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Heat Treatment of Graphene Oxide/Thiourea Mixture in the Solid State and Application for Detection of Uric acid and pH Sensing

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Abstract

The heat treatment of the graphene oxide/ thiourea mixture was done by the tube furnace equipped with an argon inlet. The graphene oxide/ thiourea sample was characterized by UV–visible spectrometry, Thermogravimetric analysis, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The UV–vis absorption spectra of graphene oxide was shown the characteristic absorbance of graphene oxide, and the Fourier transform infrared spectra showed carboxylic acid group and thiocyanate on the surface of graphene oxide/thiourea. The deconvolution of X-ray photoelectron spectra showed the sulfur and nitrogen on the surface of graphene oxide. The peak area, the percent of carbon, oxygen, nitrogen, and sulfur of modified graphene oxide based on Scofield's relative sensitivity factor (RSF), was 73, 16, 7, and 4, respectively. The fluorescence measurements of the modified graphene oxide suspension in the different pH were investigated. The alkaline solution showed the most emission intensity. The sample was shown good interaction with uric acid in the alkaline solution compared to other substances, including thiamin, nicotinamide, urea, ascorbic acid, glucose, and lauric acid, based on fluorescence spectroscopy.

Keywords: Modified graphene oxide, Fluorescence quenching, FRET mechanism, Ammonium thiocyanate.

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Introduction

Nowadays, graphene as a new carbon nanostructure has been considered a unique material [1]. The two-dimensional structure of graphene and its special characteristics, such as electronic, optical, thermal, mechanical, and chemical properties, cause to it has attracted the attention of researchers [2- 4]. So, it has been examined in many fields [5]. Graphene oxide is the significant derivative of graphene obtained by the chemical oxidation of graphene layers of graphite [1, 6]. The oxygen-containing groups and sp^2/sp^3 hybridized domains of the graphene oxide structure lead to unique optical properties such as fluorescence emission [7, 8]. So, graphene oxide was examined as a fluorophore with fluorescence emission and a highly efficient quencher for fluorescence-based detection of a wide range of samples [9]. However, graphene oxide showed low emission efficiency that was established which oxygen group of graphene oxide, lead to a nonradiative path to come back excited electron to ground state [10]. Hence, different chemical treatment was investigated for functionalizing graphene oxide with various functional group to modify this problem, for example, fluorination [10], amine [11], AgInZnS [12], nitrogen groups [13], azo-pyridine [14], cobalt porphyrin [15], manganese [16], serine, histidine [17], and ethylenediamine [18].

Besides solution-based methods for functionalizing graphene oxide, other techniques, including, arc-discharge, chemical vapor deposition, and thermal annealing in the presence of reagents, were applied [19]. The solid-state reaction is an eco-friendly method because of solvent-free it was used to produce different products by scientists many years ago [20]. The different reagent, such as urea and ammonia, was tested by the thermal solid-state method for doping nitrogen in the graphene oxide [21]. Different types of materials were applied for pH sensing based on fluorescence spectroscopy, such as hydrogel-based optical fiber, fluorescent dye in the polymer matrix, congo red dye on agarose membranes, and rhodamine-based sensor [22]. The hydroxyl and carboxylic groups on the surface of graphene oxide cause to use for sensing pH in different research [23].

Uric acid is an antioxidant in human biological fluids and a slight change in the amount of it causes health problems [24]. So, the determination of uric acid is essential, and various analytical methods and materials were investigated to detect it. The photoluminescence properties of carbon-based materials cause us to examine them for detecting uric acid based on fluorescence spectroscopy [25-26]. Thiourea was applied to reduce graphene oxide to graphene in solution by some researchers [27-29]. In this work, the solid-state treatment of graphene oxide with thiourea was investigated by the tube furnace equipped with an argon inlet. The graphene oxide/ thiourea was characterized by FT-IR and X-ray photoelectron spectroscopy spectrum (XPS). The fluorescence emission of the modified graphene oxide was examined at different pH. The interaction of modified graphene oxide suspension with substances, including thiamin, nicotinamide, urea, ascorbic acid, glucose, and lauric acid, was examined by fluorescence measurement. The uric acid showed good interaction with modified graphene oxide and decreased fluorescence emission.

