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Direct Interaction Between Gold Nanorods and Glucose

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Abstract In this work, we present the results of the study on the interactions between gold nanorods (GNRs) and glucose. The optical properties of GNRs have higher sensitivity to glucose compared with that of gold nanospheres. The long-wavelength bands of the GNRs obviously decrease as the concentration of glucose increases. At high glucose concentrations, the absorption peak in long-wavelength bands almost disappears, and the absorption intensities corresponding to the transverse plasmon band are also decrease. These results suggest that glucose could seriously affect the optical properties of GNRs. A possible interaction mechanism between gold nanorods (GNRs) and glucose has been proposed. Furthermore, the influence of glucose on different amount GNRs also has been studied.

Keywords Gold nanorods · Glucose · Interaction · UV–vis spectra

Introduction

Nanometer-size noble metallic low-dimensional structures have received much attention in recent years due to their special electronic and optical properties [1–3]. Currently, there is a great deal of interest in metallic nanorods due to their shape-dependent optoelectronic properties. Among various 1-D metallic nanostructures, gold nanorods (GNRs) are of particular importance owing to their tunable surface plasmon resonance properties [4]. In addition, because of the good biocompatibility and facile bioconjugation of gold, GNRs have been explored for biological and medical use as optical contrast agents for dark-field [5–9], two-photon luminescence diagnostic imaging [10] and photothermal therapy of cancer cells [11, 12].

GNRs exhibit more attractive optical properties when compared to gold nanospheres due to anisotropic shape. There are two major absorption bands in the electromagnetic spectrum of the nanorods: the wavelength maximum centered at ~520 nm corresponds to the transverse plasmon oscillations of nanorods. It depends on the aspect ratio and the diameter of the nanorods. The second adsorption maximum around 650–800 nm is due to the longitudinal plasmon oscillations and possesses much stronger intensity and can be tuned by varying the length of the nanorods [13]. The position and intensity of these bands can be affected by changes in the dielectric constant around the vicinity of these nanoparticles, known as localized surface plasmon resonance (LSPR) or nanoSPR [14–16]. These properties suggest that GNRs have several advantages for applications in biological sensing, imaging, and therapy, which may perhaps benefit from the geometry of these structures [17, 18]. Additionally, the elongated nanoparticles have an inherently higher sensitivity to the local dielectric environment compared to similarly sized spherical nanoparticles. More importantly, GNRs with different aspect ratios could be easily fabricated and their unique yet simple ''multiplexing'' advantage could be harnessed [19].

Successful using of GNRs in vivo at least requires engineering efforts to make them biocompatible and stable within in vivo microenvironment [20, 21]. However, the

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organism is a very complex system. There are many factors that will influence the optical properties of GNRs, and then has an effect on the use of GNRs. So it is crucial to investigate the interaction of GNRs with blood plasma and proteins [22, 23]. Blood sugar is one of the important basal components in blood plasma. As is well known, different people have different blood sugar levels, such as the normal amount of the glucose in human blood serum is 4–6 mM, and the glucose value of diabetes may more than 11 mM. It has been reported that glucose is used as a reducing agent in preparation of metal nanoparticles [24]. So it could be assumed that glucose in blood serum would affect the optical properties of GNRs when they are used in the organism. To the best of our knowledge, no paper has reported the effect of glucose on the optical properties of GNRs.

In this paper, we investigated the absorption spectrums and stability changes of GNRs in the presence of glucose for the first time. The absorption of GNRs decreased on increment of glucose concentration. The absorption peak in long-wavelength bands gradually disappeared when the concentration of glucose was higher than 5.6 mM. The influences of glucose on GNRs with different aspect ratios or different amounts had also been studied. We think this study could make a basis of research and experimentation for the study of the application of GNRs in organism.

Experimental

Chemicals and Reagents

β-D Glucose and Cetyltrimethylammonium bromide (CTAB) were purchased from Sigma. L (+)-Ascorbic acid (99%), silver nitrate ($AgNO_3$), chlorauric acid ($HAuCl_4 \cdot 3H_2O$), and sodium borohydride ($NaBH_4$) were products of Beijing Shiji Company. All the chemicals were used without further purification. All solutions were prepared with deionized water.

