Silica-covered Au nanoresonators for fluorescence modulating of a graphene quantum dot*

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We synthesize Au@SiO_2 composite particles with a core-shell structure, and utilize the Au@SiO_2 nanoparticles to modulate the fluorescence emission of the graphene quantum dot (GQD) through varying the silica shell thickness. The silica shell thickness can be easily controlled by varying the coating time. After silica coating, we investigate the influence of the silica thickness on the fluorescence emission of the GQD and find that the fluorescence property of the GQD can be changed as expected by varying the thickness of the silica shell. We propose an optimized coating time for the silica shell under the interaction of fluorescence quenching and enhancement.

Keywords: graphene quantum dot, fluorescence, nanoparticles

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1. Introduction

The graphene quantum dot (GQD), a new type of fluorophore, has become an active area of great interest,[1] and been explored for many interesting phenomena.[2] The GQD shows considerably low toxicity, high stability,[3] high electrical conductivity, and high thermal conductivity,[1] unlike the semiconductor quantum dot which has documented toxicity and is potentially an environmental hazard due to the release of metal ions such as Cd^{2+}.[4,5] The sub-10-nm sized water-soluble GQD with blue and green fluorescence property has been used as a biocompatible and low-toxicity fluorescence probe for cell imaging, biosensing, and *in situ* monitoring of drug release.[1] However, the GQD still presents some issues when applied to biological systems, such as the low quantum yield and the apparent brightness. Theoretically, we can control the emission of the GQD by the elaborate size. However, until now, it has remained a challenge to synthesize the GQD with a controlled size. So the method is difficult to use.

A powerful tool to monitor the optical properties of fluorescence emitters is the so-called plasmon-controlled fluorescence. In our previous theoretical work, we proposed to achieve the fluorescence enhancement and modulation through optimizing the distance between the silver nano-octahedron and the GQD at the nanometer scale.[2] The initial work has shown a very promising result that the plasmon-controlled fluorescence appears when a fluorescent emitter is located close to a metal nanostructure. The oscillating electrons can become resonant with the incident light radiation.[6] This can induce very strong and localized electromagnetic fields,[6] which can provoke either fluorescence enhancement or quenching depending on the distance between the metal nanostructure and fluorescence emitter.[7] So the fluorescence emission of the GQDs can be affected when they are located in the vicinity of a metal surface or a metal colloid. Colloidal Au nanoparticles, as an important type of functional metal nanoparticles, exhibit an extraordinary localized surface plasmon resonance (LSPR), which provides a means to manipulate light at the nanoscale.[8,9] The strong near-field interactions of the GQD with gold nanoparticles can lead to a substantial fluorescence enhancement. Generally, the excitation rate of the GQD can be greatly enhanced via the strong local fields created by nearby plasmonic nanoparticles.[2]

In the field of bio-applications, most reports focused on fluorescence quenching of the GQD, while the reports relating to the fluorescence enhancement of the GQD are few. Recently, Ning and colleagues used Au@SiO_2 nanoparticles to enhance the fluorescence of SiC nanoparticles, and found that a 10–15 nm spacing between Au and SiC leads to the maximum fluorescence enhancement, while a 25–30 nm spacing leads to weaker enhancement factors.[10] That report may provide a key to solve the problem of fluorescence emission of the GQD. We can modulate the fluorescence emission of the GQD by precisely tuning the spacing between the gold nanoparticle and the GQD. Coating a gold nanoparticle with silica may be a feasible solution. The SiO_2 shell can isolate the gold core from the GQD, and avoid the electron transfer between the two. Moreover, the distance between the gold core and the GQD can be controlled by changing the shell thickness. On

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the other hand, the SiO_2 shell coating the gold nanoparticles can improve the stability of the gold nanoparticles in water or ethanol[11] thus providing a biocompatible surface.[12] This kind of core-shell nanoparticle make the control of the GQD fluorescence possible.

Herein, Au@SiO_2 nanoparticles with different silica thicknesses are synthesized. Then the GQD is synthesized and adsorbed on the Au@SiO_2 nanoparticles. The structural characterization is carried out, and absorption and fluorescence properties are studied. Our aim is to investigate the influence of the silica thickness on the fluorescence emission of the GQD in the presence of a gold core.

