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Graphene Oxide as a Quencher for Fluorescent Assay of Amino Acids, Peptides, and Proteins

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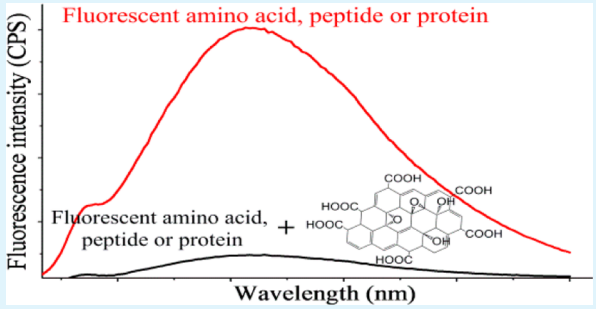
Supporting Information

ABSTRACT: Understanding the interaction between graphene oxide (GO) and the biomolecules is fundamentally essential, especially for disease- and drug-related peptides and proteins. In this study, GO was found to strongly interact with amino acids (tryptophan and tyrosine), peptides (Alzheimer's disease related amyloid beta 1-40 and type 2 diabetes related human islet amyloid polypeptide), and proteins (drug-related bovine and human serum albumin) by fluorescence quenching, indicating GO was a universal quencher for tryptophan or tyrosine related peptides and proteins. The quenching mechanism between GO and tryptophan (Trp) or tyrosine (Tyr) was determined as mainly static quenching, combined with dynamic quenching (Förster resonance energy transfer). Different quenching efficiency between GO and Trp or Tyr at different pHs indicated the importance of electrostatic interaction during quenching. Hydrophobic interaction also participated in quenching, which was proved by the presence of nonionic amphiphilic copolymer Pluronic F127 (PF127) in GO dispersion. The strong hydrophobic interaction between GO and PF127 efficiently blocked the hydrophobic interaction between GO and Trp or Tyr, lowering the quenching efficiency.



KEYWORDS: *graphene oxide, quenching, interaction, amino acid, peptide, protein*

1. INTRODUCTION

Graphene oxide (GO) is a two-dimensional, atomically thin carbon nanomaterial with functional groups, such as carboxylic acid at the edges, phenol hydroxyl and epoxide groups mainly at the basal plane, and some carbon−carbon sp^2 domains.[1] The advantages of GO over other nanomaterials lie in its unique properties, such as large specific surface area, good physisorption, high water dispersibility, and excellent biocompatibility.[2]

Since the groundbreaking research of PEGylated-GO (PEG = polyethylene glycol) used to efficiently load hydrophobic drug,[2] much progress has been achieved for explorations of graphene oxide in the biological and biomedical field, including drug and gene delivery, biological sensing, and cellular imaging.[3] The surface of GO allows electrostatic, hydrophobic, hydrogen bonding, and $\pi-\pi$ stacking interactions, which are generally favored for molecules with poor water solubility. Covalent functionalization of GO with chitosan,[4] folic acid,[5] and poly(*N*-isopropylacrylamide)[6] has recently been developed for drug delivery with pH-controlled or thermal-responsive drug release. GO was also recently studied for gene delivery.[7] The single-stranded DNA was found to be preferentially adsorbed onto the GO surface over the double-stranded form, as the later prevented the binding of GO surface to the DNA base inside the double helix.[8] Besides drug and gene delivery, GO has been exploited for near-infrared photothermal treatment for cancers and Alzheimer's disease.[9−11] GO based materials are also applied to biosensing, cellular probing, and real-time monitoring based on fluorescence.[12,13]

Although GO has shown potential applications in drug and gene delivery and photothermal treatment, one critical question needs to be addressed before any actual application: How does GO interact with biomolecules, such as amino acids, peptides, and proteins? However, there is very limited information on such a question. It was found that GO could adsorb amino acids via electrostatic interaction or $\pi-\pi$ stacking interaction,

