A Nanodiamonds-Engineered Optical-Fiber Plasmonic Interface for Sensitivity-Enhanced Biosensing

Yaofei Chen, Lu Xiao, Longqun Ni, Lei Chen, Gui-Shi Liu, Jinde Yin, Peili Zhao, Yunhan Luo, and Zhe Chen

Abstract—Benefiting from the excellent characteristics such as low cytotoxicity, functionalization versatility, and tunable fluorescence, nanodiamonds (NDs) have shown enormous application potentials in the biomedical field. Herein, we propose, for the first time to our best knowledge, to integrate NDs on a plasmonic interface constructed on a side-polished fiber using drop-casting method. The NDs engineers the plasmonic interface towards improving the sensing field thus the sensitivity, which, moreover, is dependent on the number of drop-casting cycles (DCs) and the used concentration of NDs dispersion solution. Experimental results suggest that properly increasing the NDs dispersion concentration is beneficial to obtain a higher sensitivity while using a fewer number of DCs, but the excessive concentration extremely deteriorates the resonance dip. Using the 0.2 mg/mL concentration and 3 DCs, we achieve the highest RI sensitivity of 3852 nm/RIU, which shows an enhancement of 73.8% compared to the case without NDs modification. The sensitivity enhancement in biosensing is also proved by employing bovine serum albumin as a demo. The behind mechanism is explored via characterizations and simulations. This work opens up a new application form for NDs, i.e., integrating NDs with a plasmonic interface towards high-performance biosensing.

Index Terms—Nanodiamonds, sensitivity enhancement, side-polished fiber, surface plasmon resonance biosensing.

I. INTRODUCTION

Diamand is such a kind of atomic crystal composed of pure carbon atoms infinitely-extending in the way of regular tetrahedral bonding. When its size reduces to the nanometer scale, a new interesting carbon nanomaterial namely nanodiamonds (NDs), which has great research and application value, is formed [1]. In addition to inheriting the characteristics of bulk diamonds, NDs also have the advantages of large specific surface areas, ease of surface modification, low biological toxicity, and good biocompatibility, making them ideal materials for biomedical applications [2]. NDs indeed have presented broadband application prospects in drug loading and delivery [3], selective killing of cancer cells by photothermal therapy [4], inhibition of tumor cell migration [5] and so on. Especially, after introducing the negatively-charged nitrogen vacancy (NV-) center, NDs are able to emit high-brightness and unbleached fluorescence. Moreover, the fluorescence can be modulated or affected by microwave, magnetic field, temperature, etc., due to the unique quantum spin feature of NV- [6]. Exploiting this feature, it has shown great advantages in ultra-high sensitivity biosensing [7]. For example, B. S. Miller et al. utilized a microwave field to modulate the emission intensity of NDs, which were employed as the fluorescence labels of a lateral flow assay, and then conducted frequency-domain analysis to significantly enhance the ratio of signal to noise, achieving an enhancement of $\sim10^5$ in sensitivity when compared with the case using gold nanoparticles [8]. Based on the similar idea but using magnetic field to modulate, Y. Y. Hui et al. demonstrated a highly selective, quantitative, rapid and sensitive ($\sim1$ fM in 10 seconds) platform for lateral flow immunoassays of infectious diseases using NDs as reporters [9]. Moreover, L. Nie et al. proposed the use of NDs relaxometry to detect free radicals in cells and isolated organelles, enabling to distinguish the changes caused by biological variation and intervention [10]. All the above works suggest that NDs have become a new engine to boost the performance in biosensing.