2. Experiment

All glasswares used were cleaned with aqua regia and rinsed thoroughly with deionized water. Tetrachloroauric acid ($HAuCl_4$), sodium citrate, 3-aminopropyltrimethoxysilane (APTMS), sodium silicate, hydrochloric acid (HCl), graphite, concentrated sulfuric acid (H_2SO_4), concentrated nitric acid, potassium permanganate ($KMnO_4$), hydrogen peroxide, and ammonia were purchased from Beijing chemical factory and used without further purification. The deionized water was provided by an Aquapro ED12-3002-U system.

2.1. Synthesis of Au nanoparticles

The Au nanoparticles were prepared by using the sodium citrate reduction method with $HAuCl_4$. Typically, 1 mL of 1% $HAuCl_4$ solution and 50 mL deionized water were mixed in a triangular bottle with a plug and brought to boil under vigorous magnetic stirring. Then 1.135 mL of 1% sodium citrate was added into the bottle quickly; the color of the resulting solution rapidly changed from black to reddish-purple. After the solution was kept boiling for 10 min, it was removed from heat, and stirred for another 15 min. The resultant solution was referred to as the Au nanoparticle colloid, and used for further experiments.

2.2. Synthesis of Au@Si_2 nanoparticles

For coating the Au nanoparticles each with a silica shell, we used APTMS, an amine-terminated silane coupling agent, as the primer to render the metal surfaces vitreophilic.[13] Typically, 3 mL freshly prepared 1 mM APTMS solution was added to 25 mL Au nanoparticle colloid drop-by-drop and stirred vigorously for 10 min at room temperature. Then the mixture of APTMS and Au nanoparticles was heated to a temperature between 90 °C and 95 °C with continued magnetic stirring. When it reached the desired temperature, 6 mL freshly prepared sodium silicate solution (0.54 wt.%) adjusted with HCl to pH 10–11 was added dropwise with stirring to start silica coating on the Au nanoparticles. Samples of 0.5 mL each were collected every 5 min up to 2 h.

2.3. Synthesis of GQD

In a typical procedure, multilayer graphene oxide (GO) sheets were synthesized by using a modified Hummers method.[14] The multilayer GO sheets were ultrasonically exfoliated into monolayer GO sheets in an ultrasonic cleaner within 10 h. The monolayer GO sheets were then thermally reduced into expanded grahene sheets (GSs) at 600 °C within 2 h in a nitrogen atmosphere. The GSs were oxidized in concentrated H_2SO_4 and HNO_3. 10 mL concentrated H_2SO_4 and 30 mL HNO_3 were added to 5 mg GSs, and the mixture was under ultrasonic conditions in the ultrasonic cleaner for 18 h. After the oxidization, the mixture was centrifuged several times to remove the acids. Finally, the oxidized GSs needed to be deoxidized. The oxidized GSs were added into 40 mL deionized water adjusting with 4 mL $NH_3{\cdot}H_2O$ to pH $>$ 12 and hydrothermally treated in a polytetrafluoroethylene teflon-lined autoclave (50 mL) at 200 °C for 10–12 h. After being cooled down to the room temperature, the product was filtered through a 0.22 mm microporous membrane, and then centrifuged.[1] The final product was graphene quantum dots. 2 mL GQDs were mixed with 100 μL Au@SiO_2 nanoparticles. Then the mixture was shaken for 1 min.

2.4. Sample characterization

Scanning electron microscope (SEM) images were collected on an S4800 microscope (Hitachi, Japan), and an energy dispersive spectroscopy (EDS) analysis was carried out with EMAX 250 (Horiba, Japan). Transmission electron microscopy (TEM) images were obtained using an H-800 microscope (Hitachi, Japan) to provide the morphology detail. Ultraviolet–visible (UV–visible) absorption spectra were measured with UV-310IPC (Shimadzu, Japan). Fluorescence spectra were recorded on a fluorescence spectrophotometer (SPEX, America) and the excitation wavelength was set at 320 nm.

3. Results and discussion

3.1. Synthesis of Au@SiO_2 nanoparticles

Several methods have been proposed for the synthesis of Au@SiO_2 nanoparticles so far. Herein, we use a method which requires APTMS as a coupling agent. This method is easy to operate, and feasible to synthesize Au@SiO_2 nanoparticles with a controllable and thin silica shell. The stepwise synthesis of Au@SiO_2 nanoparticles is depicted in Fig. 1. In the procedure, APTMS is allowed to adsorb onto the gold colloid surface. Because APTMS exposes an amine group at one end and a methoxy group at the other end,[15] it acts as the metal surface modifier to enhance the affinity of gold for silica, which is deposited from a sodium silicate solution. After hydrolyzing, the APTMS molecule can form a covalent bond

with the silica particles through the methoxy group, and simultaneously bind to the gold nanoparticles through the amine group. The following reaction represents the hydrolysis reaction of APTMS:

$$H_2N{-}(CH_2)_3{-}Si{-}(O{-}CH_3)_3 + H_2O \rightarrow H_2N{-}(CH_2)_3{-}Si{-}(OH)_3 + CH_3{-}OH.$$

