

Self-Assembly of Graphene Oxide with a Silyl-Appended Spiropyran Dye for Rapid and Sensitive Colorimetric Detection of Fluoride Ions

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Supporting Information

ABSTRACT: Fluoride ion (F^-) , the smallest anion, exhibits considerable significance in a wide range of environmental and biochemical processes. To address the two fundamental and unsolved issues of current F^- sensors based on the specific chemical reaction (i.e., the long response time and low sensitivity) and as a part of our ongoing interest in the spiropyran sensor design, we reported here a new F^- sensing approach that, via assembly of a F^- -specific silyl-appended spiropyran dye with graphene oxide (GO), allows rapid and sensitive detection of F^- in aqueous solution. 6-(*tert*-Butyldimethylsilyloxy)-1',3',3'-trimethylspiro [chromene- 2,2'-indoline] (SPS), a spiropyran-based silylated dye with a unique reaction activity for F^- , was designed and synthesized. The nucleophilic substitution reaction between SPS and F^- triggers



cleavage of the Si–O bond to promote the closed spiropyran to convert to its opened merocyanine form, leading to the color changing from colorless to orange-yellow with good selectivity over other anions. With the aid of GO, the response time of SPS for F^- was shortened from 180 to 30 min, and the detection limit was lowered more than 1 order of magnitude compared to the free SPS. Furthermore, due to the protective effect of nanomaterials, the SPS/GO nanocomposite can function in a complex biological environment. The SPS/GO nanocomposite was characterized by XPS and AFM, etc., and the mechanism for sensing F^- was studied by ¹H NMR and ESI-MS. Finally, this SPS/GO nanocomposite was successfully applied to monitoring F^- in the serum.

• he development of new methodologies for determination of anions is emerging as a research area of great importance because of the roles of anions in chemical and biological processes. Fluoride ion (F^-) , the smallest anion, exhibits considerable significance in a wide range of environ-mental and biochemical processes.¹⁻³ The soluble fluoride is considered as an essential micronutrient and is essential for body growth, but it is greatly toxic to the biological tissue if the concentration exceeds cellular requirements, which will cause many serious neurodegenerative diseases. For example, sodium fluoride can affect a number of essential cell-signaling components and disturb normal cellular metabolism at a higher concentration.⁴ Excess F⁻ could also produce ecological damage⁵ and cause dental or skeletal fluorosis,⁶ even nephrotoxic changes⁷ and urolithiasis⁸ in humans. Therefore, the detection of F^- has been the main focus of several research groups.

For the F^- detection, ion-selective electrode,⁹ a standard fluoride-indicating methodology, has been developed and recommended by the World Health Organization for critical information.¹⁰ However, this sensor responds to the fluoride activity in the internal electrode solution, not to the concentration. In addition, significant interference could appear with the presence of hydroxide ions.¹¹ There is still need for the

development of a new method for multipurpose determination of the anion. In the last few decades, simple and effective fluorescent or colorimetric sensors have been devised and utilized for F⁻ recognition and detection based on noncovalent or covalent interactions between the sensor molecules and F⁻, employing hydrogen bonding,¹² lewis acid coordination,¹³ chemical reaction,^{14–16} and quantum dots,¹⁷ as the attractive forces. Compared to noncovalent interaction, molecule recognition based on specific chemical reaction displays higher selectivity and stability^{15,18} and thus has recently attracted more attention by researchers.¹⁹

Pioneered by the seminal work of Yamaguchi and Tamao in 2000,^{14,15} it has been demonstrated that the Si–O bond can be broken by F⁻ through the specific nucleophilic substitution reaction between F⁻ and silica, making the Si–O containing derivatives attractive materials for F⁻ recognition and sensing with excellent selectivity. Hence, a number of sensors based on silylated dye have been designed.^{19–21} *tert*-Butyldimethylsilyl (TBDMS) or *tert*-butyldiphenylsilyl (TBDPS) was usually