Experimental

Materials

The potassium permanganate, thiourea, sulfuric acid, sodium hydroxide, sodium nitrate, lauric acid, glucose, uric acid, phosphoric acid, boric acid, and acetic acid were supplied from Merck (Germany). Graphite powder was from Dau Gen (China). The ascorbic acid, thiamin, and nicotinamide were from Damloran Razak Pharma Co. (Iran).

Instruments

The Fourier transform infrared (FT-IR) spectra, the Thermogravimetric Analysis (TGA), and the fluorescence spectra of samples were measured using Spectrum RX I (Perkin–Elmer), Thermal Analysis –TA (TGA Q50), and Cary Eclipse Agilent technology spectrophotometer, respectively. X-ray photoelectron spectroscopy spectrum (XPS) of the sample was recorded by ESCA-3400 Electron spectrometer (Shimadzu, Kyoto, Japan), which the sample was prepared by drop casting the suspension of modified graphene oxide on a cleaned silicon wafer, and it was dried at 60°C for two hours. The UV-visible spectra of the sample were taken using a Ray Leigh UV-1600 spectrometer.

Modifying graphene oxide with thiourea in solid-state

The Hummer method was applied to synthesize graphene oxide [30]. Typically, in this method, graphite powder (1 g) and sodium nitrate (1 g) were added to sulfuric acid (46 mL) concentrate in an ice bath, and the potassium permanganate (6 g) was moderately added. Then, distilled water (20 mL) and hydrogen peroxide (30%) was added to the suspension. The mixture was filtrated and washed with hydrogen chloride (0.1%) and distilled water multiple times and dried at room temperature. Next, the dried graphene oxide (0.2 g) and (0.4g) thiourea were added to the ceramic mortar, and the mixture was mixed and ground with a pestle. Afterward, the mixture was transferred to the tube furnace equipped with an argon inlet. So, it was heated at 180 °C in the presence of argon gas in the furnace for 3 hours. The remaining solid (modified graphene oxide) was cooled down and washed many times with water at room temperature.

Fluorescence experiments

The fluorescence experiments were performed in the solution containing modified graphene oxide (90 µg/ml). The Britton–Robinson buffer was used to adjust the different pH of solutions. The interaction of modified graphene oxide and the solution of (10^{-5} M) uric acid, thiamin, nicotinamide, urea, ascorbic acid, glucose, and lauric acid were investigated by fluorescence spectroscopy.

Results and discussion

Characterization of modified graphene oxide

The UV–vis absorption spectra of the graphene oxide is shown an absorption at 225 nm and a shoulder at 310 nm that is related to the π–π* electronic transition in carbon-carbon bonds and the n–π* electronic transition of non-bonding electrons of C=O band (Figure 1a) [11]. The UV–vis spectrum of modified graphene oxide also showed absorption at 225 nm, and 310 nm, which is the same as graphene oxide, and a new peak at 264 nm that can be connected to thiocyanate groups attached to the surface of graphene oxide (Figure 1.b) [31].

The Thermogravimetric Analysis curves of graphene oxide/ thiourea showed that the mass loss occurrences of graphene oxide/ thiourea at 100°C were due to water elimination, and in the range of 140- 180 °C that is because of isomerization of thiourea into ammonium thiocyanate, and over 180 °C is related to the decomposition of thiourea and ammonium thiocyanate (Figure 2) [32-33].

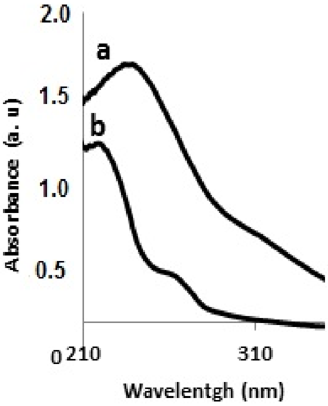

Figure 1. UV–visible absorption spectra of a) graphene oxide suspension, b) modified graphene oxide suspension.

