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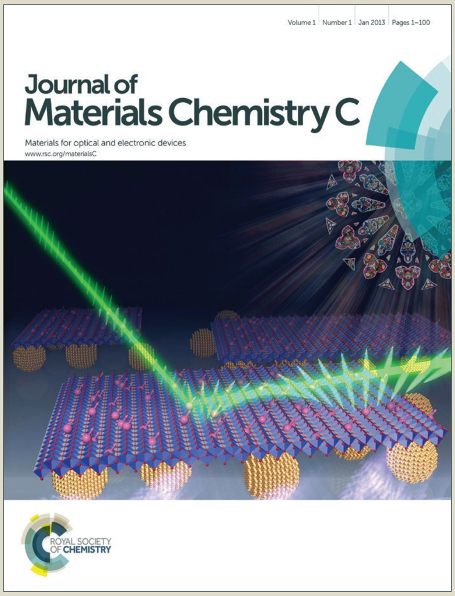

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Functional Hydrogel Film Attached with 2D Au Nanosphere Array and Its Ultrahigh Optical Diffraction Intensity as a Visualized Sensor

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A free standing 2D Au nanosphere array/hydrogel composite sensing film was prepared by attaching a 2D Au nanosphere array onto a polyacrylic acid (PAAc) hydrogel film, which could be used as visualized sensors. These 2D Au nanosphere array/hydrogel composite films displayed visually diffraction color and much stronger diffraction intensity due to their periodic structures and large scattering cross section of Au nanosphere. Their diffraction intensity was increased by more than one order of magnitude (88 times) than that of 2D PS sphere array/hydrogel composite film to external stimuli, which is useful to visual observation by naked eyes and further optical characterization. Such 2D Au nanosphere array/hydrogel composite films exhibit ultrahigh diffraction intensity to make them be used for visual determination of analyte. The presented strategy could be extended to develop different visualized sensors based on various functional hydrogel films.

1. Introduction

Responsive photonic crystals (RPCs) as chemical and biological sensors with fast, reversible optical changes in response to environmental stimuli have attracted intense interest due to their remarkable potential applications for visually identifying and quantifying chemical molecules or biological agents[1-11]. Generally, photonic crystals (PCs) can exhibit brilliant color, which is called structural color due to Bragg diffraction caused by periodic structures of PCs[12]. So the analytes could be detected by color changes caused by various periodic lengths of RPCs[13]. This is a facile, inexpensive approach to rapidly detect target analytes. Additionally, RPCs also can be tailored to selectively respond to various external stimuli, such as humidity[4], temperature[5], organic solvents[12], pH values[6,7,8], ionic strength[9], pressure[10], 3-Pyridinecarboxamide[14], metal ions[15,16], glucose[17-23], light and magnetism[24], according to the different requirements. Until now, most of related research have focused on utilizing three-dimensional (3D) PCs to prepare hydrogel RPCs (HPCs)[12,16,25,26]. 3D HPCs consist of a hydrogel network embedded with 3D PCs, creating by self-assembly of monodispersed colloidal microspheres, which cause the visible light diffraction. The hydrogel carriers are functionalized with the appropriate molecular recognition agents[15], leading to change of hydrogel volume or refractive index in response to corresponding target analytes due to interactions between the analysts and functionalized hydrogel[16], which shifts the diffraction wavelength and causes the changes of diffraction color in visible range[27]. However, the formation of the 3D PCs embedded in hydrogel is quite time consuming and it is difficult to prepare uniform 3D PCs/functionalized hydrogel composites[1,28], which limits their further applications as sensors.

Recently, much attention has been paid to two-dimensional (2D) HPCs with fast detection to the analytes as well as easy fabrication and functionalization due to the simple preparing procedure, low cost and high production efficiency of 2D PCs compared with traditional 3D PCs[15,28]. 2D HPCs could be prepared by directly incorporating the 2D PCs into stimulus-responsive hydrogel, so the constructed 2D HPCs could be acted as optical sensors for various external stimuli. Furthermore, 2D HPCs were successfully fabricated to visually detect analytes such as pH value[15,29], temperature[15], Pb^{2+}[15,30], chemical and biological species[1,28,31,32,33]. For instance, Asher et al. prepared the poly(acrylamide-co-acrylic acid) (PAAm-co-AAc) hydrogel film embedded with a monolayer polystyrene (PS) colloidal crystal, demonstrating diffract light in the visible spectral region under changes of pH values[15]. In a certain pH value, the interspace among adjacent microspheres in monolayer colloidal crystal will increase or decrease in the hydrogel composite system due to the volume changes. The interspace change between two adjacent microspheres can be visually monitored by changes of the diffraction light color. In a similar approach, Xue et al. applied a 2D PS array onto hydrogel film modified with phenylboronic acid (PBA) to develop a visual glucose sensor[28]. The rapid changes of structural color and diffraction wavelength quickly offer synchronized signals when such 2D HPCs suffered the