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chosen as the F⁻ acceptor that was covalently attached to the chromophore or fluorophore molecule to render the dye unreactive to potentially interfering compounds and thus sensitive only to the presence of F⁻. Even though the silvlated dye has high selectivity and affinity toward F⁻, it is difficult to overcome the strong hydration effect of fluoride in aqueous environments, making the time necessary to reach equilibrium tens of minutes or even hours.²² For advanced, sophisticated approaches, employing surfactant micelles²³ and hydrogels²⁴ have recently been developed by Yang et al. to achieve the desired reaction speed; however, the systems are known as organic media and suffer from their intrinsic limits, such as poor long-term stability due to physical entrapment. Therefore, to further improve the performance of F⁻ detection in the complex biological environment, the development of a new sensing method that can alleviate these problems is highly desirable.

The current trend of nanoscale science has been the integration of functionalized nanomaterial and technology with biology and chemistry to develop new analytical tools. Graphene oxide (GO), a chemically exfoliated graphene derivative, exhibits good biocompatibility and low cytotoxicity,^{26,27} making GO attractive nanomaterials in analytical chemistry for biological applications, such as recognizing various analytes²⁸ and improving the catalytic activity of enzymes,²⁹ delivering drugs,³⁰ and exploiting intracellular imaging studies.³¹ Inspired by the success of the aforementioned work, and as a continuation of our studies on sensors based on carbon nanomaterials,³² herein, we present a new F⁻ sensing approach, coupling the specific molecule recognition ability of silvlated dyes and the unique features of GO to develop a nanocomposite for rapid and sensitive colorimetric detection of F⁻ in aqueous solution. In this paper, a TBDMSfunctionalized chromophore, 6-(tert-butyldimethylsilyloxy)-1',3',3'-trimethylspiro[chromene-2,2'-indoline] (SPS), was designed, and the SPS and GO hybrid nanocomposite (SPS/GO) was prepared and applied to F⁻ sensing. Significantly, the response time of SPS/GO for F⁻ was shortened from 180 to 30 min, and the detection limit was lowered more than 1 order of magnitude compared to the free SPS. Furthermore, due to the protective effect of nanomaterials, the SPS/GO nanocomposites can function in a complex biological environment, making it a promising material for bioanalytical applications.

EXPERIMENTAL SECTION

Materials and Apparatus. All chemicals were of analytical reagent grade and were supplied by Alfa Aesar or Sigma Aldrich. GO used in this work was purchased from Carbon Nanotechnologies, Inc. The solutions of anions were prepared from NaF, NaCl, NaBr, NaI, NaNO₃, NaHSO₄, AcONa, NaH₂PO₄, NaClO₄, respectively. They were dissolved in sterilized Milli-Q ultrapure water (18.2 M Ω) as stock solutions. Working solutions were prepared by successive dilution of the stock solution with Tris-HCl buffer (20 mM, pH 8.0).

Nuclear magnetic resonance spectra were recorded at 400 MHz and carbon spectra were recorded at 100 MHz on an Invoa-400 (Invoa 400) spectrometer. Mass spectra were obtained on an LCQ/Advantage high-performance liquid chromatography (HPLC)-mass spectrotometer. Atomic force microscopy (AFM) measurements were performed by using a Nanoscope Vmultimode atomic force microscope (Veeco Instruments). Samples for AFM images were prepared by depositing a dispersed SPS/GO solution onto a freshly cleaved

mica surface, allowing them to dry in air. Tapping mode was used to acquire the images under ambient conditions. Energydispersive X-ray (EDX) analysis was carried out using a HITACHI S-4500 instrument. UV—vis absorption spectra were recorded in 1.0 cm path length quartz cuvettes on a Hitachi U-4100 UV—vis spectrometer (Kyoto, Japan). pH was measured by model 868 pH meter (Orion).