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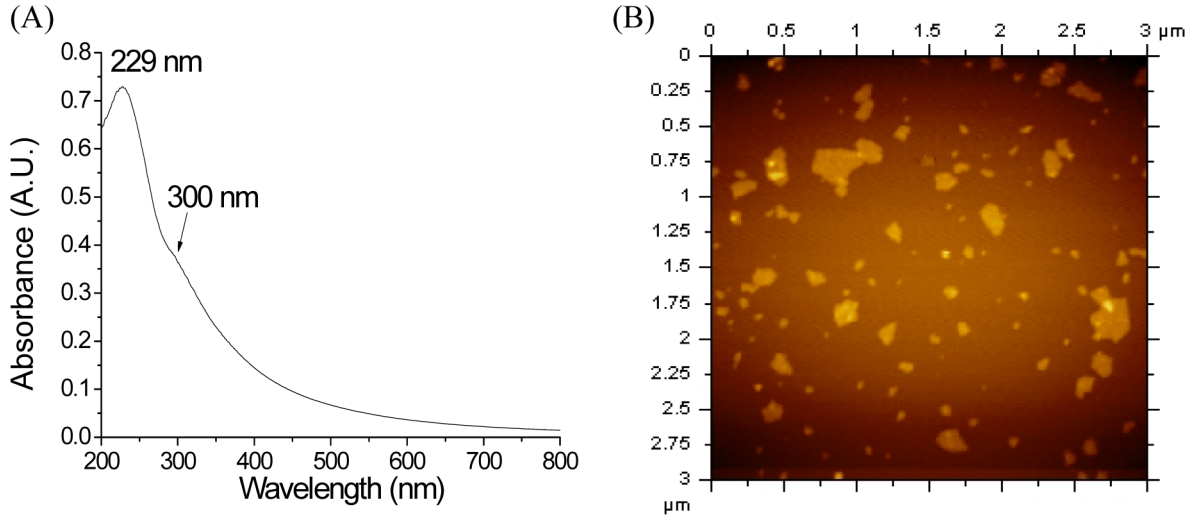

Figure 1. UV−vis absorption spectrum of 15 μg/mL GO aqueous dispersion (A). Tapping mode AFM image of GO deposited on a freshly cleaved mica surface with height of ∼0.9 nm (B).

such as arginine, histidine, lysine, tryptophan, tyrosine, and phenylalanine.[13] GO could quench the fluorescence of several dye-labeled peptides for biosensing,[13−15] but the quenching mechanism of GO has not been studied. Furthermore, there is no fluorescence study based on the interaction between GO and amino acids, peptides, and proteins without fluorescent dye-labeled probe. Understanding the interaction between GO and biomolecules is fundamentally essential, especially for disease- and drug-related peptides and proteins. The present study is intended to investigate the interaction between GO and fluorescent assay of amino acids (tryptophan and tyrosine), peptides (Alzheimer's disease related amyloid beta 1-40 and type II diabetes related human islet amyloid polypeptide), and proteins (drug related bovine and human serum albumin) using fluorescence spectroscopy.

2. EXPERIMENTAL SECTION

2.1. Materials. Single-layer GO was purchased from ACS Material LLC (Medford, MA). L-Tyrosine (Tyr), L-tryptophan (Trp), and Pluronic F127 were bought from Sigma (St. Louis, MO). Amyloid beta 1-40 ($A\beta_{40}$), human islet amyloid polypeptide (hIAPP), human serum albumin (HSA), bovine serum albumin (BSA), and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) were obtained from MP Biomedicals (Solon, OH). All these chemicals were used without any further purification. The deionized water used in the experiments was obtained from a Modulab 2020 Water purification system. The resistivity, surface tension, and pH of deionized water were 18 MΩ·cm, 72.6 mN/m, and 5.6 at 20.0 ± 0.5 °C, respectively.