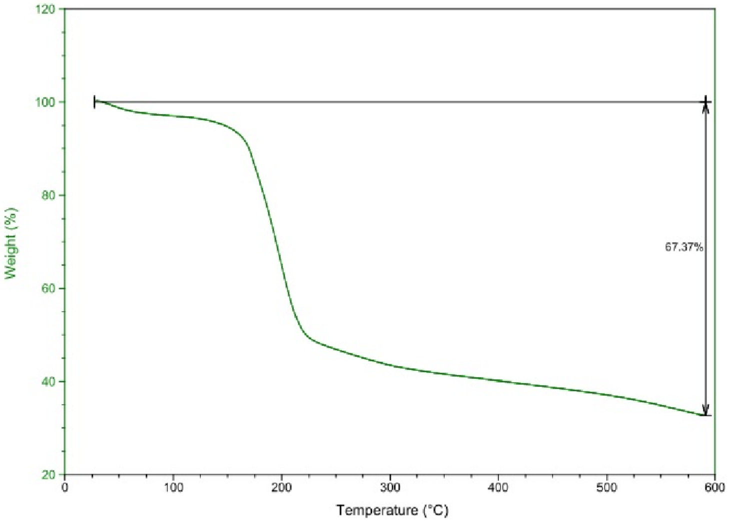

Figure 2. Thermogravimetric Analysis curves of graphene oxide/ thiourea.

FT- IR spectrum of graphene oxide showed the strong and intense peak 1735cm^{-1} that is ascribed to the stretch of the C=O band of the carboxylic acid group of GO (Figure 3, a) that it can be seen in the FT- IR spectrum of modified graphene oxide at 1740 cm^{-1} (Figure 3.b) [8]. The peak observed at about 2035 cm^{-1} can be connected to the thiocyanate (-S-C≡N) antisymmetric vibration of the ammonium thiocyanate group (Figure 3.b) [34]. So, the thiourea decomposed to ammonium thiocyanate at 180 °C based on TGA data, and the UV–vis, and FT-IR spectrum showed the peaks related to the ammonium thiocyanate group over the surface of graphene oxide.

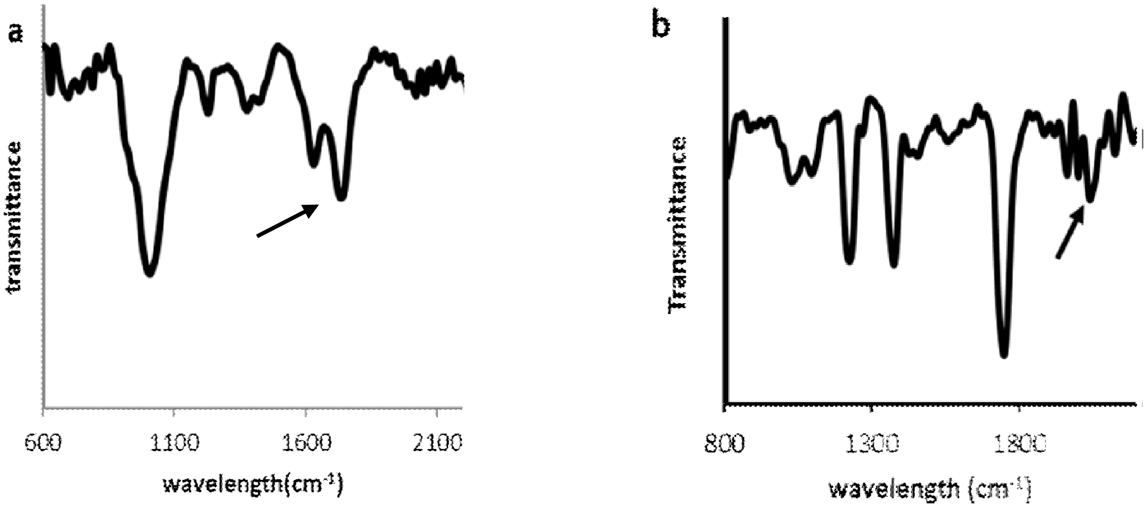

Figure 3. Fourier transform infrared spectra of a) graphene oxide, b) modified graphene oxide.