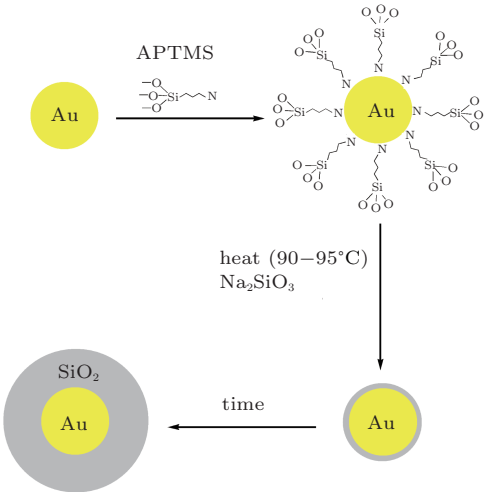


Fig. 1. (color online) Schematic depiction of the formation of a silica shell on a gold nanoparticle.

After dripping APTMS, the freshly prepared sodium silicate solution is added to the dispersion, which promotes the formation of a relatively homogeneous silica layer around the particle using the silanol groups as the anchor points. The thickness of the silica layer can be increased by carefully increasing the coating time.[13] Therefore, the coating time can be used to represent the average thickness of the shells.[13,16] This method allows a good control over the size and the morphology of the silica shell. This resulting silica layer can provide the gold core with both mechanical and chemical stabilities. It is reported that the silica coating renders a gold core amenable to be used in a variety of solvents, such as water, ethanol, methanol, and acetone.[12] Then it can protect the core from degradation in the subsequent steps. Moreover, due to the chemical stability of silica, it has no obvious influence on the optical property of the gold nanoparticles.[17] Furthermore, the silica shell can be used to control the distance between the gold core and the GQD by changing the shell thickness.

3.2. Characterization of Au@SiO_2 nanoparticles

SEM and TEM images in Fig. 2 show that silica coating is obtained for all gold nanoparticles. The average gold core diameter is about 40 nm, while the average thickness of the silica shell is from 2 nm to 10 nm depending on the coating time. Nanoparticle formation occurs in several steps: (i) nucleation in a very short time, (ii) growth of the nuclei, and (iii) Ostwald ripening (dissolution of smaller particles and redeposition of the dissolved species on larger particles).[18] Whatever the shape of the gold colloids (spherical or nonspherical), the silica shell growth always follows well the shape (or outline) of the gold colloids as shown in Fig. 2. In fact, it has been reported that increased silica deposition leads to spherical and nearly monodisperse particles, regardless of the shape and the size of the original gold colloids.[19,20]

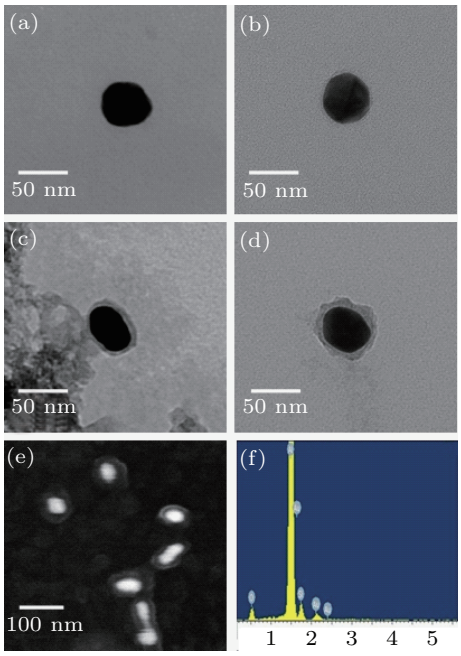


Fig. 2. (color online) TEM images of Au@SiO_2 nanoparticles with different coating time: (a) 0 min, (b) 30 min, (c) 60 min, and (d) 120 min. (e) SEM image of Au@SiO_2 nanoparticles. (f) EDS image of Au@SiO_2 nanoparticles on an aluminum substrate.

