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ULTRABINAFSHA SPEKTROSKOPIYA YORDAMIDA sS-rGO NANOKOMPOZITI HOSIL BO‘LISHINI TAHLIL QILISH

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Annotatsiya. Ushbu tadqiqotning maqsadi seritsin va grafen oksidi asosida nanokompozit sintez qilish hamda uning hosil bo‘lish jarayonini ultrabinafsha-ko‘rinadigan (UB) spektroskopiya yordamida baholashdan iborat. Tadqiqot davomida seritsin, grafen oksidi va seritsin–grafen oksidi nanokompozitining UB- yutilish spektrlari o‘rganildi hamda ularning yutilish maksimumlari, optik zichliklari va spektral profillaridagi o‘zgarishlar bo‘yicha qiyosiy tahlil o‘tkazildi. Olingan natijalar asosida komponentlar o‘rtasidagi o‘zaro ta’sirning spektroskopik belgilari aniqlandi va seritsin–grafen oksidi nanokompozitining hosil bo‘lishi baholandi.

Kalit so‘zlar: ipak tolasi chiqindilari, seritsin, grafen oksidi, nanokompozit, ultrabinafsha spektroskopiya.

Аннотация. Целью данного исследования является синтез нанокompозита на основе серицина и оксида графена, а также оценка процесса его образования с помощью ультрафиолетовой и видимой (УФ) спектроскопии. В ходе работы были изучены спектры поглощения серицина, оксида графена и нанокompозита «серицин — оксид графена» в УФ- и видимом диапазонах, а также проведен сравнительный анализ их максимумов поглощения, оптической плотности и изменений спектральных профилей. На основе полученных результатов выявлены спектроскопические признаки

взаимодействия между компонентами и дана оценка образования нанокompозита «серицин — оксид графена».

Ключевые слова: отходы шелкового волокна, серицин, оксид графена, нанокompозит, ультрафиолетовая спектроскопия.

Abstract. The aim of this study is to synthesize a nanocomposite based on sericin and graphene oxide and to evaluate its formation using ultraviolet-visible (UV-Vis) spectroscopy. During the study, the UV-Vis absorption spectra of sericin, graphene oxide, and the sericin–graphene oxide nanocomposite were investigated, and a comparative analysis was conducted regarding their absorption maxima, optical densities, and changes in spectral profiles. Based on the obtained results, the spectroscopic signatures of the interaction between the components are identified, and the formation of the sericin–graphene oxide nanocomposite is evaluated.

Keywords: silk fiber waste, sericin, graphene oxide, nanocomposite, ultraviolet spectroscopy.

1. INTRODUCTION

In recent years, the creation of novel functional nanocomposite materials by combining natural biopolymers and carbon-based nanomaterials has emerged as a promising direction in modern materials science. In such systems, the biocompatibility, biodegradability, and abundance of functional groups characteristic of biopolymers are combined with the high specific surface area, good dispersibility, and advanced surface chemistry of graphene oxide (GO). Consequently, composite materials possessing physicochemical and functional properties distinct from those of the individual components can be formed. For this reason, protein–graphene oxide-based nanocomposites are being actively investigated in fields such as biomedicine, drug delivery, tissue engineering, and environmental technologies [1–3].

II. LITERATURE REVIEW

Sericin is a water-soluble natural protein that surrounds the fibroin fibers within silk; its molecular structure contains polar functional groups associated with serine, aspartate, glycine, and other amino acids. In particular, the presence of hydroxyl, amino, and carboxyl groups enables sericin to form hydrogen bonds and other intermolecular interactions with various molecules and nanomaterials. Sericin’s high hydrophilicity, biocompatibility, bioactivity, and abundance of functional groups make it a promising biomaterial for the production of biocomposites and nanostructured materials [4,5].

Graphene oxide (GO) is a carbon-based nanomaterial with a two-dimensional layered structure, obtained through the chemical oxidation of graphite. The presence of oxygen-containing functional groups—such as hydroxyl, epoxide, and carboxyl groups—on the carbon backbone of GO enhances its hydrophilicity and dispersibility in aqueous media. Furthermore, the high surface area of GO creates favorable conditions for the adsorption of protein molecules onto its surface and facilitates various intermolecular interactions. These properties enable the use of GO as an effective nanofiller for creating nanocomposites with proteins, polymers, and other biological materials [6,7].

Combining sericin and graphene oxide (GO) makes it possible to integrate the functional properties of the biopolymer with the advanced nanostructured surface characteristics of GO into a single system. In a study conducted by Vedakumari et al., a sericin-modified graphene oxide nanocomposite was successfully synthesized, and its physicochemical and biological properties were investigated. The authors demonstrated the formation of a new composite system resulting from the attachment of sericin molecules to the GO surface. This study represents a significant scientific contribution that directly confirms the potential of the sericin-GO system to form a stable nanocomposite material [8].