As one of the powerful biosensing technologies, surface plasmon resonance (SPR) refers to an optics-physical phenomenon, which occurs at the metal/dielectric interface when the momentum matching condition between the incident light wave and surface plasma wave is satisfied [11]. Using magnetic field to modulate, Y. Y. Hui et al. demonstrated a highly selective, quantitative, rapid and sensitive ($\sim1$ fM in 10 seconds) platform for lateral flow immunoassays of infectious diseases using NDs as reporters [9]. Moreover, L. Nie et al. proposed the use of NDs relaxometry to detect free radicals in cells and isolated organelles, enabling to distinguish the changes caused by biological variation and intervention [10]. All the above works suggest that NDs have become a new engine to boost the performance in biosensing.
have the advantages of miniature size, remote sensing, and ease of alignment, thus attracting great attentions [12]–[14]. However, the intrinsic sensitivity for the conventional silica fiber SPR sensors is limited by the inherent structure and parameter of fiber. Among the various fiber SPR configurations, the side-polished fiber (SPF) SPR sensor is outstanding because its flat polished surface provides an ideal platform to be functionalized and engineered [15], which pave a way to the breakthrough of limitation in sensitivity. S. Q. Hu et al. designed a side-polished few-mode-fiber SPR sensor coated with a layer of Ag/TiO$_2$ hyperbolic metamaterials, and the plasmonic interface can be flexibly engineered by the metal filling fraction and the number of bilayers, theoretically improving the sensitivity to 5114.3 nm/RIU (1.33–1.40 RIU) at the optimized parameters [16]. Subsequently, the similar configuration was experimentally-implemented by C. Li and W. Yang et al., who fabricated an Au/Al$_2$O$_3$ or Ag/MgF$_2$ multilayer composite hyperbolic metamaterial on a D-shaped plastic optical fiber, achieving a sensitivity up to 4461 nm/RIU or 1875 nm/RIU during 1.34–1.356 RIU, respectively [17]–[18]. Moreover, only one pair of Ag/MgF$_2$ layer, where the MgF$_2$ layer was sandwiched between the Ag layer and a SPF to generate the long-range SPR, was also performed to improve the sensitivity [19]. Even so, the requirement of expensive equipment and complex manufacturing processes for precisely controlling the thickness of each layer within nanometer makes the sensors high cost and difficult to prepare.

In this paper, an SPF-based SPR biosensor, whose plasmon interface is engineered by NDs to enhance the sensitivity, is proposed. The NDs are modified on the plasmon interface by drop-casting method. The impact of the key parameters, including the concentration of NDs dispersion and the number of drop-casting cycles (DCs), on the performance of sensor characterizations and simulations. These work provides guidance for the designing of nanomaterials-engineered SPR sensor. The proposed sensor in this paper shows great potentials in the field of biomedical test with high sensitivity.

II. METHODS AND MATERIALS

A. Structure and Principle of the Sensor

As shown in Fig. 1, the sensor is composed of a side-polished fiber, a gold film layer coated on the polished surface, and a NDs layer modified on the gold film. The side polishing of the fiber not only leaks the evanescent field, which is originally confined in fiber, to interact with the surrounding media, but the resulted flat surface also provides an excellent platform for subsequently coating gold film and depositing NDs. At a specific wavelength $\lambda_R$, when the momentums between the light propagating in the fiber and the surface plasmon polariton (SPP) in the gold film match with each other, the SPR will occur. The p-polarized component of the light, whose electric field is perpendicular to side-polished surface, will be coupled with the SPP and be attenuated after propagating along the gold film/fiber interface within a certain distance due to relatively-high ohmic loss of gold. Consequently, a dip centered at $\lambda_R$ will be generated in the transmittance spectrum, which is extremely sensitive to the surrounding refractive index (RI) variation on the gold surface. The addition of NDs not only enhances the evanescent field at the plasmon interface, but increases the surface area as well, meaning an improvement of the carrying capacity to biological probes thus the sensitivity. Obviously, the NDs modification parameters have an important impact on sensitivity enhancement, which will be emphatically-explored in this work.

B. SPF-SPR Sensor

A self-developed wheel-based polishing system was used to the side-polishing of fiber. First, a piece of multi-mode fiber (SI2012-J, YOFC) with the core/cladding diameter of 105/125 $\mu$m was clamped by two fiber clamps. The left clamer was fixed, while the right one was mounted on a movable slider. To avoid breakdown of the MMF fiber during side-polishing, a tension controller is used to adjust the tension along the fiber by pushing the slider. Then, a polishing wheel, to which was affixed 6 $\mu$m particle size abrasive paper, was moved from the bottom to the midpoints of the MMF until the MMF was bent and had a 1–2 cm long section overlapped with the abrasive paper. The polishing wheel was then controlled by computer to rotate clockwise and anticlockwise to polish the MMF. The MMF was first coarsely polished for 5 mins and then finely polished for $\sim$120 mins. The residual thickness error of the fabricated SPF can be controlled within $\pm$0.5 $\mu$m.

Then a vacuum deposition machine (ZZS-700B, Chengdu Vacuum Machinery) was used to successively coat a layer of chromium ($\sim$5 nm) and gold ($\sim$50 nm) on the polished surface to complete the fabrication of SPF-SPR sensor, wherein the chromium layer was used to enhance adhesion between the SPF and the gold film. The prepared sensor was characterized with an optical microscope and a scanning electron microscopy (SEM). As shown in Fig. 2(a), the total length of the side-polished region is about 13 mm, including two symmetrical transition regions ($\sim$4 mm) and a flat region ($\sim$5 mm), where the residual thickness is measured as $\sim$73.2 $\mu$m. The cross-section of the SPF presents as a D-shape [Fig. 2(b)].