By increasing the coating time, the silica thickness can be increased, and then silica-coated Au nanoparticles with continuously variable silica thicknesses can be obtained. The silica shell can influence the plasmon resonance of the gold nanoparticles through changing the local optical environment around them. The position of the gold plasmon band after silica coating is detected by UV–visible absorption spectroscopy. The influence of the silica thickness on the plasmon band of aqueous gold colloids is shown in Fig. 3. The nano-sized gold colloids show a very intense surface plasmon absorption band at around 520 nm.[21] The gold core used in the present experiment shows a maximum at 525.5 nm. As the coating time increases from 0 to 60 min, a weak red shift is observed depending on the silica shell thickness. It is known that the position of the surface plasmon resonance band is extremely sensitive not only to the particle size and shape but also to the refractive index of the medium surrounding the particle.[22–24] Silica is electronically inert, which does not exchange charge with the gold core,[25] however its refractive index is higher than that of water.[26] So the red shift is the result of an increase in the local refractive index of the medium surrounding the gold core

after the formation of the silica shell. When the coating time is more than 60 min, scattering becomes important, resulting in a strong increase in the absorbance at shorter wavelengths. This effect promotes a weak blue shift of the surface plasmon band. In turn, the weak swing of the plasmon absorption peak proves that the silica thickness is increased by increasing the coating time.

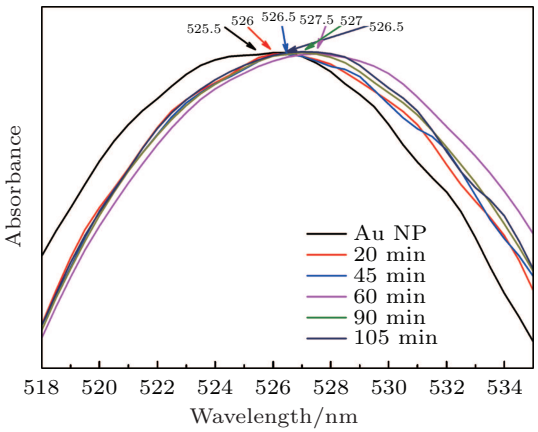


Fig. 3. (color online) UV–visible absorbance spectra of Au@SiO_2 nanoparticles with different silica thicknesses.

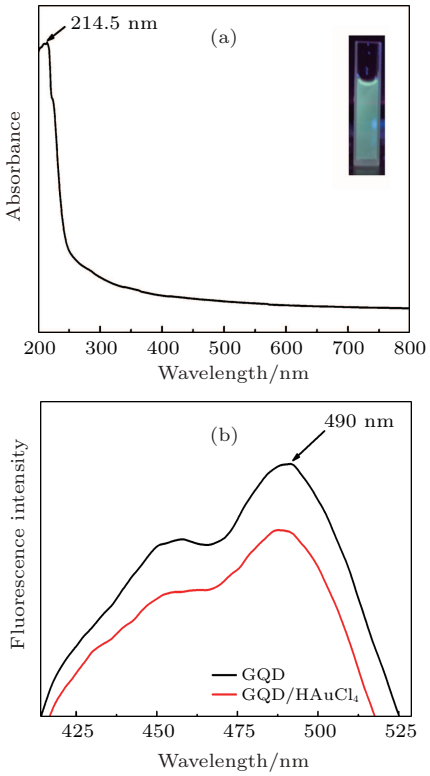


Fig. 4. (color online) (a) UV–visible absorption spectrum of GQD; inset: photograph of the GQD aqueous solution taken under ultraviolet light. (b) Fluorescence spectra of the original water-soluble GQD and the water-soluble GQD in the presence of Au^{3+} ions.

3.3. Fluorescence properties of Au@SiO_2/GQD

The optical properties of the GQD are shown in Fig. 4. From the UV–visible absorption spectrum of the GQD aqueous solution (Fig. 4(a)), the typical absorption peak at 214.5 nm can be observed, which is assigned to the π–π^* transition of graphitic sp^2 domains.[27] When the GQD is irradiated with ultraviolet light, bright blue-green fluorescence is observed (Fig. 4(a)). To further explore the optical properties of the water soluble GQD, a detailed fluorescence investigation is carried out. As shown in Fig. 4(b), the spectrum shows that the fluorescence maximum appears at 490 nm.

In order to avoid the interference of the Au^{3+} ions, the $HAuCl_4$ solution is added into the GQD solution. As shown in Fig. 4(b), the fluorescence intensity of the GQD is not increased. It proves that the Au^{3+} ions cannot enhance the fluorescence of the GQD.