2.2. Methods. One mg/mL GO aqueous solution was obtained by dissolving 5.00 mg of GO into 5 mL of pure water, followed by sonication for 1 h in a cold water bath (Branson, model 1510, Danbury, CT). Then, the as-prepared GO solution was diluted to 100 μg/mL. The concentrations of the fluorescent assay of amino acid (Tyr and Trp) and protein (HSA and BSA) were prepared individually as 2.5×10^{-6} M, if not specifically mentioned. The concentration of both $A\beta_{40}$ and hIAPP for the fluorescence emission was prepared as 2.5×10^{-5} M as the fluorescence intensity of 2.5×10^{-6} M solution was too weak. Due to the propensity of aggregation, peptide $A\beta_{40}$ or hIAPP was first dissolved into HFIP to render the monomeric form and then was put in a vacuum desiccator for 2 h to remove the solvent HFIP. In order to fix the final concentration of fluorescent assay as 10^{-6} M (10^{-5} M for $A\beta_{40}$ and hIAPP) with gradually increased concentration of GO in the range of 0−30 μg/mL, a total volume of 400 μL of mixture was obtained by mixing 160 μL of 2.5×10^{-6} M (2.5×10^{-5} M for $A\beta_{40}$ and hIAPP) fluorescent assay, a certain volume of 100 μg/mL GO (from 0 to 120 μL, 20 μL as each increment), and pure water (from 240 to 120 μL, 20 μL as each decrement). In the fluorescence lifetime study of Trp or Tyr mixed with different amounts of GO, the concentrations of Trp and Tyr were fixed at 2.5×10^{-5} and 5×10^{-5} M, respectively.

2.3. Characterization. Atomic force microscopy (AFM) images were taken with tapping mode using Agilent 5420 AFM instrument (Agilent, Santa Clara, CA). The cantilever had a resonance frequency of 342 kHz with typical force constant 42 N/m, a silicon probe at the tip. The fluorescence spectra were measured by Fluorolog-3 spectrofluorimeter (Horiba Scientific, Edison, NJ) using a 1 cm × 0.2 cm quartz cell. The slit widths in spectrofluorimeter for both excitation and emission were set at 5 nm. The excitation wavelength for Tyr, $A\beta_{40}$, and hIAPP was set as 270 nm, Trp, BSA, and HSA as 290 nm, and GO as 425 nm. The excitation wavelengths were selected to ensure that the Raman scattering peak did not interfere with the emission wavelength. Frequency-domain fluorescence lifetime measurements were performed using a ChronosFD spectrofluorometer (ISS, Champaign, IL). Samples were excited with a 280 nm modulated diode, and emission was collected using 305 nm long-pass filters (Andover, Salem, NH). 2,5-Diphenyoxazole (PPO) in ethanol (lifetime = 1.4 ns) was used as a lifetime reference, and polarizers were set at a magic angle configuration (54.7°). All measurements were conducted at room temperature in 0.5 × 1 cm quartz cells. Modulation-phase data were analyzed using GlobalsWE software, and the χ^2 parameter was used as criterion for goodness of fit. The average intensity decay lifetime was obtained by fitting the data with a multiple-exponential decay model. UV−vis absorption was performed by a Lambda 900 UV/vis/NIR spectrophotometer (Perkin-Elmer, Norwalk, CT) using a 1 cm × 1 cm quartz cell. In order to observe the UV−vis absorption more clearly, the final concentration of 10^{-5} M instead of 10^{-6} M Trp and Tyr was analyzed with the presence and absence of GO.

3. RESULTS AND DISCUSSION

3.1. Characterization of GO by UV−vis and AFM. To confirm that the commercial available GO used in this study had similar properties as previously reported, UV−vis absorption and AFM were applied to characterize it. The sample of diluted GO aqueous dispersion (15 μg/mL) was examined by a UV−vis absorption spectrum, as shown in Figure 1A. It displayed a maximum absorption at 229 nm due to the $\pi-\pi^*$ transition of aromatic C=C bonds and a shoulder around 300 nm due to the $n-\pi^*$ transition of C=O bonds.