C. NDs and Interface Modification

The NDs powders were purchased from FND Biotech Inc. and the morphology was characterized by transmission electron microscopy (TEM). Overall, the NDs particles exhibit an irregular shape and a size of $\sim$35 nm [Fig. 2(c)]. We have additionally measured the diameter distribution of NDs using the dynamic
represents the effective RI of the
\( \text{imag}(\lambda) \) refers to the imaginary part of the effective RI; \( n_{\text{eff},i} \) is the number of modes, and we only consider the first 10 modes in the simulations (i.e., \( N = 10 \)). Before each DC, the NDs dispersion should be sonicated at least 30 mins to ensure its uniformity.

### D. Other Materials

In order to evaluate the sensing performance to RI, the ethylene glycol water solutions with various concentrations were prepared, and their RIs ranging from 1.331 to 1.379 were calibrated by an Abbe refractometer (NT52-975, Edmund Optics Co.) at room temperature. Besides, the bovine serum albumin (Jietewei Bioengineering Co.) solutions with different concentrations were prepared, and their RIs ranging from 1.331 to 1.379 were calibrated by an Abbe refractometer (NT52-975, Edmund Optics Co.) at room temperature. In Fig. 2(d), the average diameter of NDs is 35.6 nm with a standard deviation of 10.8 nm, agreeing well with the TEM result. The NDs modification layer was simplified to a dense diamond film model, and the NDs refractive index was selected as 2.4. The photonic crystal cladding was simplified to a uniform structure, and the cladding RIs 1.4457 and 1.4378, respectively. The finite element method (FEM, COMSOL Multiphysics) was employed to calculate the mode field and transmittance spectrum of the sensor. The RIs of the fiber core and cladding were set as 1.4457 and 1.4378, respectively. The dispersion relationship of the gold film adopted the Drude model, and the NDs refractive index was selected as 2.4. The NDs modification layer was simplified to a dense diamond film (see the Discussion for details). The transmittance at wavelength \( \lambda \) was calculated by the following formula [20]:

\[
T(\lambda) = \frac{1}{N} \sum_{i=1}^{N} \exp \left[ -\frac{4\pi}{\lambda} \text{imag}(n_{\text{eff},i})L \right]
\]  

where \( n_{\text{eff},i} \) represents the effective RI of the \( i \)-th mode; \( \text{imag}(n_{\text{eff},i}) \) refers to the imaginary part of the effective RI; \( L \) is the length of the flat side-polished region, namely 5 mm herein; \( N \) is the number of modes, and we only consider the first 10 modes in the simulations (i.e., \( N = 10 \)), which is reasonable because only the first few modes can be efficiently excited in a multi-mode fiber if a Gaussian beam is launched to the fiber end without radial offset [21].

### III. RESULT

First, the RI sensing performance of the sensors modified by various DCs using 0.2 mg/mL NDs dispersion were tested. The test results [Fig. 4(a)–(d)] indicate the number of DCs playing a significant role in the spectral response to RI. As the DC increases, the initial spectrum, which is defined as the one at 1.331 RIU, consistently shifts to the longer wavelength, suggesting that the plasmon interface can be regularly modulated by the NDs modification. Moreover, the spectral shift amount induced by a fixed RI variation increases with the DC, meaning a higher RI sensitivity. The sensitivity can be obtained by linearly fitting the resonant wavelengths and RIs as shown in Fig. 4(e), and it is significantly increased from 2061 to 3582 nm/RIU within the RI range of 1.331–1.379 RIU when the DC increases from 0 to 3, corresponding to an improvement of 73.8%. Since the resonant wavelength would move beyond the working wavelength range of 200–1100 nm. The sensor was fixed on a glass slide and at the same time, it was surrounded by UV glue to form an open sample cell. During test, a 200 \( \mu \)L RI sample or BSA solution was dropped in the sample cell, making the sensor completely immersed in the solution. Before changing the sample solution, the sample cell was repeatedly rinsed with deionized water or PBS solution and dried with a nitrogen gas gun. All the tests were performed at room temperature.