Preparation of GNRs

GNRs were prepared by a seed-mediated growth approach reported by Murphy et al. [25, 26]. First, the gold seeds were prepared. An aqueous solution containing 0.62 mM CTAB and 2.2×10^{-3} mM $HAuCl_4$ was prepared in a conical flask. Next, 5×10^{-2} mM of ice-cold $NaBH_4$ solution was added to the solution while stirring. The solution turned brownish yellow immediately after adding $NaBH_4$, indicating particle formation. Next, the growth solution was prepared as follows: 0.6 mM $AgNO_3$ was added to 0.95 mM CTAB solution. To this solution, 6.72×10^{-3} mM $HAuCl_4$ was added, and after gentle mixing of the solution, 1×10^{-2} mM ascorbic acid was added. The final step was the addition of 0.02 mL of the seed solution to the growth solution. The temperature of the growth medium was kept constant at 25° in all the experiments. Then the precipitate was centrifuged, washed with deionized water, and diluted to 5 mL with deionized water. Gold nanospheres were prepared by the following steps: (1) An aqueous solution containing 0.95 mM CTAB and 6×10^{-4} mM $AgNO_3$, 6.72×10^{-3} mM $HAuCl_4$ was prepared in a conical flask; (2) 4.6×10^{-3} mM $NaBH_4$ solution was added into the solution. The solution turned dark red immediately indicating particle formation, at last the precipitate was centrifuged, washed with deionized water, and diluted to 5 mL with deionized water.

Apparatus and Measurements

Transmission electron microscope (TEM) of gold nanorods was obtained with a JEM-1230 electron microscope (JEOL, Japan), operating at 120 kV.

The UV–vis spectra of the samples were taken using a V-570 UV/VIS/NIR spectrophotometer (Jasco, Japan). Quartz cells of 1 cm optical path length were used for all spectrum measurements. The sample was prepared as follows: GNRs were dissolved into 2 mL by PBS buffer (pH = 6.8) with different concentration of glucose solution (concentration from 0.6 to 6.7 mM) for 2 min. Then, samples were contained in 1-cm path length quartz, and the UV–vis absorption intensities of the solution were recorded by JASCO V-570 UV/VIS/NIR spectrophotometer. The UV–vis absorption signal was recorded over a range from $\lambda = 400$ nm to $\lambda = 800$ nm.

Results and Discussion

Figure 1a shows the changes in the UV–vis spectra of the GNRs interaction with different concentrations of glucose ($R = 2.4$, R is the aspect ratio of GNRs). These nanorods have two absorption maxima at 522 and 667 nm corresponding to the transverse and longitudinal mode, respectively. As the concentration of glucose increases, the long-wavelength bands at 667 nm of the GNRs obviously decreases. The absorption bands at 522 nm also slightly decrease. When the concentration of glucose is higher than 5.6 mM, the longitudinal absorbance shifts to higher wavelength, and the absorption peak around 667 nm gradually disappears. Figure 1b shows the calibration curve derived from the changes in the absorbance at $\lambda = 667$ nm as the concentration of glucose increases. The linear range scans the concentration of glucose from 1.1 to 6.7 mM with a correlation coefficient of 0.993.

Figure 1c shows the changes in the absorbance of the GNRs with larger aspect ratio interaction with different