The interactions between sericin and graphene oxide are primarily attributable to their functional groups. Hydroxyl, amino, and carboxyl groups within sericin can form hydrogen bonds and electrostatic interactions with the epoxide, hydroxyl, and carboxyl groups on the GO surface. Such intermolecular interactions influence the dispersibility, structural stability, and surface properties of the nanocomposite. Research has also noted that the interaction of sericin derivatives with graphene-based materials can alter the structural arrangement of carbon layers and modify the material's functional properties [8, 9].

The functional properties of materials based on sericin and graphene oxide have also been investigated in other multi-component composite systems. Jiang and colleagues developed an injectable nanocomposite hydrogel based on alginate, sericin, and graphene oxide, and studied its structural, mechanical, and biological properties. The research results demonstrated that the combined use of sericin and GO can enhance the functional properties of the composite material. Subsequent studies involved the development of multi-component hydrogels based on sericin, GO, and nano-hydroxyapatite, with a comprehensive evaluation of their structural and biological properties [10,11].

Spectroscopic methods play a crucial role in investigating the nanocomposite formation process. In particular, ultraviolet-visible (UV-Vis) spectroscopy is a rapid instrumental technique used to study optical absorption processes associated with transitions between the electronic states of substances. This method allows for the comparison of the composite material's spectrum with the absorption spectra of individual components, as well as the identification of changes in the position and intensity of absorption maxima. Such spectral changes can provide preliminary information regarding the interactions between components and the composite formation process [8,12].

Investigating the sericin-graphene oxide nanocomposite using UV-Vis spectroscopy is particularly important because the individual components of this system possess characteristic optical absorption properties. Vedakumari and colleagues utilized UV-Vis spectroscopy to study the sericin-modified graphene oxide nanocomposite and compared the optical properties of the composite material with the spectral characteristics of the individual components. These results demonstrate that UV-Vis spectroscopy can be employed for the preliminary assessment of the formation of the sericin-GO system [8].

At the same time, a significant portion of existing scientific literature focuses on investigating the biological, morphological, mechanical, and adsorption properties of materials based on sericin and graphene oxide. A comparative study of the spectra of sericin, graphene oxide, and their nanocomposite—specifically analyzing the spectral changes

observed via UV–Vis spectroscopy—provides additional scientific insight into the formation mechanism of this system.

3. Research methodology

Natural sericin protein was used as the biopolymer matrix in the study. Sericin was extracted during the silk fiber degumming process, then purified and dried under laboratory conditions. The purified sericin served as the primary polymer component in subsequent experiments. A graphene oxide (GO) dispersion was used as the nanofiller. Analytical-grade ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) reagent was employed to create an alkaline environment during the synthesis process. Distilled water served as the reaction medium.

The SS-rGO nanocomposite was synthesized using a condensation method. Initially, a 1% (w/v) aqueous solution of sericin protein was prepared. The purified sericin was mixed with the required amount of distilled water using a magnetic stirrer until completely dissolved. An aqueous dispersion of graphene oxide was prepared in a separate vessel. Subsequently, the sericin solution and the graphene oxide dispersion were mixed at a mass ratio of 1:0.5.

The reaction was carried out via the condensation method at a temperature range of 85–100°C.

Upon completion of the reaction, the resulting composite was cooled to room temperature and dried until a constant mass was achieved. The dried sample was then prepared for subsequent physicochemical analyses.

4. Analysis and results

To prepare the nanocomposite material, a sericin solution and a graphene oxide dispersion were mixed at a mass ratio of 1:0.5. This ratio was selected to ensure the uniform distribution of graphene oxide particles within the sericin matrix and to enhance the structural stability of the nanocomposite. Ammonium carbonate was added to the reaction mixture because the composite formation was carried out in an alkaline medium. The alkaline environment enhances the activation of functional groups in sericin molecules, facilitating the formation of hydrogen bonds and other intermolecular interactions with graphene oxide. UV spectra of the obtained material were recorded using a Shimadzu 1800 instrument (Japan).