### F. Simulations

The finite element method (FEM, COMSOL Multiphysics) was employed to calculate the mode field and transmittance spectrum of the sensor. The RIs of the fiber core and cladding were set as 1.4457 and 1.4378, respectively. The dispersion relationship of the gold film adopted the Drude model, and the NDs refractive index was selected as 2.4. The NDs modification layer was simplified to a dense diamond film (see the Discussion for details). The transmittance at wavelength \( \lambda \) was calculated by the following formula [20]:

\[
T(\lambda) = \frac{1}{N} \sum_{i=1}^{N} \exp \left[ -\frac{4\pi}{\lambda} \text{imag}(n_{\text{eff},i})L \right]
\]  

where \( n_{\text{eff},i} \) represents the effective RI of the \( i \)-th mode; \( \text{imag}(n_{\text{eff},i}) \) refers to the imaginary part of the effective RI; \( L \) is the length of the flat side-polished region, namely 5 mm herein; \( N \) is the number of modes, and we only consider the first 10 modes in the simulations (i.e., \( N = 10 \)), which is reasonable because only the first few modes can be efficiently excited in a multi-mode fiber if a Gaussian beam is launched to the fiber end without radial offset [21].
TABLE I
COMPARISON OF THE TYPICAL SPR SENSORS WITH ENHANCED SENSITIVITY BY NANOMATERIALS

| SPR Configuration | Nanomaterials     | Detection range (RIU) | Sensitivity (nm/RIU) | Enhancement | Reference |
|-------------------|------------------|-----------------------|----------------------|-------------|-----------|
| Prism             | MoS₂             | 1.334-1.360           | 2793.5               | 30.7%       | [24]      |
| Prism             | GeSe             | 1.333-1.361           | 3581.2               | 79.5%       | [25]      |
| Prism             | Bi₂Se₃           | 1.333-1.361           | 2929.1               | 52.0%       | [26]      |
| Prism             | MoS₂             | 1.333-1.360           | 2524.8               | 36.3%       | [27]      |
| Prism             | Graphene oxides  | 1.333-1.360           | 2715.1               | 20.2%       | [28]      |
| SP-FMF            | HMM (Ag/ TiO₂)   | 1.334-1.361           | 5114.3               | 36.6%       | [16]      |
| SP-POF            | Graphene-HMM     | 1.340-1.352           | 4461                 | 119.4%      | [17]      |
| SP-POF            | HMM (Ag/MgF₂)    | 1.340-1.356           | 1875                 | 59.5%       | [18]      |
| SP-MMF            | MoS₂             | 1.332-1.359           | 2153.9               | 37.3%       | [29]      |
| SP-MMF            | NDs              | 1.331-1.379           | 3582                 | 73.8%       | This paper |

SP, side-polished; FMF, few-mode fiber; POF, plastic optical fiber; MMF, multi-mode fiber; HMM, hyperbolic metamaterials.

Fig. 4. (a)–(d) Spectral responses to RI for the sensors modified with 0.2 mg/mL NDs dispersion and 0–3 DCs, respectively. (e) The corresponding sensitivities obtained by linear fittings, and (f) the comparisons between the averaged sensitivities over multiple tests. (g) The surfaces of the sensors observed by an optical microscope.

of the spectrometer, no more than 3 DCs is performed. At each DC, the RI response test was repeated multiple times, and the measured sensitivity remained within a small error range, as shown by the error bars in Fig. 4(f). This indicates that the sensor has a good measurement repeatability. In other words, the NDs have been firmly modified on the surface of sensor, because the surface is sufficiently rinsed with deionized water before each RI test.

The surfaces of the sensors were observed under an optical microscope (MJ30, Mshot Photoelectric Technology Co.). It can be clearly seen from Fig. 4(g) that the increase in DC makes more NDs modified on the gold film surface, suggesting a stronger modulation on the plasmon interface thus an enhanced sensitivity, and the mechanism will be explored in the discussion section. Meanwhile, the surface roughness increases as well, leading to the full width at half maximum (FWHM) of the resonance dip rising from 103.1 to 204.9 nm when the DC was up to 3. Even so, because the sensitivity improves at the same time, the figure of merit (FOM), which is defined as FOM = Sensitivity/FWHM, only shows a little degradation (from 20.0 to 17.5).

The impact from the NDs dispersion concentration on the plasmon interface was investigated as well. We can obviously see that the color of the NDs dispersion gradually changes from transparent to opaque milky white as the increase of concentration [Fig. 5(a)]. The measured absorption and scattering spectra show that an increased concentration results in a stronger absorption and scattering, as shown in Fig. 5(b). Moreover, it is suggested that there is no obvious absorption peak similar to SPR dip located in the wavelength range of 450–1100 nm, which is exactly the range where the SPR occurs in our experiments.

