordingly, 1 mL

Table 5: The antibacterial activities of blank and modified wool fibers by Ch-NGQDs nanocomposites against S. aureus bacteria.

Samples	Modified wool fibers by (5% owf)	Reduction (%) S. aureus
1	-	0
2	Ch-NGQDs1	82
3	Ch-NGQDs2	91
4	Ch-NGQDs3	99
5	Ch-NGQDs4	96
6	Ch-NGQDs5	85

a bacterium with 10^6-10^7 CFU/mL concentration was cultivated. In the next step, all 6 samples were incubated at 37˚C for 24 h. Then, 100 µL of each sample was separately spread on agar plates. After 24 h, the plates were taken out of the incubator and the surviving bacteria were counted. Eq (1) represents the bacteria reduction rate:

$$\%R = \frac{B - A}{B} \times 100 \quad (1)$$

Stands for the survived bacteria (CFU/mL) on the modified wool fibers (samples 2-6), and B shows the survived cells on sample 1 (blank). In order to ascertain the tests, all of them were performed 3 times. Findings of antibacterial tests approved that about 80-99% of S. aureus were killed following the adding Ch-NGQDs nanocomposites to wool fibers. Sample 4 indicated the highest antibacterial effect. These findings are shown in Table 5. The results of this experiment prove that the nanocomposites resulting from the combination of chitosan and NGQDs could be used in wool fibers as a strong antibacterial substance. Additionally, NGQDs revealed antibacterial activity to kill the *S. aureus* bacteria even by itself and without chitosan (sample 2).

CONCLUSIONS

The present study signifies an unparalleled surface modification of wool fibers by Ch-NGQDs nanocomposites. To do this, first, NGQDs were synthesized via pyrolysis of citric acid and triethanolamine. Next, Ch-NGQDs nanocomposites including varying weight percentages were prepared and their formation of them was approved and analyzed using spectroscopic instruments and methods. Then, wool fibers were modified by Ch-NGQDs nanocomposites. At last, fastness properties, colorimetric values, and developed antibacterial features were evaluated. Findings proved that modification of wool fibers by synthesized nanocomposites not only caused remarkable changes in the various characteristics of wool fibers but also led to a partial improvement in optical and light fastness, as well as some colorimetric values. Moreover, the modification of wool fibers by prepared nanocomposites caused the *S. aureus* bacteria elimination. It is worth mentioning that synthesized nanocomposites of graphene quantum dots and chitosan biopolymers could create durable bonds with wool fibers due to the functional groups present on their surface that offer an affordable and a bio-based way for surface modification of wool fibers.

Declaration of Conflicting Interests

No declaration was reported by the author(s) related to conflicts of interest.

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