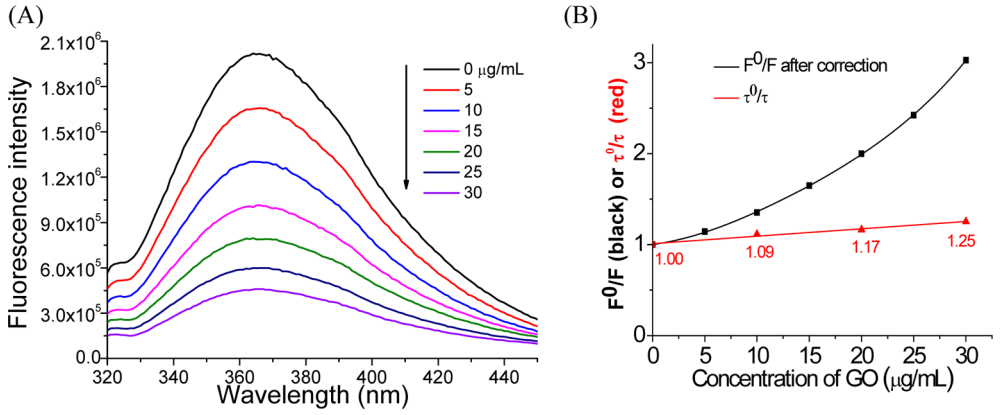

Figure 2. (A) The fluorescence quenching of Trp (10^{-6} M) by mixing with different concentrations of GO. (B) The quenching of Trp (F^0/F after inner filter effect correction, black) and fluorescence lifetime ratio (τ^0/τ, red) as a function of GO concentrations.

Both were consistent with previous reports.[16,17] To further verify the single-layer morphology of GO by AFM, 5 μL of 15 μg/mL GO aqueous dispersion was spread onto a freshly cleaved mica surface and left to dry in the air. The AFM image showed that all heights of GO sheets were around 0.9 nm (Figure 1B and extracted profile in Figure S-1 in the Supporting Information), which were also similar to previous reported single-layer GO.[10,14,16,17] All these results confirmed that the GO used in this study was truly a single-layer sheet.

3.2. Fluorescence quenching of Trp or Tyr by GO. It has been known that GO can quench the emission of fluorescent molecules or particles, such as organic dye molecules,[18−20] fluorescent labels,[12,14,15,21−23] and quantum dots (QD),[17,24,25] through the process of Förster resonance energy transfer (FRET) from the fluorescent moiety to GO. The fluorescent dyes or labels usually contain aromatic rings, and the quenching is via noncovalent interactions, such as electrostatic interaction, hydrogen bonding, hydrophobic and $\pi-\pi$ interactions between GO, and the dye molecules or fluorescent labels.[14,15,19,22,23] On the basis of the structure and component of fluorescent amino acids, peptides, and proteins, there should be a noncovalent interaction between them and GO, affecting the fluorescent intensity of the fluorescent assay. Indeed, the experiments in the present study showed the strong quenching effect of GO.

When mixed with GO aqueous dispersion, the fluorescence intensity of the 10^{-6} M Trp assay was strongly reduced without any shift of the emission maximum, as shown in Figure 2A. Very similar phenomenon of reduced fluorescence intensity was also found for the 10^{-6} M tyrosine (Tyr) assay (Figure S-2 in the Supporting Information). Due to the fact that GO had strong absorption in the range of 270−360 nm, which overlaps with the excitation and emission of Trp or Tyr, the change of fluorescence after the addition of GO could be caused by the so-called "inner filter effect". This effect refers to the absorbance of light at the excitation or emission wavelength by the molecules present in the solution.[26] Therefore, it must be properly considered before any discussion of interaction or binding between the fluorescent molecules and GO. As the fluorescence intensity was collected from the center of a cuvette, the inner filter effect could be estimated from the following equation:[26,27]

$$F_{abs} = F_{corr} \times 10^{-\frac{A_{ex}\times d_{ex}}{2} - \frac{A_{em}\times d_{em}}{2}} \quad (1)$$

where F_{obs} is the measured fluorescence, F_{corr} is the correct fluorescence intensity that would be measured in the absence of inner filter effect, d_{ex} and d_{em} are the cuvette path length in the excitation and emission direction (in cm), respectively, and A_{ex} and A_{em} represent the measured absorption value at the excitation and emission wavelength with the addition of compound, respectively. Due to the fact that the UV−vis absorption of 10^{-6} M Trp or Tyr in the range of 270−360 nm was negligible compared with the high absorption of GO dispersion, A_{ex} and A_{em} used for correction were the absorption of GO alone at room temperature as an approximation. After this correction, Stern−Volmer plot of F^0/F against the concentration of GO showed that there did exist quenching when GO was added to the solution of Trp (Figure 2B, black color), where F^0 and F were the fluorescence intensity at the maxima in the absence and in the presence of GO, respectively. All F^0/F discussed below had been corrected by the inner filter effect.