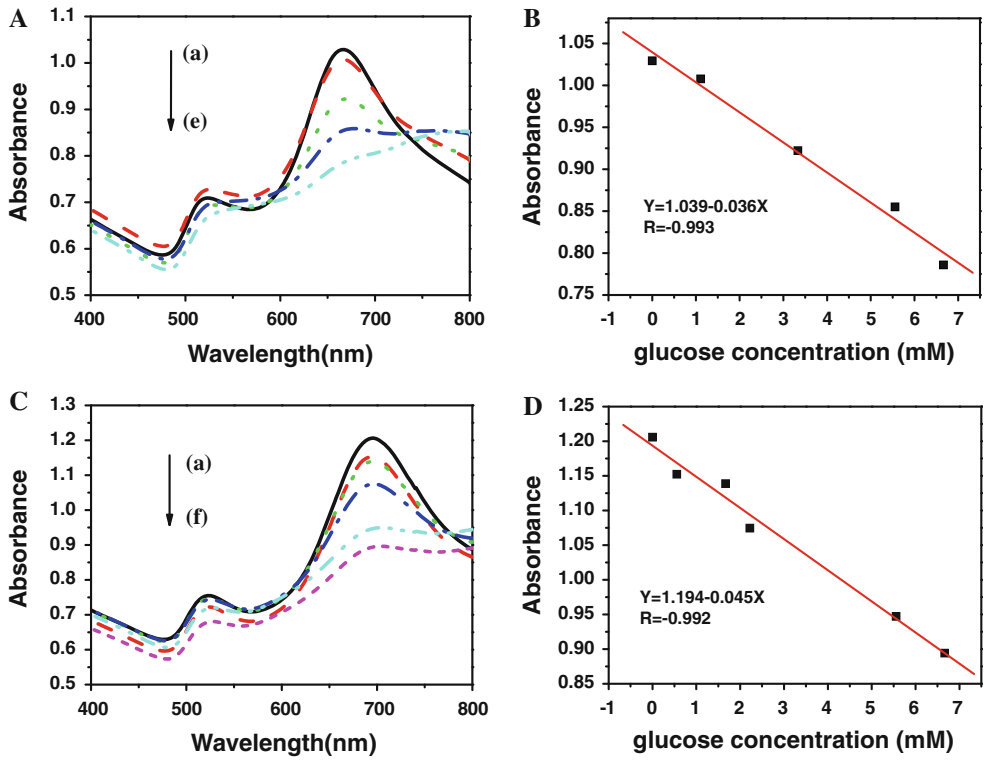

Fig. 1 **a** The UV–vis spectra of the GNRs ($R = 2.4$) interaction with different concentrations of glucose (from *a* to *e* the amount of the glucose is 0, 1.1, 3.3, 5.6, 6.7 mM respectively); each sample is recorded after reacting the GNRs (0.22 mg) with variable amounts of glucose for 2 min. **b** The linear calibration plot for different amounts of glucose. **c** The UV–vis spectra of the GNRs ($R = 3.0$) interaction with different concentrations of glucose (from *a* to *f* the amount of the glucose is 0, 0.6, 1.7, 2.2, 5.6, 6.7 mM, respectively); each sample is recorded after reacting the GNRs (0.25 mg) with variable amounts of glucose for 2 min. **d** The linear calibration plot for different amounts of glucose

concentrations of glucose ($R = 3.0$). These nanorods have two absorption maxima at 523 and 696 nm corresponding to the transverse and longitudinal mode, respectively. The absorbances of the GNRs make the same changes with the concentration of glucose increasing. Figure 1d shows the calibration curve derived from the changes in the absorbance at $\lambda = 696$ nm as the concentration of glucose increase. The linear range scans the concentration of glucose from 0.6 to 6.7 mM with a correlation coefficient of 0.992.

We also investigated the interaction between gold nanospheres and glucose. Figure 2 shows the changes in the UV–vis spectra of the gold nanospheres interaction with different concentrations of glucose. The absorption peak at $\lambda = 526$ nm shows no changes following the concentration of glucose increases.

Based on the above results, we assumed the interaction mechanism between GNRs and glucose. This may be related to the anisotropy of the GNRs. Previous studies have reported that CTAB forms bilayers on the GNRs. High-resolution crystallography on individual nanorod in earlier research has shown that GNRs are pentatetrahedral twins, with the {1 1 1} faces of gold at the ends, and {1 0 0} faces