We then modified and tested the sensors using other three NDs dispersion concentrations, i.e., 0.05, 0.1, and 0.5 mg/mL. For the case of 0.05 and 0.1 mg/mL concentrations, the resonance wavelength remains less than 1000 nm, i.e., within the working range of the spectrometer, without significant broadening or shallowing even after 6 DCs (see the Figs. S1 and S2 in the file posted on ArXiv [22]). The sensitivity continues improving from 2267 to 2648 nm/RIU for the case of 0.05 mg/mL concentration and from 2032 to 2564 nm/RIU for the 0.1 mg/mL, as the DC
Fig. 5. (a) Absorption and scattering spectrum of the NDs layer deposited on a glass slide using different dispersion concentrations. The spectrum of a clean glass slide is used as the control line. (b)–(c) The RI sensitivity varying with the number of DC at 0.05 and 0.1 mg/mL concentrations, respectively. (d) Sensitivity enhancement at various DCs for the sensors modified with 0.05, 0.1, and 0.2 mg/mL NDs concentrations. (e)–(g) For the sensors modified by 0 and 3 DCs using 0.2 mg/mL NDs dispersion, the spectral responses to the BSA concentrations and the corresponding sensitivities obtained by linear fitting. (h) Measured Zeta potentials of NDs dispersion, bare and NDs-modified gold surfaces of the sensors. The PH value was adjusted to 7.4, equaling to the one of PBS, during the Zeta potential measurements.

In our case, the sensitivity enhancement arises from the modification NDs on the sensor surface, and the mechanism behind it has been explored by characterizations and simulations as well. Through SEM characterization on the sensors surfaces that are modified with 0.2 mg/mL NDs and 0–3 DCs, it can be clearly observed that the NDs particles randomly stack and distribute on the sensor surface, and the coverage ratio of NDs particles on the surface increases with the DC [Figs. 6(a)–(d)]. Meanwhile, the thickness of the NDs modification layer rises from 99 to 176 nm [Fig. 6(e)–(g)].

Based on the above results, we developed a model for simulation as shown in Fig. 7(a). In the model, the ND particles layer that originally stacks on the gold surface in a loose state is simplified to a dense diamond dielectric layer, and simulated electric field amplitude distribution of the 1st p-polarized mode is also presented. An enhanced evanescent field that penetrates into the sample solution can be observed, proving the generation of SPR at the sensor surface. In addition, it has been confirmed that the sensitivity enhancement of 39.4% in BSA biosensing is smaller than that in RI sensing (~73.8%), and this is related with the NDs-modification-induced decrease of Zeta potential at the sensor surface. The Zeta potential of sensor surface reduces from ~19.8 to ~25.3 mV after modified with NDs, providing a stronger repulsive force to drive the BSA molecules, which are negatively charged in PBS solution, to leave the sensor surface.

Arousing from the $-1.0 \times 10^{-4}$ RIU/$^\circ$C thermo-optical coefficient of water, the $\pm 0.5 ^\circ$C temperature drift during the test, and the 3580 nm/RIU sensitivity, the temperature drift induced the resonant wavelength uncertainty of 0.36 nm, which was much smaller than the signals measured in our experiments. Even so, if a thermo-stabilized microfluidic system was used, the thermal fluctuation can be further controlled within $\pm 0.03 ^\circ$C [23], by which the influence induced is ignorable.

IV. DISCUSSIONS

In our case, the sensitivity enhancement increases from 0 to 6 [Fig. 5(c)–(d)]. However, when the NDs dispersion concentration rises to 0.5 mg/mL, the resonance dip at RI = 1.331 has almost shifted beyond the working range of spectrometer after 1 DC, and exhibits an obvious distortion, making the current sensor unsuitable for further test. This can be understood by that the high concentration makes more NDs modified on the plasmon interface, giving rise to a stronger absorption and scattering loss to surface plasmon wave.

The dependences of the sensitivity enhancement on the DCs and concentration are presented in Fig. 5(e), which suggests that although the sensitivity improvement can be obtained by repeating the DC, employing a higher concentration is more preferable because a less DC number is enough to achieve a larger enhancement. However, the concentration should be lower than 0.5 mg/mL to avoid the excessive distortion of the resonance dip. For the NDs (~35 nm in diameter) used in our experiments, the optimal NDs dispersion concentration is 0.2 mg/mL, at which the sensitivity can be improved by 73.8% after 3 DCs.