The decrement of fluorescence intensity after removing the inner filter effect meant that there was strong quenching effect between GO and Trp. A previous theoretical investigation had shown that Trp could be strongly adsorbed on the surface of graphene via $\pi-\pi$ interactions with a preferring parallel orientation with respect to the plane of graphene.[28] Although GO was the oxidized form of graphene with carboxylic acid group at the edge and hydroxyl and epoxy groups on the basal plane, it still had plenty of small aromatic areas with sp^2 carbons.[29,30] Therefore, GO could still have $\pi-\pi$ interaction or hydrophobic interaction with Trp or Tyr.

3.3. Quenching Mechanism of Trp by GO. After the correction of inner filter effect, the possible quenching mechanisms of Trp by GO were: (1) collisional quenching due to random collision; (2) static quenching through the ground-state complex formation; (3) dynamic quenching due to Förster resonance energy transfer (FRET) from the donor as Trp to the acceptor as GO; (4) static and dynamic combined quenching.[26,27] These possibilities are discussed below.

The observed reduction of fluorescence intensity could be possibly due to collisional quenching, which could be described by the classical Stern−Volmer equation:

$$\frac{F^0}{F} = 1 + K_D[Q] \quad (2)$$

where F^0 and F are the fluorescence intensity at the maxima in the absence and in the presence of the quencher, respectively;

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[Q] is the concentration of the quencher; K_D is the collisional quenching constant.[27] One good way to discriminate collisional quenching from binding-related quenching was to study how temperature affected the quenching efficiency. For collisional quenching, higher temperature increased the probability of collision and resulted in higher quenching efficiency, while less quenching was observed at lower temperature. The fluorescence emission data of Trp mixed with GO were collected at three different temperatures, namely 5, 20, and 45 °C. The Stern–Volmer plot in Figure 3 showed that temperature did

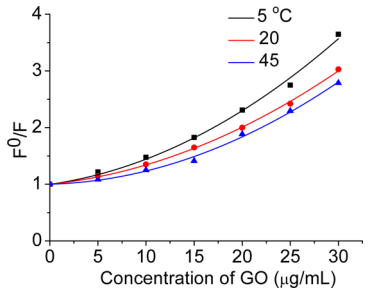

Figure 3. Stern–Volmer plot of 10^{-6} M Trp against the concentration of GO as the quencher at 5, 20, and 45 °C.

affect the quenching efficiency. However, a higher quenching efficiency was observed at lower temperature, indicating that the collisional quenching was not the main mechanism of quenching by GO. Similar observation was also found for Tyr (Figure S-3 in the Supporting Information).

In the static quenching alone mechanism, the nonfluorescence complex is formed between the ground state of chromophore and the quencher, decreasing the population of fluorophore and thus resulting in the reduction of fluorescence intensity. The fluorescence lifetime remains the same during quenching, as this process does not affect the excitation state of the fluorophore.[27] Also, neither the concentrations of chromophore nor the inner filter effect affects fluorescence lifetime. Due to observation that there was a slightly linear decrement of the fluorescence lifetime of Trp when GO was added, the quenching mechanism could not be attributed to the static quenching only.

Förster resonance energy transfer (FRET) is a distance dependent interaction between the electronic excited states of two fluorescent molecules in which excitation is transferred from a donor molecule to an acceptor molecule without emission of a photon. Because of the overlap between the emission of Trp and the absorption of GO, as shown in Figure 4A, and the adsorption of Trp on GO sheet,[13] the reduction of emission of GO was possibly due to the energy transfer from the excited state of Trp to GO. One could observe slight increments of the emission of GO from Figure 4B. However, this energy transfer was not the only factor for the fluorescence quenching due to the fluorescence lifetime study, which is independent of the concentrations of fluorophore, inner filter effect, and photobleaching. If there was only FRET present, the values of the fractional fluorescence F^0/F at each concentration of GO should be equal to the ratio of the fluorescence lifetime τ^0/τ, where τ^0 and τ were the fluorescence lifetime without and with the presence of the corresponding concentration of GO, respectively. However, the plot of F^0/F against concentration of GO was clearly upward compared with the linear τ^0/τ at the same concentration of GO (Figure 2B, red color), indicating a dynamic and static combined mechanism for the fluorescence quenching.[27]