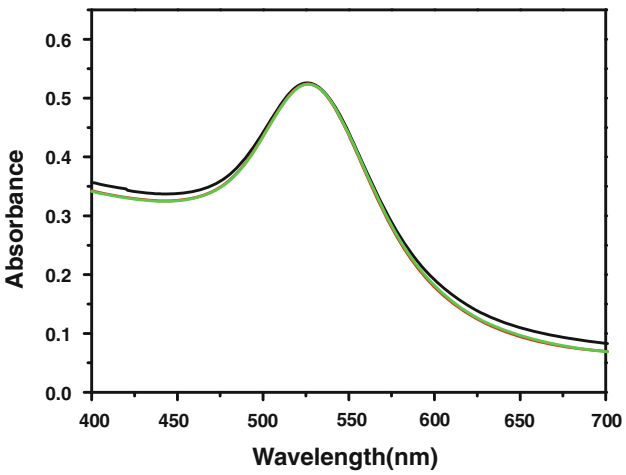

Fig. 2 The UV–vis spectra of the gold nanospheres interaction without or with different concentrations of glucose (4.4, 6.7 mM, respectively)

along the length of the rods [27, 28]. The CTAB preferentially binds to the {1 0 0} faces, along the length of the rods. So the glucose molecules preferentially bind to the {1 1 1} ends of the rods, and the GNRs tend to connect together end to end (see Fig. 3b). The absorption intensities of GNRs

around 690 nm decrease in the low glucose concentration due to this longitudinal plasmon band corresponding to the length of the GNRs. The absorption intensity around 520 nm changes little, because of the small changes in the width of the GNRs during the aggregation. When the glucose concentration increases, the GNRs aggregated seriously and then the absorption intensities corresponding to both the longitudinal plasmon band and the transverse plasmon band are greatly affected. On the other hand, since gold nanospheres are isotropy (see Fig. 3d), only transverse surface plasmon resonance will take effect. So, glucose little effects on their morphology, and their absorption intensity has no significant change. This also proves that the GNRs with anisotropy have a higher sensitivity and they are more suitable for the application in sensor.

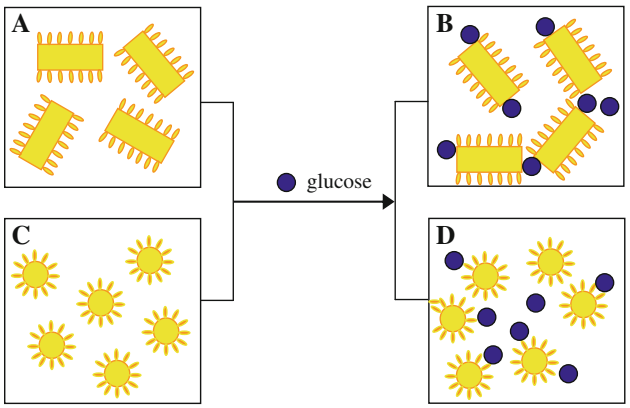

Fig. 3 Proposed mechanism of the interaction between GNRs and glucose

In order to verify our hypothesis about the interaction mechanism between GNRs and glucose, we analyzed the GNRs with transmission electron microscope (TEM). Figure 4a shows the GNRs without glucose. The average diameter of nanorods is 15 nm, and the average length is 43 nm. Figures 4b and c show the images of GNRs mixed with low (2.2 mM) and high (8.3 mM) concentration of glucose, respectively. It is obvious that there are some aggregation and some distortion of GNRs. Even some GNRs connect end to end (see the arrows shown in Fig. 4b). This may be result in lower absorption of GNRs. When the concentration of glucose is further increased (see Fig. 4c), the GNRs complete the aggregation, which may be result in the disappearance of the absorption peak. The TEM images of gold nanospheres with and without glucose were also investigated. Figure 4d shows the typical TEM image of the gold nanospheres, which indicates that the sample is composed of a large quantity of well-dispersed spherical nanoparticles. The average diameter of these