For the GQD located in the vicinity of a laser-irradiated gold nanostructure, the observed fluorescence emission of the GQD is a function of the gold nanostructure–GQD distance.[12] The most important property of the surface-enhanced fluorescence is the distance dependence, because there is a continuous transition from fluorescence quenching to fluorescence enhancement when varying the distance between the GQD and the gold nanostructure.[28–31] The gold nanoparticles are well-known fluorescence quenchers for both organic fluorophore and GQD.[32–34] So we increase the distance between the gold nanoparticle and the GQD to interdict the charge transfer and improve the fluorescence. Silica is chosen to separate the GQD from the gold nanoparticle because the silica shell can establish a tunable and consistent barrier layer between the gold core and the GQD.[35] We can modulate the fluorescence emission of the GQD through changing the silica thickness. The fluorescence properties of Au/GQD and Au@SiO_2/GQD are displayed in Fig. 5. The fluorescence intensity of Au/GQD is so weak on account of intense fluorescence quenching, while the fluorescence intensities of Au@SiO_2/GQD are higher than that of Au/GQD. This phenomenon can be understood by the photon-induced electron transfer between the gold nanoparticle and the GQD. When the GQD is adsorbed onto the uncoated gold nanoparticles, the quenching effect dominates at such a short separation distance.[32–34] There is a large overlap between the GQD emission and the surface plasmon resonance absorption bands of the gold core. Photon-induced electron transfer from the GQD to the gold nanoparticle occurs. After coating the gold nanoparticle with silica, the silica shell isolates the gold nanoparticle from the GQD, which prevents the electron transfer from the GQD to the gold nanoparticle. As the coating time increases from 0 to 60 min, the fluorescence intensity is increased, because the fluorescence quenching mechanism and the fluorescence enhancement mechanism coexist and weaken as the distance between the gold nanoparticle and the GQD increases. Surface plasmon absorption and scattering of the gold nanoparticles contradictorily affect the emission of the

GQD in the vicinity.[36] As reported, the larger the emission of a chromophore overlaps with the scattering of the plasma in the spectrum, the larger the enhancement will be.[37] Absorption and scattering are both affected by the distance, and the distance is more critical for the absorption function.[37] Therefore when the distance is increased, the absorption decreases faster than the scattering, consequently, the quenching is decreased while the scattering is not significantly affected. The results is the fluorescence quenching is weakened more obviously than the fluorescence enhancement. So the fluorescence emission of the GQD appears to be enhanced. With the optimal silica thickness, the highest fluorescence enhancement is obtained. However, when the coating time is more than 60 min, the fluorescence intensity is decreased. As the distance becomes long, the scattering is decreased obviously, thus the enhancement is weakened more obviously than the quenching. So the fluorescence emission of the GQD is weakened. No red-shift or blue-shift of the fluorescence peak can be observed. The fluorescence intensity at the fixed wavelength can be increased or decreased. We propose using a silica coating with the optimal thickness for the enhancement of the GQD fluorescence.

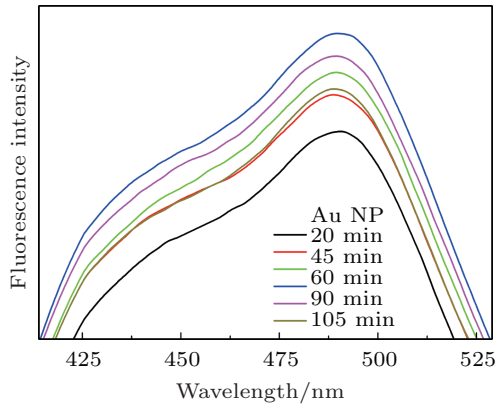


Fig. 5. (color online) Fluorescence spectra of water-soluble GQD in the presence of Au nanoparticles and Au@SiO_2 nanoparticles with different silica thicknesses.

4. Conclusion

We choose gold nanoparticles to influence the GQD emission because their surface plasmon resonance overlaps with the GQD emission. For the Au@SiO_2 nanoparticles, a weak swing of the plasmon absorption peak is found due to the increase in the local refractive index around the gold core. We show the fluorescence quenching dependence of the silica shell thickness. The overlap of the surface plasmon resonance and the GQD emission leads to fluorescence quenching by energy transfer or charge transfer when the gold nanoparticle without silica coating contacts with the GQD directly. The fluorescence intensities of Au@SiO_2/GQD become higher than that of Au/GQD. The fluorescence intensity reaches the maximum when the silica coating time is 60 min. This research provides a basis for the further study of metal nanoparticles enhancing and modulating the GQD emission, and contributes to in depth exploration of the application of the GQD.

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