The curve fitting of the XPS spectrum peaks of modified graphene oxide was performed using a Lorentzian peak shape (Figure 4). The peaks of the C 1s deconvoluted spectrum at 258.5 eV (FMWH=0.87), 286 eV (FMWH=0.8), 287.2 eV (FMWH=0.8), and 289.3 eV (FMWH=0.8) are related sp2 hybridizes non-oxygenated carbon cycles (c-c and c = c), the carbon of N-C bond, carbonyl group, and the carboxylic group, respectively [35-37].

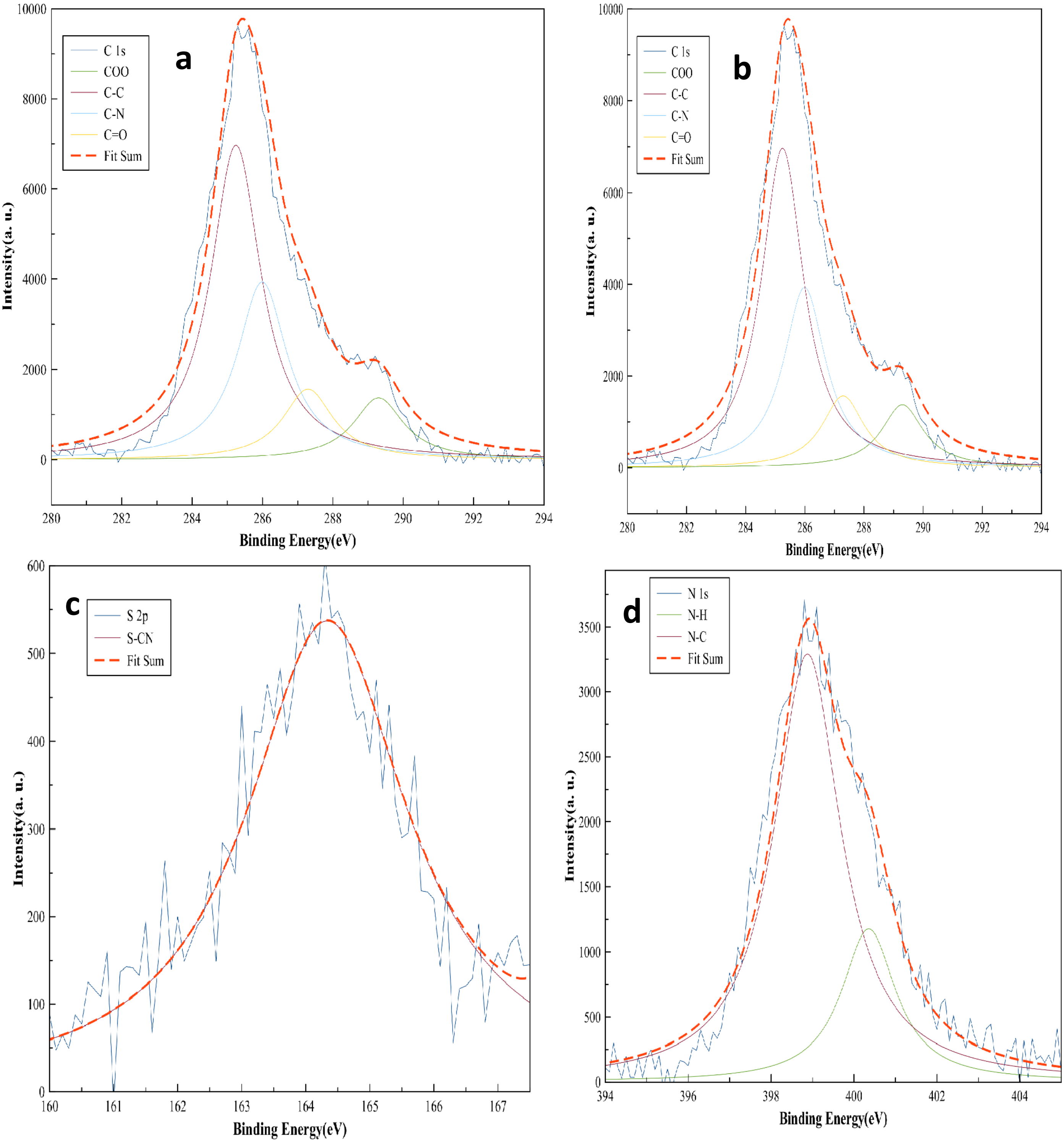

Figure 4. The deconvoluted XPS spectrum for modified graphene oxide a) C 1s, b). O 2p, c) S 2p, d) N 1s.

The peaks of O 2p deconvoluted spectrum at 532 eV (FMWH=1.1), 532.9 eV (FMWH=0.9), and 534 eV (FMWH=1.1) are attributed to the carboxylic, carbonyl and hydroxyl groups, respectively [38]. The peaks of the S 2p spectrum at 164 eV (FMWH=1.5) can be related to the thiocyanate group that attached graphene oxide. The peaks of N 1s deconvoluted spectrum at 399 eV (FMWH=0.9), and 400.5 eV (FMWH=0.9) could be related to the nitrogen of cyanide and ammoniums groups [39]. So, the thiourea produced the ammonium thiocyanate at a high temperature that it was attached to the surface of graphene oxide. Based on Scofield's relative sensitivity factor (RSF) and the measured peak areas, the percent of carbon, oxygen, nitrogen, and sulfur in the modified graphene oxide was 73, 16, 7, and 4, respectively [40-41]. Accordingly, in the following TGA, UV–vis, and FT-IR measurements, the