Synthesis of SPS. The synthesis route of SPS is shown in Scheme 1 (for details see the Supporting Information). 6-

Scheme 1. Synthetic Pathways for SPS



Hydroxyl spiropyran (SP–OH) was synthesized via the Knoevenagel condensation reaction of 2,4-dihydroxybenzaldehyde and 1, 2, 3, 3-tetramethyl-3H-indolium in an 80% yield. To introduce the F^- reaction site to the spiropyran compound, *tert*-butyldimethylsilyl chloride was linked to SP–OH by the Williamson reaction, giving rise to the product of SPS in a 60% yield. The new synthesized compound was characterized by ¹H NMR and ESI-MS.

Preparation of SPS/GO Nanocomposite. GO nanosheets were synthesized from natural graphite by a modified Hummers' method,³³ and the characterization data as shown in Figure S1 (see the Supporting Information). The stock solution of GO (4.0 mg/mL) was obtained by sonicating the final product of GO for 2 h in Tris-HCl aqueous solution. The mixture solution of SPS and GO was obtained by the addition of 10 μ L of GO to 0.5 mL of SPS (10.0 μ M) solution. Then, the mixture was stirred for about 2 h. After centrifugation for three times with water, the SPS/GO nanocomposite and free SPS were further separated by the dialysis method, and then the product was dried under vacuum at 60 °C overnight. The structure feature and chemical composition of GO and SPS/ GO were characterized by AFM and EDX spectroscopy.

F⁻ Detection. GO was first sonicated in doubly deionized water for 2 h to give a homogeneous black solution. After the pretreatment, an aliquot of the freshly made GO suspension (less than 1%, v/v) was added to 1.0 mL of Tris-HCl buffer containing 10 μ M of SPS and the absorption spectra were then measured. Different concentrations of F⁻ were added to the complex system of GO and SPS for incubating at 25 °C for 30 min, and the absorption spectra were then measured. The addition was limited to 20 μ L so that the volume change was insignificant. To study the kinetics and time-dependence of the reaction between SPS and F⁻ in the absence and presence of GO, the absorption peak of mero form at 490 nm was recorded in 10% (v/v) CH₃CN/Tris-HCl solution. For determination of F⁻ in the real samples, bovine serum was diluted 10-fold, and the measurements were conducted 30 min after the addition of F⁻.

Analytical Chemistry

RESULTS AND DISCUSSION

Design of SPS/GO Sensor Platform. Spiropyrans, an important class of photoswitchable molecules, are an attractive starting point in construction of optical molecular sensors,³⁴ due to their reversible structure conversion between the closed spiropyran (spiro-) form and the opened merocyanine (mero-) form upon external optical, thermal, or chemical stimulation. In recent years, our group has developed a number of spiropyran fluorescent or colorimetric sensors for metal ions,³⁵ anions,³⁶ amino acids,³⁷ and GSH³⁸ by empolying the noncovalent host–guest interaction. However, this strategy has generally displayed moderate sensitivity and specificity over other competitive species, even interference. In the continuation of our studies of spiropyran sensors, we designed a new spiropyran derivative containing a silylate moiety as a unique reaction activity for F⁻. Scheme 2A showed the molecular structure of the new

Scheme 2. Possible Scheme of the Structure Conversion of SPS in (A) Polar Solvent and on (B) GO Surface Triggered by F^-



synthesized spiropyran compound, 6-(*tert*-butyldimethylsily-loxy)-1',3',3'-trimethylspiro[chromene-2,2'-indoline] (SPS), and the mechanism of structure conversion of SPS triggered by F⁻. The design strategy exploits the specific nucleophilic substitution reaction between F⁻ and SPS that triggers the cleavage of the Si–O bond and promotes the closed spiropyran to convert to the opened merocyanine form in the polar solvent, leading to the color changing from colorless to orange-yellow. However, in our primary experiment, we found that this F⁻ recognition process, as the common challenge, usually needed a few hours in aqueous solution to complete the detection process due to the low concentrations of the probe, which severely reduced the reaction rate between F⁻ and the silyl moieties.