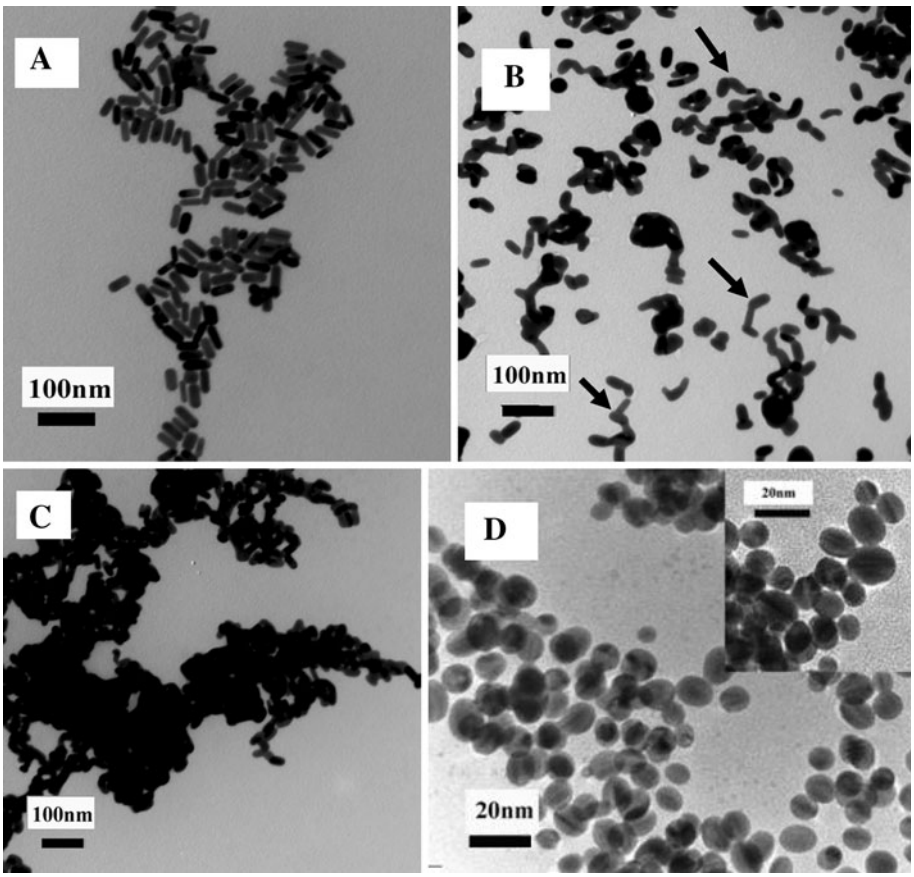

Fig. 4 TEM images of the **a** GNRs and **b** GNRs with a low concentration of glucose (2.2 mM), **c** GNRs with a high concentration of glucose (8.3 mM), **d** gold nanospheres, the *inner* shows gold nanospheres with 2.2 mM glucose

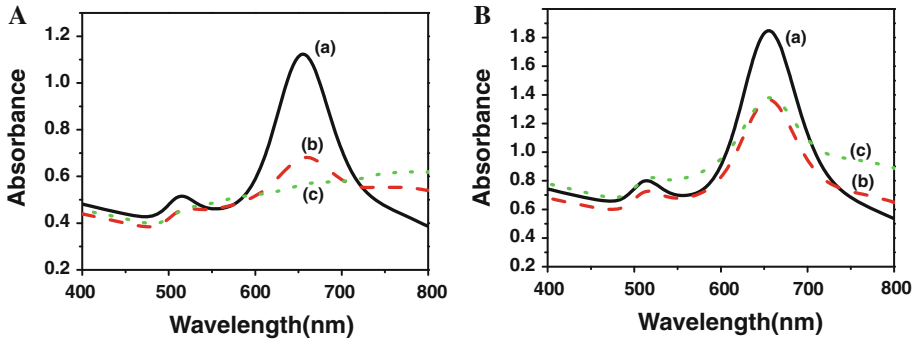

Fig. 5 The UV–vis spectra of **a** GNRs (0.24 mg) interaction in the absence (*a*) and presence of different concentrations of glucose (*b*) 5.6 mM; (*c*) 6.7 mM; each sample is recorded after reacting the GNRs with variable amounts of glucose for 2 min. **b** The UV–vis spectra of GNRs (0.40 mg) interaction in the absence (*a*) and presence of different concentrations of glucose (*b*) 6.7 mM; (*c*) 8.3 mM; each sample is recorded after reacting GNRs with variable amounts of glucose for 2 min