XPS spectrum also showed that ammonium thiocyanate attached to the surface of graphene oxide (Figure 5). So, the surface of the graphene oxide was functionalized by a simple method in compression to other methods that used for functionalizing graphene oxide.

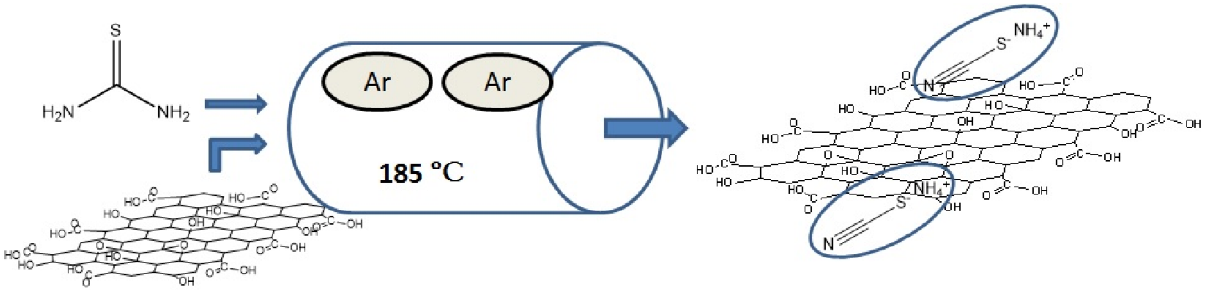

Figure 5. Schematic illustration modifying the surface of graphene oxide.

Fluorescence measurements of modified graphene oxide

The modified graphene oxide solution (90µg/ml) at an excitation wavelength of 280 nm emitted fluorescence at 376 nm (Figure 6 a). The fluorescence in the graphene oxide-based materials was emitted because of the electron-hole pairs owing to sp^2 domains in the sp^3 matrix [42]. It was established that the graphene oxide solution consists of two types of structure, including oxidized graphene-like sheets and heavily oxidized small organic fragments that the oxidized small organic fragments emitted higher intensity [43]. The fluorescence emission of modified graphene oxide at 376 nm has changed in the different pH (Figure 6.b). The intensity in the acidic solution (pH 3 and 5) was lower than neutral and alkaline pH (7, 9) which could be related to the interaction of ammonium thiocyanate with the surface of oxidized small organic fragments and the decrease of non-radiative relaxation paths induced by surface passivation of ammonium thiocyanate in the natural and alkaline solution [44-45].