3.4. UV–vis Absorption of Trp and GO. To further verify the quenching mechanism, it was necessary to study the UV–vis absorption spectrum. Due to the formation of complex between the ground state of the fluorophore and the quencher during the static quenching, the UV–vis absorption spectrum of the fluorophore would change, while no absorption spectrum change should be observed in the dynamic quenching.[31] As the quenching of Trp was static and dynamic combined quenching, one would expect that the absorption peak of Trp shifted after mixing with GO. The UV–vis absorption peak of Trp in the presence of 30 μg/mL GO did show some small differences with the one without GO, as shown in Figure 5A. The absorption peaks of GO did not seem to be shifted, as shown in Figure 5B. On one hand, it was possible that one may not be able to observe clear differences of absorption due to the nature of the complex formed. On the other hand, one may not exclude the possibility that these small differences of UV–vis absorption of Trp were due to the experimental error. A similar observation was found for Tyr (Figure S-4 in the Supporting Information).

3.5. Hydrophobic Interaction Study between Trp and GO Using Pluronic F127 as a Screening. On the basis of the discussion above, there was a strong interaction between GO and Trp or Tyr. Both Trp and Tyr had a hydrophobic moiety, indicating that the hydrophobic interaction with GO

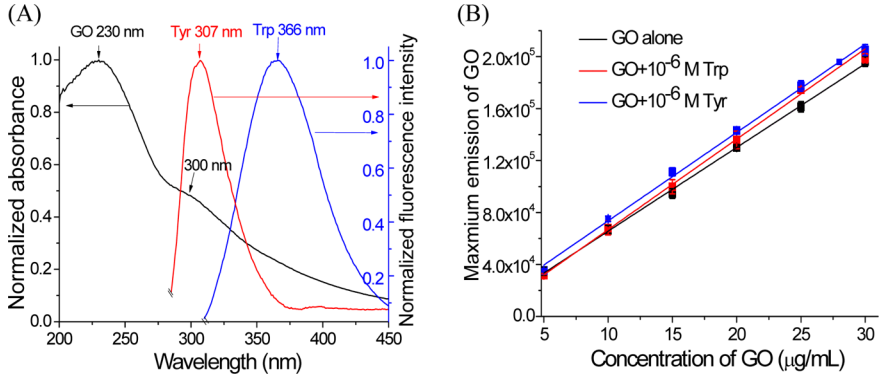

Figure 4. (A) Normalized UV–vis absorption spectra of GO aqueous solution (black) and normalized fluorescence emission of Tyr (red, excited at 270 nm) and Trp (blue, excited at 290 nm). (B) The fluorescence intensity of GO at the maximum without (black) and in the presence of 10^{-6} M Trp (red) and Tyr (blue), excitation wavelength of 425 nm.

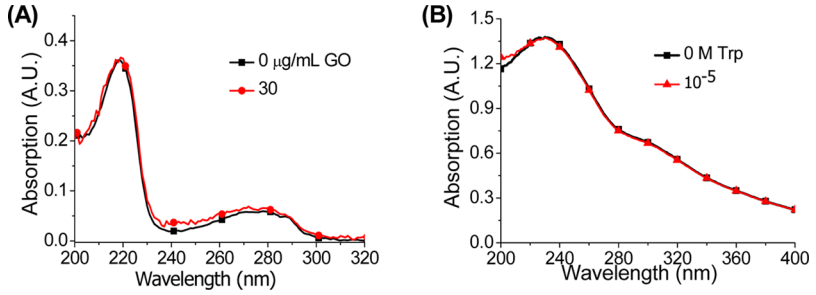

Figure 5. (A) UV−vis absorption spectra of 10^{-5} M Trp with and without the presence of 30 μg/mL of GO. Water and 30 μg/mL GO aqueous dispersion were used as the corresponding background solutions. (B) UV−vis absorption spectra of 30 μg/mL GO aqueous dispersion without and with the presence of 10^{-5} M Trp. Water and 10^{-5} M Trp were used as the corresponding background solutions.