In recent years, GO has been used to construct a sensing platform for detection of biomolecules by adsorbing lipophilic organic molecules on the surface. The abundance of carboxy, hydroxy, and epoxy groups on the surface of GO sheets makes the system more water-soluble, and these groups are the essential chemical skeletons for an ideal adsorbent,^{39,40} making the sensor molecule and the target enriched in GO surface with high concentration to bring some positive effects on the reaction rate of the detection process. Moreover, the high specific surface area of GO makes GO a promising material for a catalyzing reaction.⁴¹ Therefore, GO was employed to construct the rapid F^- sensing platform of SPS. The basic concept of the proposed approach was shown in Scheme 2B.

Due to the specific nucleophilic substitution reaction between SPS and F^- that occurs on the GO surface, the reaction rate between F^- and silicon ether was greatly accelerated.

F⁻ **Induced SPS Ring Opening.** The photophysical property of a spiropyran is related to the chemical structure of the molecule and the surrounding media, such as the solvent polarity and the nature of the substituents, displaying reversible structural transformation from the closed spiro form to the opened mero form, which has been shown to exhibit extremely sensitive absorption and color changes in the visible range. Figure S2 of the Supporting Information showed the UV–vis absorption spectra of free SPS in different organic solvents, and one could see that the free SPS was colorless with a strong absorption band at around 300 nm in either the polar or the nonpolar organic solvent, but no obvious absorption could be observed in the longer wavelength, reflecting that SPS mainly existed as the closed spiro form. Figure 1a showed the UV–vis



Figure 1. (A) UV–vis absorption spectra of (a) 10 μ M SPS in 10% (v/v) CH₃CN/Tris-HCl solution; (b) a + 5.0 × 10⁻⁴ M F⁻; (c) CH₃CN/Tris-HCl solution containing 40 μ g/mL GO; (d) c + SPS; and (e) d + 5.0 × 10⁻⁴ M F⁻. (B) Corresponding solution colors of a, b, c, d, and e.

absorption spectrum of SPS (10 μ M) in the Tris-HCl buffer solution (20 mM, pH 8.0) containing 10% CH₃CN (v/v); the absorbance was obviously weaker than that in the organic solvent due to the poor solubility in the aqueous solution, and no absorption in the visible region was observed. When NaF (500 μ M) was added to the SPS solution, as shown in Figure 1b, a new peak centered at around 490 nm ($\varepsilon = 2.6 \times 10^4$ M⁻¹ cm⁻¹) appeared, concomitant with the solution color changed from colorless into an orange-yellow color (Figure 1B), which indicated that closed SPS was activated by specific nucleophilic substitution reaction between the F⁻ and Si–O bond to give a free phenoxy anion. Then, the $p-\pi$ conjugation effect between the electron pair at the oxygen atom and the aromatic rings caused the structural transition from the closed form to the open mero form in the polar solvent (Scheme 2A).

The reaction mechanism of the as-proposed in Scheme 2A was confirmed by ¹H NMR and ESI-MS spectra. The ¹H NMR (Figure S3 of the Supporting Information) of SPS were exhibited upon reaction with F^- ; the chemical shift of the vinyl

protons at δ 5.60 ppm and δ 6.81 ppm were upfield shifted to δ 7.02 ppm and δ 7.52 ppm, respectively. And the corresponding protons of the *t*-butyldimethylsilyl group at the upfield (δ 0.7–1.1) disappeared after its removal by F⁻. Besides, the ESI-MS spectra for both the sensor and the product as shown in Figure S4 (see the Supporting Information). After treatment of SPS with F⁻, a new peak at *m*/*z* 293.20 appeared, corresponding to the merocyanine structure of SPS.