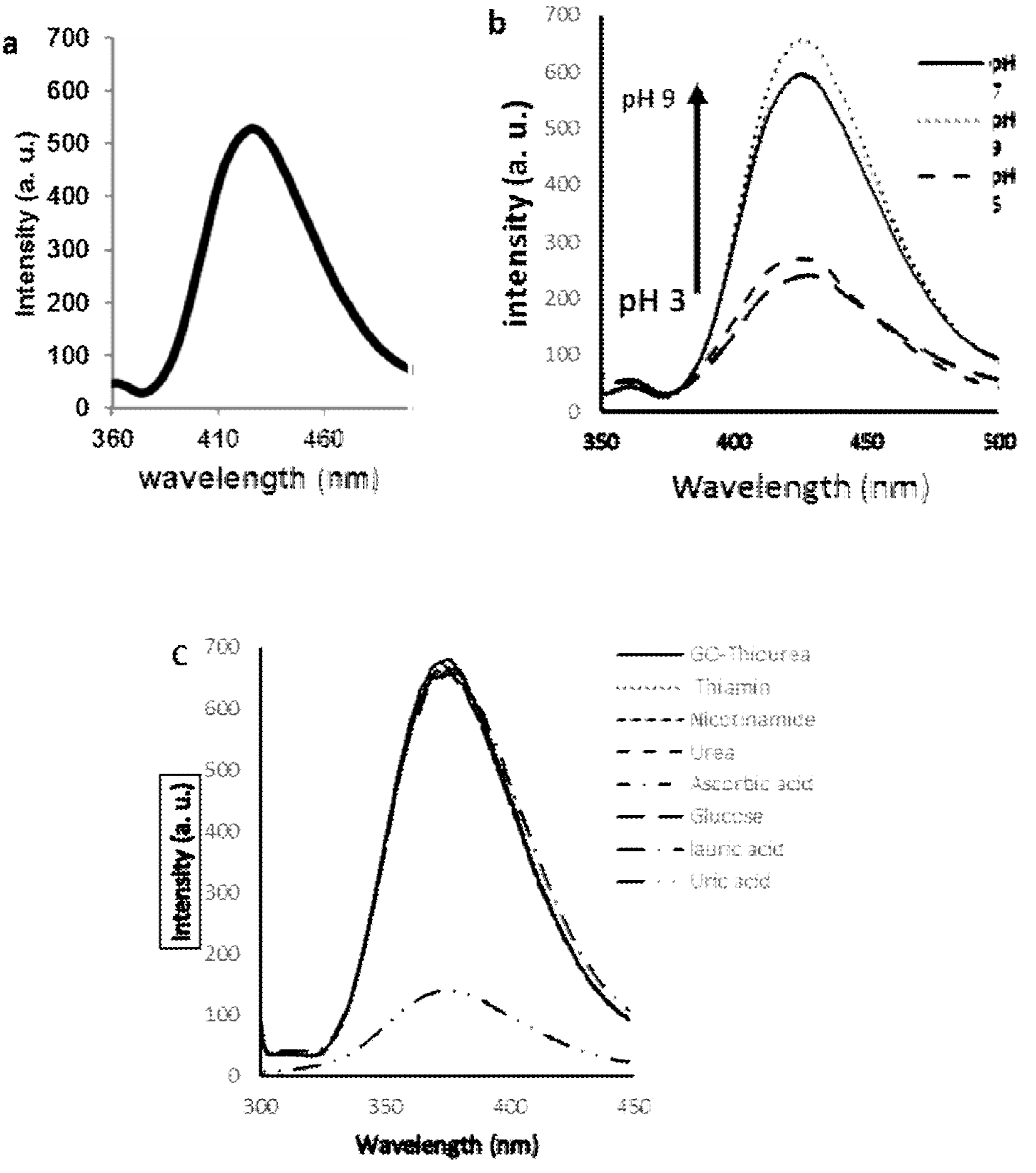

Figure 6. The fluorescence emission of the solution (250µg/ml) at an excitation wavelength of 280 nm emitted fluorescence at 376 nm a) modified graphene oxide, b) modified graphene oxide in the different buffered pH (3,5,7,9), c) In the solution of (10 $^{-5}$ M) uric acid, thiamin, nicotinamide, urea, ascorbic acid, glucose, lauric acid.