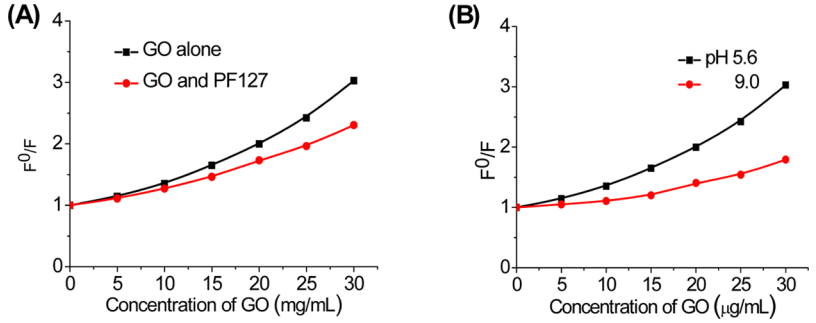

Figure 6. (A) Stern−Volmer plot of 10^{-6} M Trp against the concentration of GO alone and the mixture of GO/PF127 (1:1, w/w). (B) Stern−Volmer plot of 10^{-6} M Trp against the concentration of GO at pH 5.6 and 9.

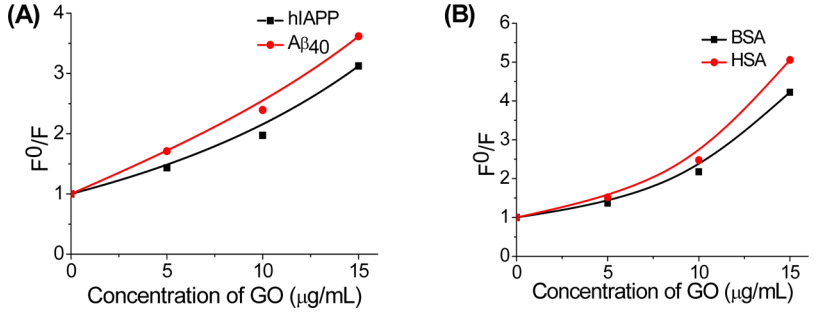

Figure 7. (A) Stern−Volmer plot of 10^{-5} M hIAPP and 10^{-5} M Aβ_{40} against the concentration of GO. (B) Stern−Volmer plot of 10^{-6} M BSA and 10^{-6} M HSA against GO.

might play a critical role during quenching. To verify this assumption, Pluronic F127 (PF127) was utilized to block the interaction between GO and Trp or Tyr, as PF127 was previously shown to have strong hydrophobic interaction with GO[32] and graphene.[33] PF127 was a triblock copolymer consisting of a central hydrophobic block of polypropylene glycol flanked by two hydrophilic blocks of polyethylene glycol. The hydrophobic segments had previously been shown to interact with the hydrophobic part of GO while the hydrophilic chains extended to the aqueous solution.[32] When mixing GO with PF127, the hydrophobic moiety of GO would be expected to be covered by the hydrophobic part of PF127, therefore screening the hydrophobic interaction between GO and Trp. As PF127 had no effect on the fluorescence emission of 10^{-6} M Trp in experiments (data not shown), one would expect to observe a lower quenching efficiency for the mixture of GO and PF127. Indeed, as shown in Figure 6A, the mixture of GO/PF127 (1:1, w/w) did have a lower quenching efficiency than the corresponding GO concentration without the presence of PF127. This observation supported the assumption that the added PF127 blocked the hydrophobic interaction between GO and Trp. A lower quenching effect of the mixture of GO and PF127 was also observed for Tyr, as shown in Figure S-5 in the Supporting Information.

3.6. Electrostatic Interaction Study between Trp and GO. Another possible interaction between GO and Trp during quenching could be electrostatic interaction. The carboxylic groups of GO were readily deprotonated when dispersed in water, making it negatively charged. If electrostatic interaction was important for the quenching, decreased quenching efficiency between GO and Trp at basic pH was expected, as GO and Trp were both negatively charged (the isoelectric point for Trp was 5.9). To eliminate any change of pH during mixing, all solutions were prepared at pH 9. The experimental results were shown in Figure 6B. As expected, the value of F^0/F was lower at pH 9 compared with that at pH 5.6, suggesting that electrostatic interaction did participate in the quenching process. Similar to Trp, the quenching efficiency between GO and Tyr at pH 9 was also lower than that at pH 5.6, as shown in Figure S-6 in the Supporting Information.