To characterize the biosensing performance, the BSA solutions with different concentrations were successively flowed over the sensor surface. The measured results [Fig. 5(f)–(h)] indicate that as the concentration of the BSA solution increases, the resonant wavelength shifts to the longer wavelength direction, and they show a good linear relationship. Moreover, the sensitivity of 0.3183 nm/(mg/mL) for the sensor modified with NDs using 0.2 mg/mL and 3 DCs is higher than the 0.2283 nm/(mg/mL) for the unmodified sensor, which proves the sensitivity enhancement effect of NDs modification layer in SPR biosensing. Note that the sensitivity enhancement of 39.4% in BSA biosensing is smaller than that in RI sensing (~73.8%), and this is related with the NDs-modification-induced decrease of Zeta potential at the sensor surface. The Zeta potential of sensor surface reduces from ~19.8 to ~25.3 mV after modified with NDs, providing a stronger repulsive force to drive the BSA molecules, which are negatively charged in PBS solution, to leave the sensor surface.

Arising from the $-1.0 \times 10^{-4}$ RIU/$^\circ$C thermo-optical coefficient of water, the $\pm 0.5 ^\circ$C temperature drift during the test, and the 3580 nm/RIU sensitivity, the temperature drift induced the resonant wavelength uncertainty of 0.36 nm, which was much smaller than the signals measured in our experiments. Even so, if a thermo-stabilized microfluidic system was used, the thermal fluctuation can be further controlled within $\pm 0.03 ^\circ$C [23], by which the influence induced is ignorable.

Authorized licensed use limited to the terms of the applicable license agreement with IEEE. Restrictions apply.
Fig. 6. (a)–(d) SEM images on the surface of sensors modified with 0.2 mg/mL NDs dispersion and 0–3 DCs, respectively. (e)–(g) SEM images on the section profile of the plasmon interface modified with 0.2 mg/mL NDs dispersion and 1–3 DCs, respectively. The scale bars in (b)–(g) all represent the 500 nm length.

sensitivity. By varying the diamond layer thickness in simulation model from 0 to 20 nm, which mimics the thickness and coverage increase of NDs modification layer in experiments, the electric field distribution of the fundamental mode in the vicinity of plasmon interface were obtained by simulations and presented in Fig. 7(b). It is found that the amplitude and penetration depth of the evanescent field are significantly enhanced by 80.3% and 55.6%, respectively, when the diamond layer thickness is changed from 0 to 20 nm. Not only the fundamental mode, but the high-order modes also exhibit the enhancement of evanescent field with the same behavior (please see Fig S3 in the file posted on ArXiV [22]). The above discussion well explain the mechanism for the sensitivity enhancement induced by the NDs modification.

The transmittance spectrum of the sensor and its response to RI were simulated as well. As shown in Fig. 7(b)–(e), redshift of the resonant wavelength occurs with the increase of the sample RI, and the addition of 10 nm diamond layer significantly improves the sensitivity from 3828 to 4637 nm/RIU with an enhancement of 21.1%, which further evidences the sensitivity enhancement mechanism coming from the modulation on plasmon interface by NDs modification layer. We also note that the thickness of the diamond layer used in the simulation is smaller than the measured value of NDs modification layer in Fig. 6(e)–(g). This arises from that in actual conditions NDs particles are randomly stacked on the gold surface with a loose state, whereas it is condensed as a diamond layer in our simulation model. Moreover, because only part of the modes transmitted in multi-mode fiber are considered and the light energy is assumed to be evenly distributed in each modes, the simulated sensitivity is higher and the resonance dip is deeper than those obtained in experiments. Even so, the simulated and experimental results agree well in trends, giving a theoretical insight into the NDs-engineered plasmon interface.