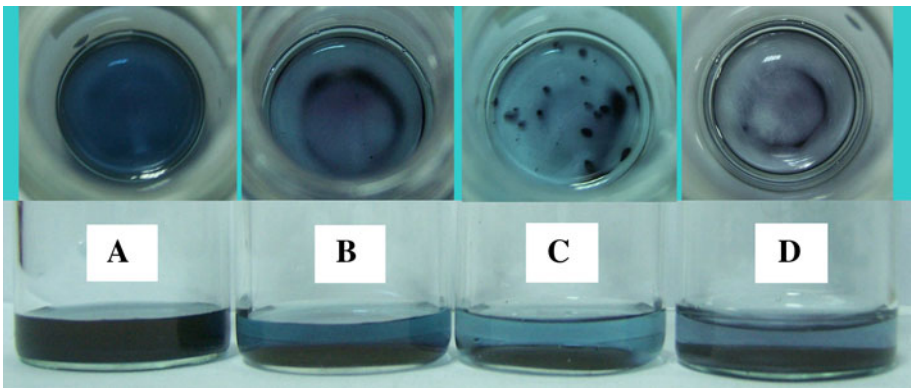

Fig. 6 The photographs of the GNRs (0.24 mg) in the absence (**a**) and presence of different concentrations of glucose (**b**) 4.4 mM; (**c**) 6.7 mM; (*D*) 8.3 mM after 64 h. The planforms show above and the side elevations shown below

particles estimated from the TEM image is about 13 nm. After mixed with glucose, the TEM image of the gold nanospheres (the inset of Fig. 4d) shows no obvious change. The image of well-dispersed gold nanospheres indicates that the morphology of gold nanospheres is not affected by the glucose, so the absorption peak of gold nanospheres shows no changes.

The changes in the absorbance of the different amounts of GNRs interacting with glucose were also investigated. It could be found the absorption peak around 655 nm almost disappears in 6.7 mM glucose with 0.24 mg GNRs (Fig. 5a). When the amount of GNRs increased to 0.40 mg (Fig. 5b), the absorption peak still maintains in 8.3 mM glucose. This result also indirectly proves our conjecture. In the same glucose concentration, more GNRs will reduce the extent of aggregation, so that the absorption intensity of the GNRs will reduce more slowly. This important finding confirms that keeping the amount of GNRs help to maintain these optical properties.

We also examined the stability of GNRs with or without glucose. In the first 15 h, GNRs show good stability in all solution with or without glucose. After 24 h, the aggregation of GNRs could be seen in the solution with 8.3 mM glucose. The aggregation of GNRs also could be seen in the solution with 6.7 mM glucose after 40 h. And all the solutions with glucose (4.4, 6.7, and 8.3 mM, respectively) show obvious aggregation of GNRs after 64 h. The photographs of these solutions are shown in Fig. 6. It could be seen the color of solutions with glucose all fade compared with the solution without glucose from side elevation photographs. From the planforms of the solutions, the aggregations of GNRs show more obvious in the solution with glucose (Fig. 6b–d). As the amount of glucose increases, the aggregations of GNRs show more seriously. Therefore, the concentration of glucose in the solution has significant influence on the stability of GNRs.

Summary

The present study has demonstrated the direct interaction between GNRs and glucose. The UV–vis spectrum results show that the glucose has more significant influence on the longitudinal plasmon band of GNRs. As the concentration of glucose increase, the long-wavelength bands of the GNRs obviously decrease. This is probably due to the anisotropy of the GNRs. When the concentration of glucose is higher than 5.6 Mm, the absorption intensities

corresponding to both the longitudinal plasmon band and the transverse plasmon band are greatly affected and the absorption peak in long-wavelength bands almost disappears. The experimental results prove that glucose has seriously affected the optical properties and stability of GNRs. This effect could be weakened by increasing the amount of GNRs. So this study would help the biomedical applications of GNRs.

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