Thus enhancing the intensity of emission occurred in pH 7 and 9, but in the acidic pH, the oxygenated group protonated, and the ammonium thiocyanate groups separated from it, which caused lower intensity. Then, the interaction of different materials such as thiamin, nicotinamide, urea, ascorbic acid, glucose, lauric acid, and uric acid by fluorescence spectroscopy was investigated in the optimized pH. As shown in Figure (6.c), the fluorescence emission of modified graphene oxide was quenched after adding uric acid compared to other substances. The usual mechanism of quenching fluorescence in the graphene oxide-based material is fluorescence Resonance Energy Transfer (FRET). In the FRET mechanism, the quenching reagent absorbs energy at the emission wavelength of the fluorophore by long-range interactions such as dipole-dipole interactions [24]. Hence, exciting nitrogen and sulfur groups as electron-donating at the surface of modified graphene oxide can cause higher interaction between modified graphene oxide and uric acid as a fluorophore and quencher, respectively. The absorption band of the uric acid is between 230- 500 nm, which overlaps with fluorescence excitation and emission of modified graphene oxide. Therefore, the uric acid leads to the non-radiative path to come back excited electrons. So, the modified graphene oxide in the presence of uric acid showed low emission efficiency based on the FRET mechanism (Figure 7).

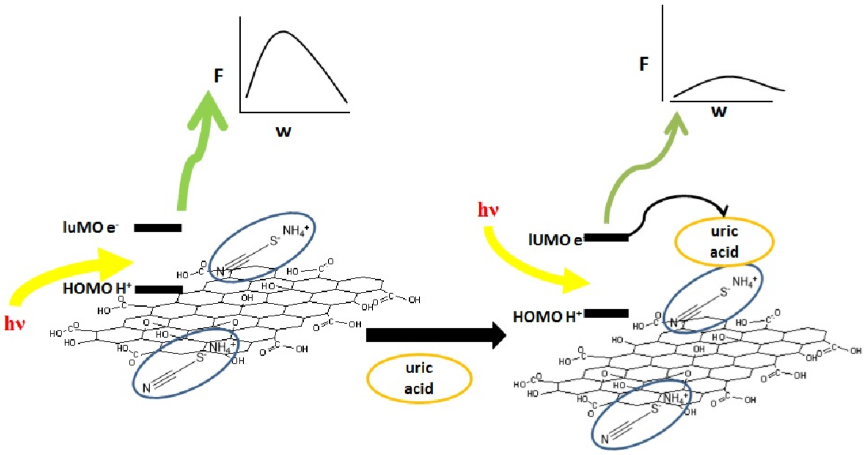

Figure 7. Schematic illustration mechanism of the detecting uric acid by modified graphene oxide.

Conclusion

The solid-state heat-modifying graphene oxide with thiourea was done by the tube furnace.

Then the Fourier transform infrared, and XPS spectra were used to characterize different functional groups of the graphene oxide layers. The percent of different elements was calculated based on Scofield's relative sensitivity factor (RSF). Fluorescence spectroscopy was used to measure the fluorescence emission of modified graphene oxide in the different buffered pH media that the acidic pH had a quenching effect on the intensity and alkaline pH enhanced it. Then, the interaction of modified graphene oxide suspension with thiamin, nicotinamide, urea, ascorbic acid, glucose, and lauric acid was investigated by fluorescence spectroscopy. The uric acid showed the quenching effect on the fluorescence emission of modified graphene oxide that can be related to the FRET quenching mechanisms.

Acknowledgments

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