The comparison between the typical SPR sensors with sensitivity enhancement using nanomaterials has been presented in Table I. The sensor proposed in this paper possesses a competitive sensitivity with an outstanding enhancement. Compared to the prism-based SPR configuration, the all-fiber structure makes the proposed SPR sensor more integrated, miniaturized and portable. In addition, the plasmon interface can be flexibly engineered by varying the NDs dispersion concentration and the times of DCs, which is a more accessible method than that constructing a HMM using complex deposition technology for nanoscale multilayer [16]. Although the 2D materials, such as

![Fig. 7. (a) Schematic diagram of the developed simulation model and the electric field amplitude distribution of the fundamental p-polarized mode in the fiber. (b) The normalized 1D electric field amplitudes along the white dash line in (a), namely in the vicinity of plasmon interface, for the diamond layer thickness of 0, 10, and 20 nm, respectively. The resonant wavelengths chosen in simulations for 0, 10 and 20 nm diamond layer thicknesses are 577, 763, and 942 nm, respectively. From (b), we can obtain the penetration depth of 153, 207, 238 nm, and the maximal electric field amplitude of 0.066, 0.093, and 0.119 V/m, for the diamond layer thickness of 0, 10, and 20 nm, respectively. In (a) and (b), the RIs of the sample solutions are all set as 1.331. (c)–(e) Transmittance spectral response to the RI variation and the corresponding sensitivity obtained by linear fitting for the diamond layer thickness of 0 and 10 nm, respectively.](image-url)
the graphene, MoS2, and Bi2Se3 as shown in Table I, have also widely been demonstrated the potentials in improving SPR sensing performance, the NDs exploited in this work holds the specific advantage of ease of surface modification and functionalization, which provides more versatile strategies for biosensing.

V. CONCLUSION

A new application method of NDs that integrating NDs with a plasmonic interface for sensitivity-enhanced biosensing is introduced. In this work, the NDs is modified onto the surface of an SPF-SPR sensor using drop-casting method. Measurement results suggest that introducing NDs modification layer can obtain the sensitivity enhancement, which, moreover, extremely depends on the times of DCs and the concentration of NDs dispersion, because both of them play an important role in the thickness, occupation rate, and roughness of the ND layer. It is found that there exists an optimal concentration, at which the sensitivity can be enhanced to be a preferable level without the extreme deterioration of resonant dip. We have achieved a highest sensitivity of 3582 nm/RIU using 0.2 mg/mL concentration and 3 DCs by experiments. The biosensing is also proved with an improvement of 39.4% for the BSA sensing. Through characterization and simulation, the mechanism behind the sensitivity enhancement is mainly ascribed to the evanescent field engineered by the NDs modification layer. This work provides a clue for exploiting NDs towards high-performance SPR biosensing, and through further research such as on the specificity, accuracy, and sensing speed, it is expected to be applied in practical fields.