To assess the feasibility of SPS/GO nanocomposite for F⁻ detection, the effects of GO on the absorption spectra of SPS in the absence and presence of F^- were investigated. The GO dispersion displayed a maximum absorption at 231 nm and a shoulder at 290-300 nm (Figure 1c and Figure S5 of the Supporting Information), corresponding to the π - π * transition of aromatic C=C bonds and the $n-\pi^*$ transition of the C=O bond,⁴² respectively. Upon addition of GO to the SPS solution, no new absorption band could be observed, but the intensities of the 285-330 nm bands obviously increased (Figure 1d). After further increasing the GO concentrations, the absorbance increased gradually concomitant with the absorption band red shift (Figure S5 of the Supporting Information). We also noted that the intensities at the two bands of Figure 1d were greater than the sum of the absorbance of the above two individual systems of SPS (Figure 1a) and GO (Figure 1c), indicating that the solubility of SPS in aqueous solution has a considerable improvement due to the decoration of SPS on the GO surface to form the SPS/GO nanocomposite. Next, the effect of GO on the Si-O cleavage of SPS was studied. As shown in Figure 1e, reaction of SPS with 500 μ M F⁻ in the presence of GO, a very strong absorption band maximum centered at 490 nm appeared $(\varepsilon = 5.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$, and the absorbance was larger than that of SPS at this wavelength after reaction with F⁻. On the other hand, there was no difference in the position of the maximum absorption between the SPS system and SPS/GO system, suggesting that no structural perturbation of merocyanine molecules of SPS occurs in the presence of GO. This absorbance enhancement clearly indicated that it could achieve higher response sensitivity with the aid of GO than free SPS due to the improvement of the solubility and signal intensity of SPS in aqueous solution.

Effect of GO on the Si–O Cleavage Rate. Not only the response sensitivity but also the Si-O cleavage rate of of SPS by F⁻ was promoted by GO. To demonstrate, we evaluated the absorption enhancements of SPS by F⁻ as a function of time in the absence and the presence of GO. From Figure S6 (panels A and B) of the Supporting Information, the SPS absorbance around 490 nm increased gradually with time upon addition of F⁻ in the both cases, but there was a rather large difference in the response time and the intensity change for the same concentration of F⁻. Figure S6C of the Supporting Information compared the change of absorbance at 490 nm with time in the two cases. In the absence of GO, the SPS absorption enhancement reached maximum ($\Delta A = 0.27$) within 3.0 h after interaction with 500 μ M F⁻, while in the presence of GO in the SPS solution, a maximal absorbance enhancement of 0.49 was observed within and around 30 min. Moreover, rapid color change from colorless to orange-yellow in a very short time (about 10 min) could be observed in the SPS/GO system after addition of F- (Figure S6D of the Supporting Information), while producing an observable yellow color in the SPS system need about 2.0 h (Figure S6E of the Supporting Information).

To further study the effect of GO on the sensing system, the reaction kinetics of the structure conversion of SPS after

addition of F⁻ (500 μ M) in the absence and presence of GO was examined. As shown in Figure 2A, in the absence of GO,



Figure 2. Effect of GO on the reaction kinetics of F⁻ with SPS. (A) The time courses of the ring-opening reaction between 10 μ M SPS and 500 μ M F⁻ in the presence of different amounts of GO (0, 10, 25, and 40 μ g/mL) in 10% CH₃CN/Tris-HCl solution at 25 °C. Absorbance was recorded at 490 nm. (B) Kinetic plot of reaction of 10 μ M SPS with 500 μ M F⁻ in the presence of different amounts of GO ($(\bullet, 0; \blacktriangle, 10; \triangledown, 25; \text{ and } \blacksquare, 40 \, \mu$ g/mL). (C) Kinetic curves of SPS/GO (10 μ M) with different concentrations of F⁻ (0, 50, 100, 250, and 500 μ M) in the presence of 40 μ g/mL GO. (D) Plot of the apparent rate constant k' vs the concentrations of F⁻.