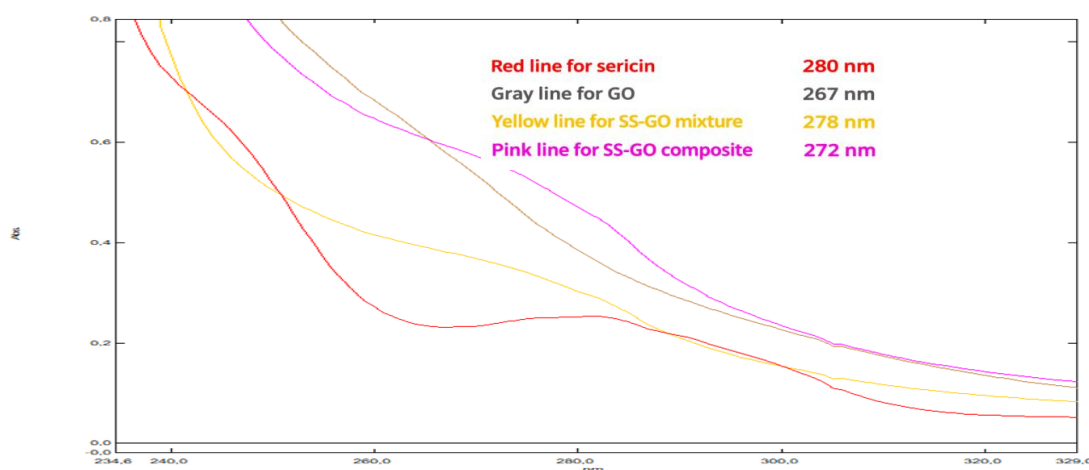


Figure 1. UV–Vis spectrum of the SS-rGO nanocomposite.

UV–Vis spectroscopy is a widely used physicochemical method for evaluating the electronic structure of polymer and nanocomposite materials, interactions between functional groups, and the nanocomposite formation process. In particular, changes in the wavelength and intensity of electronic transitions in protein-polymer and graphene-based nanomaterials allow for the identification of intermolecular bond formation.

UV spectrum of sericin. As shown in the graph, the main absorption maximum for sericin (red line) is observed at 280 nm. This maximum is primarily associated with $\pi \rightarrow \pi^*$ electronic transitions of aromatic amino acids—such as tyrosine, tryptophan, and phenylalanine—present in sericin and serves as a characteristic spectral feature of protein molecules. Additionally, $n \rightarrow \pi^*$ electronic transitions of carbonyl fragments in amide groups contribute to some extent to absorption in this region (13).

UV spectrum of graphene oxide. For the graphene oxide (GO) sample, a maximum was observed at 267 nm. Conjugated C=C bonds present in the sp^2 -hybridized carbon domains of GO give rise to $\pi \rightarrow \pi^*$ electronic transitions. At the same time, oxygen-containing functional groups (–OH, –COOH, and epoxy groups) reduce the degree of conjugation in the electronic system; consequently, the maximum is observed at a shorter wavelength compared to pure graphene (14).

Analysis of the SS+GO physical mixture. In the physical mixture of sericin and GO, the maximum shifted to 278 nm. This indicates the presence of a certain level of intermolecular interactions between the components, including hydrogen bonds, van der Waals forces, and electrostatic attractions. However, the overall spectral profile closely resembles a superposition of the individual component spectra, showing no evidence of strong chemical bonding or the formation of a new electronic system. Therefore, this sample is characterized as a system dominated by physical adsorption (6, 15).

UV spectrum of the SS-rGO nanocomposite. The observation of a peak at 272 nm in the SS-rGO nanocomposite indicates the formation of strong interfacial interactions between sericin and graphene oxide. The shift of the characteristic sericin peak from 280 nm to 272 nm represents a hypsochromic (blue) shift. Such a shift is attributed to the redistribution of electron clouds and an increase in electron transition energy. The primary cause of this hypsochromic shift is the formation of strong hydrogen bonds between the amide (–CONH–), amino (–NH₂), and hydroxyl (–OH) groups of the sericin macromolecule and the carboxyl and hydroxyl groups on the graphene oxide surface. Consequently, the electron density in the amide groups decreases, and the energy required for electron transition increases. Furthermore, π – π stacking interactions may occur between the aromatic sp^2 planes of graphene oxide and the aromatic amino acids in sericin. This interaction alters electron delocalization, leading to a shift of the UV spectral peak toward shorter wavelengths (6, 15).

The relationship between electron transition energy and wavelength is described by the expression:

$$E = hc/\lambda$$

Therefore, the shift of the peak from 280 nm to 272 nm indicates an increase in electron transition energy and the formation of new interfacial electronic states within the nanocomposite (16).

Conclusion.

UV–Vis spectroscopic results confirm the existence of strong intermolecular interactions between sericin and graphene oxide. The hypsochromic shift of the characteristic sericin peak from 280 nm to 272 nm indicates the formation of hydrogen bonds and π – π stacking interactions between the amide groups and the oxygen-containing functional groups of graphene oxide. In contrast, the retention of the peak at 278 nm in the physical mixture suggests that primarily physical adsorption occurred. Thus, the UV spectral results suggest the successful synthesis of the SS-rGO nanocomposite and the stable immobilization of sericin macromolecules onto the graphene oxide surface.

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