REFERENCES

[1] V. N. Mochalin, O. Shenderova, D. Ho, and Y. Gogotsi, “The properties and applications of nanodiamonds,” Nature Nanotechnol., vol. 7, no. 1, pp. 11–23, 2012.
[2] S. Kumar, M. Nehra, D. Kedia, N. Dilbaghi, K. Tankeshwar, and K.-H. Kim, “Nanodiamonds: Emerging face of future nanotechnology,” Carbon, vol. 143, pp. 678–699, 2019.
[3] V. S. Madamsetty et al., “Development of multigrain loaded PEGylated nanodiamonds to inhibit tumor growth and metastasis in genetically engineered mouse models of pancreatic cancer,” Nanoscale, vol. 11, no. 45, pp. 22006–22018, 2019.
[4] J. Li, R. Liu, Q. Zhao, Y. Shi, G. Gao, and J. Zhi, “Nanodiamond-based photosensitizer: Enhancing photodynamic therapy and inhibiting tumor metastasis,” Carbon, vol. 174, pp. 90–97, 2021.
[5] Q. Guo, L. Li, G. Gao, R. Liu, Y. Einaga, and J. Zhi, “Nanodiamonds inhibit cancer cell migration by strengthening cell adhesion: Implications for cancer treatment,” ACS Appl. Mater. Interfaces, vol. 13, no. 8, pp. 9620–9629, 2021.
[6] H.-C. Chang, W. W.-W. Hsiao, and M.-C. Su, Fluorescent Nanodiamonds, New York, NY, USA: Wiley, 2018.
[7] T. Zhang et al., “Toward quantitative Bio-sensing with nitrogen–vacancy center in diamond,” ACS Sensors, vol. 6, no. 6, pp. 2077–2107, Jun. 2021.
[8] B. S. Miller et al., “Spin-enhanced nanodiamond biosensing for ultrasensitive diagnostics,” Nature, vol. 587, no. 7835, pp. 588–593, 2020.
[9] Y. Y. Hui et al., “Magnetically modulated fluorescence of nitrogen-vacancy centers in nanodiamonds for ultrasensitive biomedical analysis,” Anal. Chem., vol. 93, no. 18, pp. 7140–7147, 2021.
[10] L. Nie et al., “Quantum monitoring of cellular metabolic activities in single mitochondria,” Sci. Adv., vol. 7, no. 1, 2021, Art. no. eabf0573.
[11] S. Zeng, D. Baillargeat, H.-P. Ho, and K.-T. Yong, “Nanomaterials enhanced surface plasmon resonance for biological and chemical sensing applications,” Chem. Soc. Rev., vol. 43, no. 10, pp. 3426–3452, 2014.
[12] L. Liu et al., “Ultrasonic detection of endocrine disruptors via superfine plasmonic spectral combs,” Light: Sci. Appl., vol. 10, no. 1, pp. 1–14, 2021.
[13] M. Lobry et al., “Plasmonic fiber grating biosensors demodulated through spectral envelopes intersection,” J. Lightw. Technol., vol. 39, no. 22, pp. 7288–7295, 2021.
[14] Y. Liu et al., “Plasmonic fiber-optic photothermal anemometers with carbon nanotube coatings,” J. Lightw. Technol., vol. 37, no. 13, pp. 3373–3380, 2019.
[15] J. Zhao et al., “Surface plasmon resonance refractive sensor based on silver-coated side-polished fiber,” Sensors Actuators B Chem., vol. 230, pp. 206–211, 2016.
[16] S. Hu et al., “High-performance fiber plasmonic sensor by engineering the dispersion of hyperbolic metamaterials composed of Ag/TiO2,” Opt. Exp., vol. 28, no. 17, pp. 25562–25573, 2020.
[17] C. Li et al., “Optical fiber SPR biosensor complying with a 3D composite hyperbolic metamaterial and a graphene film,” Photon. Res., vol. 9, no. 3, pp. 379–388, 2021.
[18] W. Yang et al., “High performance D-type plastic fiber SPR sensor based on a hyperbolic metamaterial composed of Ag/MgF2,” J. Mater. Chem. C, vol. 9, pp. 13647–13658, 2021.
[19] H. Zhang et al., “Long-Range surface plasmon resonance sensor based on side-polished fiber for biosensing applications,” IEEE J. Sel. Topics Quantum Electron., vol. 25, no. 2, pp. 1–9, Mar./Apr. 2019.
[20] J. Dong et al., “Side-polished few-mode fiber based surface plasmon resonance biosensor,” Opt. Exp., vol. 27, no. 8, pp. 11348–11360, 2019.
[21] A. Amphawan, F. Payne, D. O’Brien, and N. Shah, “Derivation of an analytical expression for the power coupling coefficient for offset launch into multimode fiber,” J. Lightw. Technol., vol. 28, no. 6, pp. 861–869, 2009.
[22] Y. Chen et al., “A nanodiamonds-engineered optical-fiber plasmonic interface for sensitivity-enhanced biosensing,” 2022, arXiv:2202.13583.
[23] F. Chiavaioli, C. A. J. Gouveia, P. A. S. Jorge, and F. Baldini, “Toward a uniform metrological assessment of grating-based optical fiber sensors: From refractometers to biosensors,” Biosensors, vol. 7, no. 2, 2017, Art. no. 23.
[24] Y. Chen et al., “MoS2 nanosheets modified surface plasmon resonance sensors for sensitivity enhancement,” Adv. Opt. Mater., vol. 7, no. 13, 2019, Art. no. 1900479.
[25] Y. Zhao, S. Gan, L. Wu, J. Zhu, Y. Xiang, and X. Dai, “GeSe nanosheets modified surface plasmon resonance sensors for enhancing sensitivity,” Nanophotonics, vol. 9, no. 2, pp. 327–336, 2020.
[26] J. Zhu et al., “Topological insulator overlayer to enhance the sensitivity and detection limit of surface plasmon resonance sensor,” Nanophotonics, vol. 9, no. 7, pp. 1941–1951, 2020.
[27] Y. Luo et al., “Sensitivity-enhanced surface plasmon sensor modified with mos2 overlayer,” Opt. Exp., vol. 26, no. 26, pp. 34250–34258, 2018.
[28] X. Xiong et al., “Plasmonic interface modified with graphene oxide sheets overlayer for sensitivity enhancement,” ACS Appl. Mater. Interfaces, vol. 10, no. 41, pp. 34916–34923, 2018.
[29] Y. Zhang et al., “Sensitivity-enhanced fiber plasmonic sensor utilizing molybdenum disulfide nanosheets,” J. Phys. Chem. C, vol. 123, no. 16, pp. 10536–10543, Apr. 2019.