the absorbance at 490 nm reached its saturation value in about 3.0 h upon reaction with F⁻ at 25 °C. Then the effect of temperature on the response time was investigated, and the reaction rate constants^{43,44} (pseudo-first-order rate constants k'_{SPS} and pseudo-second-order rate constants k_{SPS}) at different temperature were calculated as shown in Table S1 of the Supporting Information, which indicated that the reaction rate could be improved as the temperature went up. However, high temperature is not conducive to the analysis of practical samples. When GO was presented to SPS solution at the fixed F⁻ concentration, the time to reach the equilibrium value sped up with the increasing GO amount, indicating that the reaction kinetics of SPS/GO with F⁻ was a GO-concentrationdependent manner. When the amount of GO reached 40.0 μ g/mL, the recognition process could be complete within 30 min with $k'_{\text{SPS/GO}}$ values as 2.45 × 10⁻³ s⁻¹, which was 24-fold faster than that of free SPS $(1.02 \times 10^{-4} \text{ s}^{-1})$ at 25 °C (Figure 2B). Then, the reaction kinetics of SPS with F⁻ were measured by varying the concentrations of F⁻ at the fixed GO amount of 40.0 μ g/mL (Figure 2C) to determine the pseudo-secondorder rate constants $k_{\text{SPS/GO}}$ for the reaction of SPS/GO with different concentrations of F⁻. As shown in Figure 2D, the plot of $k'_{SPS/GO}$ versus $[F^-]$ was a straight line passing through the origin, indicating that the reaction is second-order overall, firstorder with respect to nucleophilic substitution reaction, and second-order with respect to the ring-opening in the polar solvent, with $k_{\text{SPS/GO}} = 0.95 \text{ M}^{-1} \text{ s}^{-1}$. These results can most reasonably be attributed to rate-limiting attack of F⁻ at the Si-



Figure 3. AFM images and line profile of (A) GO, (B) A + SPS, and (C) B + F^- and the corresponding EDX data of (D) GO, (E) D + SPS, and (F) E + F^- .

O bond followed by cleavage of the C–O bond in the polar solvent to afford merocyanine form. Therefore, the results further proved that GO could accelerate the reaction rate for sensing F^- .

The F⁻ sensing kinetics of SPS/GO was analyzed to gain insight into the sped-up process. It could be explained by three possible mechanisms. First, GO shows good adsorption ability to aromatic compounds though $\pi-\pi$ stacking interactions, so GO can improve the solubility of SPS in aqueous solution which leads to the reaction concentration of SPS increase effectively. Second, GO provides a relatively hydrophobic reaction interface for the Si–O cleavage reaction, as that observed by Yang in organic medium.^{23,24} Finally, the high active surface area, multiple surface oxygen-containing functional groups, and unique electronic structure of GO presented the good catalysis toward organic reactions.^{29a}

Preparation and Characteristics of SPS/GO Nanocomposite. To achieve a real F⁻ sensor, the SPS/GO nanocomposite was prepared. The homogeneous GO dispersion was mixed with SPS solution, after being vigorously stirred for two hours; the SPS/GO nanocomposite and free SPS were separated by centrifugation and dialysis method. The prepared SPS/GO nanocomposite was characterized by UVvis absorbance measurements, atomic force microscopy (AFM), and energy-dispersive X-ray (EDX) spectroscopy. Firstly, the SPS/GO nanocomposite was established through UV-vis absorbance measurements. The dried nanocomposites dispersed in aqueous solution again, as shown in Figure S7 of the Supporting Information; the distinct characteristic absorption band of spiro form was observed, indicating that SPS was assembled onto the surface of GO successfully. The coverage of SPS on GO was calculated to be about 62.5% by comparing the

absorbance of SPS/GO before and after centrifugation and dialysis.

Then, the morphology and thickness of the GO and SPS/ GO nanocomposite were studied by AFM observation. As shown in Figure 3, the average thickness of the GO sheets is about 0.9 nm (Figure 3A), which is consistent with that observed by other researchers.⁴⁵ In comparison, the average thickness of SPS/GO in the absence and presence of F⁻ were determined to be about 1.8 nm (Figure 3B) and 1.4 nm (Figure 3C), respectively. There was a 0.9 nm increment compared with that of the unmodified GO, owing to the presence of SPS with a three-dimensional structure on the GO sheet surfaces. While, after reaction with F⁻, SPS was converted to the merocyanine form (MC) with a planar structure, and the average thickness of MC/GO decreased about 0.4 nm compared with SPS/GO. Considering that the thicknesses of the closed and opened forms of one SPS molecule were calculated to be 1.0 and 0.4 nm respectively, we could assume that GO sheets were covered by a monolayer of SPS and MC.