3.7. Fluorescence Quenching of Peptides and Proteins by GO. As GO has recently been exploited for drug delivery and near-infrared photothermal treatment for cancers and Alzheimer's disease,[9−11] the understanding of the biophysicochemical interaction between GO and peptides or proteins is fundamentally essential, especially for those drug- or disease-related peptides or proteins, such as amyloid peptides (Aβ) and human islet amyloid polypeptide (hIAPP). Aβ_{40} is the most abundant form of Aβ peptides, associated with Alzheimer's disease. hIAPP, a 37 amino acid residues peptide, is the major source of the amyloid deposits found in the islets of Langerhans of around 95% type 2 diabetic patients.[34] Both had only one fluorophore, the Tyr residue at position 10 for Aβ_{40} and position 37 for hIAPP in the amino acid sequence, respectively. Serum albumin is the most abundant protein in the circulatory system in mammals, contributing to the osmotic blood pressure and aiding in the transport, distribution, and metabolism of many endogenous and exogenous ligands.[35] Bovine serum albumin (BSA) and human serum albumin (HSA) have similar structures and are among the most widely used and characterized proteins in the pharmaceutical field.

When mixed with GO, the fluorescence of Tyr in peptides Aβ_{40} or hIAPP was quenched, as shown in Figure 7A. The emission maxima of both peptides were not shifted. The quenching meant that there was noncovalent interaction between GO and peptide Aβ_{40} or hIAPP, changing the chemical environment of Tyr residue. The difference of quenching efficiency should not be due to the charge differences of Aβ_{40} and hIAPP (The isoelectric points for Aβ_{40} and hIAPP were 5.4 and 8.8, respectively). Instead, the structure differences between Aβ_{40} and hIAPP were probably responsible for the quenching efficiency. The only Tyr residing in Aβ_{40} was located at the hydrophilic N-terminal domain (residues 1−28), which had six aromatic amino acid residues (three phenylalanine and three histidine). It was possible that there existed strong $\pi-\pi$ interaction or hydrophobic interaction between these residues and GO. While the Tyr residue in hIAPP was located at the hydrophilic domain of the C-terminus (residues 28−37), there was no aromatic residues in this domain for the interaction with GO.

GO could also strongly quench the fluorescence of BSA and HSA, with a higher quenching efficiency for HSA, as shown in Figure 7B. From the view of fluorescent spectroscopy, the main difference between these two proteins was the number of Trp residues. BSA had two Trp (Trp^{135} and Trp^{214}), and HSA only had one (Trp^{214}).[36] As the Trp^{214} in both proteins were located in a similar environment, the lower quenching efficiency of GO for BSA was considered to be due to the additional presence of the Trp^{135} in its sequence. Another possibility could be due to conformational changes of protein due to the interaction between GO and these proteins, decreasing the fluorescence intensity. On the basis of the observation of the quenching of fluorescent assay of amino acids, peptides, and proteins, it is possible that GO is a universal quencher for tryptophan or tyrosine related peptides and proteins.

4. CONCLUSION

In conclusion, GO was found to interact with amino acids (Trp and Tyr), peptides (Alzheimer's disease related Aβ_{40} and type 2 diabetes related hIAPP), and proteins (drug-related BSA and HSA) by fluorescence quenching. On the basis of the Stern−Volmer plot and fluorescence lifetime study between Trp or Tyr and GO, the main quenching mechanism was determined as static quenching, slightly combined with dynamic quenching (Förster resonance energy transfer). Both electrostatic interaction and hydrophobic interaction contribute to the interaction between Trp or Tyr and GO. The electrostatic interaction was confirmed by pH effect, while the hydrophobic interaction was proved by the presence of nonionic amphiphilic copolymer PF127. The strong hydrophobic interaction between GO and PF127 efficiently blocked the hydrophobic interaction between GO and Trp or Tyr, lowering the quenching efficiency. On the basis of the present study, it is possible that GO could be a universal fluorescent quencher for tryptophan or tyrosine related peptides and proteins.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental results of graphene oxide and Tyr. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

GO = graphene oxide
Trp = tryptophan
Tyr = tyrosine
Aβ_{40} = amyloid beta 1-40
PF127 = Pluronic F127
hIAPP = human islet amyloid polypeptide
BSA = bovine serum albumin
HSA = human serum albumin
FRET = Förster resonance energy transfer
PEG = polyethylene glycol

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