Energy-dispersive X-ray (EDX) spectroscopy was also employed to further explore the interactions between GO and SPS in the absence and presence of F⁻. The survey of GO showed the absence of any detectable amounts of Si at about 1.74 KeV and N at about 0.392 KeV (Figure 3D). Compared with GO, the survey of SPS/GO showed the presence of Si and N originate from SPS (Figure 3E), indicating that the noncovalent functionalization of GO by SPS successfully occurred. After reaction with F⁻, F⁻-mediated cleavage of the Si–O bond from SPS/GO led to nearly no detectable peak of Si (Figure 3F), due to the disappearance of the π - π stacking interaction between the *tert*-butyldimethylsilyl group and GO.

Performance of F^- Sensing with SPS/GO Nanocomposite. As spiropyran is sensitive to pH, the effect of the pH (from 4.0 to 10.0) on the signal response was first investigated. Figure S8 of the Supporting Information showed the absorbance at 490 nm of SPS/GO before and after the addition of F^- as a function of different pH values. At acidic conditions, spiropyran converted to its protonated merocyanine form (HME⁺), which was not in favor of sensing F⁻ because of the strong background signal at 456 nm. On the contrary, at alkaline conditions, spiropyran existed in the closed spiro form, resulting in the lack of appearance of an absorption band in the visible range, which would get a high signal-to-background after addition of F⁻. Therefore, the results indicated that the performance of SPS toward F⁻ work under a pH range from 7.0 to 10.0.

To demonstrate the applicability of the proposed approach for quantitative detection of F⁻, we measured the absorption spectra of SPS/GO containing F⁻ at varied concentrations. As shown in Figure 4A, the SPS/GO nanocomposite exhibited very weak absorption in the absence of F⁻; however, with the addition of F⁻, the absorbance around 490 nm gradually increased. Moreover, the obvious change could be observed at a sufficiently low concentration of 1.0×10^{-6} M in the absorption spectra, and the absorbance leveled off when the concentration



Figure 4. Sensitivity and selectivity of F⁻ detection with GO/SPS nanocomposite. (A) UV-vis absorption spectra of SPS/GO (10 μ M SPS, 40 μ g GO) in the presence of increasing amounts of F⁻ in 10% CH₃CN/Tris-HCl (v/v) aqueous solution (20 mM, pH 8.0). The arrow indicates that the signal changes with increases in F⁻ concentrations (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180, 200, 250, 300, and 400 μ M). (B) Absorbance enhancement $(A - A_0)$ of SPS and SPS/GO at 490 nm as a function of the concentrations of F^- , respectively. Here, A_0 and A are the absorbance of SPS in the absence and the presence of different concentrations of F⁻, respectively. The magnitudes of the error bars were calculated from the uncertainty given by three independent measurements. (C) Absorption spectra of SPS/GO after addition of selected competing anions (1.0 mM) in the 10% CH₃CN/Tris-HCl solution. Inset: the color change of SPS/GO solution after addition of selected anions (from left to right: F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, NO₃⁻, ClO₄⁻, AcO⁻, HCO_3^- , and $H_2PO_4^-$), respectively. (D) Absorbance enhancement, A $-A_0$, of SPS/GO at 490 nm by selected competing anions (1.0 mM, x axis markers) and the mixture of each competing anion (1.0 mM) and F⁻ (500 μM).

of F⁻ reached 4.0×10^{-4} M. This dynamic response range of SPS/GO was obviously better than the free SPS system which needed as high as 1.0×10^{-4} M F⁻ to produce an obvious change in the absorption spectra (Figure S9 of the Supporting Information). The calibration curves were also established by plotting the increment of absorbance at 490 nm versus F⁻ concentration (Figure 4B). One can see that the absorbance increased considerably as F⁻ with a good linearity concentration was raised from 5.0×10^{-6} to 1.0×10^{-4} M. The detection limit that was taken to be 3 times the standard derivation of a blank solution was estimated to be 8.6×10^{-7} M, which was much lower than the free SPS system for the detection of F⁻ (1.0×10^{-5} M), indicating that the SPS/GO nanocomposite is potentially appropriate for highly sensitive quantification of F⁻ in aqueous solution.

The selectivity of the nanocomposite described herein has been determined by examining the absorption response toward the common anions in the form of sodium salts, such as Cl⁻, Br⁻, I⁻, HSO₄⁻, NO₃⁻, ClO₄⁻, AcO⁻, HCO₃⁻, and H₂PO₄⁻. As shown in Figure 4C, the characteristic absorption peak at 490 nm accompanied with remarkable color response from colorless to orange-yellow was found only in SPS/GO holding F⁻ solution, and no other anions caused observable color changes, which indicated that nanocomposite can selectively target F⁻ due to the highly special affinity between fluorine and silicon. To further characterize the binding specificity of SPS/GO for F⁻, competition experiments were conducted in which SPS/ GO was first mixed with the competitive anion, and F⁻ was then added to the mixture. Figure 4D showed the absorption responses of SPS/GO toward F⁻ in the presence of other competitive anions. Evidently, the coexistence of these anions did not interfere with the sensing system of SPS/GO for F⁻ as well as the subsequent absorption enhancement. These results suggested that the SPS/GO nanocomposite can function as a high selective and anti-inference sensor for F-.

Preliminary Application. To extend the practical application of the SPS/GO nanocomposite, we performed the F^- sensing in 10% bovine serum. As shown in Figure S10 of the Supporting Information, SPS/GO exhibited excellent stability and anti-interference ability in the serum compared with free SPS, due to the protective effect of nanomaterials.⁴⁶ Upon addition of F⁻ to the serum-containing sample, the absorption spectra of SPS/GO displayed an obvious increase around 490 nm (Figure S10A of the Supporting Information), while only a slight change was observed in serum-containing SPS alone (Figure S10B of the Supporting Information). So the SPS/GO nanocomposite can serve as a good candidate for F⁻ detection in a complex system. Then, the nanocomposite was applied to quantitative determination of F⁻ in 1:10 dilution of bovine serum samples. The bovine serum samples were spiked with F⁻ at concentrations of 20.0, 50.0, and 100.0 μM and then analyzed by the proposed method and compared with the traditional F⁻ ion-selective electrode (ISE), which served as a referential standard. The results were shown in Table 1, which revealed high consistency in determination of the F⁻ in biological samples by the present approach and conventional instrument, demonstrating the excellent performace of this sensor in practical application.

CONCLUSION

In conclusion, a SPS/GO nanocomposite has been successfully prepared and applied to the F^- sensing in aqueous media. The nanomaterial as a novel nanosensor exhibited good solubility

Table 1. Detection of F⁻ in Bovine Serum Samples

sample	F ⁻ added (µM)	ISE (μM)	this method (μM)	recovery (%)
1	0	-	-	_
2	20.0	19.6 ± 0.5^{a}	18.5 ± 1.0	92.5
3	50.0	51.0 ± 1.2	47.8 ± 0.9	95.6
4	100.0	101.5 ± 1.6	96.2 ± 1.2	96.2
^{<i>a</i>} Mean \pm standard deviation of three determinations.				

and stability in the aqueous solution. Additionally, the SPS/GO could accelerate the reaction rate of F^- and silicon ether and showed higher sensitivity and a lower detection limit for detecting F^- in comparison with most of reported fluoride sensors. Furthermore, it showed an excellent anti-interference ability in complicated real samples. This nanosensor showed a great potential application in sensing analytes in a complex system rapidly and sensitively. More importantly, this approach could provide a new design strategy for developing a general platform to make the water-insoluble sensors detect the components in aqueous solution.

ASSOCIATED CONTENT

S Supporting Information

Experimental details and additional spectroscopic data as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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