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external environmental stimuli, which have potential applications in sensors. However, the reported 2D HPCs sensors are limited to 2D monolayer PS colloidal crystals, which have relatively low scattering cross section. The high reflective mirror, such as Al or Au mirror, was applied on such 2D HPCs and the diffraction intensity was increased to some extent during the diffraction measurement and color identification process[15,28,29,31,33], but the diffraction intensity is still not strong due to the low scattering cross section of PS itself. As for the design of sensors, high diffraction intensity is an important factor to determine sensitivity. Therefore, it still keeps a great challenge to obtain the high diffraction intensity for the 2D HPCs sensors made of 2D periodic arrays.

In this work, we develop a strategy to prepare an interesting, free standing 2D periodic Au nanosphere array/hydrogel composite sensor. The 2D Au nanosphere array was prepared using monolayer colloidal crystal as a template and it was coated onto stimulus-responsive hydrogel film to form 2D periodic Au nanosphere array/hydrogel composite system, which displayed visually diffraction color and much stronger diffraction intensity without using high reflective mirror to external stimuli. The diffraction intensity of 2D periodic Au nanosphere array/hydrogel composite sensor on a quartz slide was increased by more than one order of magnitude (88 times) than that of 2D PS sphere array/hydrogel composite film on Al mirror. Such high diffraction intensity originates from the large scattering cross section of Au and periodic structure of Au nanosphere array and it is highly helpful for visual observation by naked eyes and further quantitative detection by monitoring the diffraction peak position and intensity. This presented synthesizing route is universal and could be extended to various functional hydrogel to further develop different sensors. Herein, taking polyacrylic acid (PAAc) hydrogel with attached 2D Au nanosphere array to response to pH as an example, we show that the free standing 2D Au nanosphere array/hydrogel composite sensing film can be formed by the strategy presented in this work. To the best of our knowledge, this is the first report on 2D Au nanosphere array/hydrogel composite sensor with diffraction wavelength and diffraction color variation induced by pH change.

2. Experimental

2.1 Materials

Polystyrene (PS) microspheres with diameter of 350 nm in aqueous suspension (2.5 wt%) were purchased from Alfa Aesar Corporation. Acrylic acid (AAc), dimethyl sulfoxide (DMSO), sodium hydroxide, boric acid, phosphoric acid and acetic acid were obtained from Sinopharm Chemical Reagent Co, Ltd. N, N'-methylenebisacrylamide (MBAAm) was purchased from Aladdin Industrial Corporation. 2-hydro-xy-1-[4-(2-hydroxyethoxy)-phenyl]-2-methyl-1-propanone (Irgacure 2959) was obtained from Tianjin Heowns Biochemical Technology Co., Ltd. They were directly used without further purification. Water (18.2MΩ•cm) was obtained from an ultrafilter system (Milli-Q, Millipore, Marlborough, MA).

2.2 Preparation of 2D PS monolayer colloidal arrays

The 2D PS monolayer colloidal array was prepared on a cleaned glass slide by an air/water interfacial self-assembly method, as previously reported[34-45]. Briefly, the aqueous PS microsphere suspension and alcohol were mixed at a volume ratio of 1:1. An appropriate amount of deionized water was dropped onto a cleaned glass slide. Then PS microsphere suspension was applied onto the water surface drop by drop and a 2D PS monolayer colloidal crystal was thus fabricated by self-assembly at air-water interface. Finally, it would stay on the substrate after complete evaporation of water at room temperature (Fig. 1a).

2.3 Preparation of 2D periodic Au nanosphere array

Firstly, an as-prepared 2D PS colloidal crystal was transferred onto a SiO_2 substrate from the glass slide using water surface as a media[46,47] (Fig. 1b). Subsequently, a thin layer of Au was deposited on the 2D PS colloidal crystal with the supporting substrate by using an ion-beam coater (Fig. 1c). The 2D PS colloidal array with Au coating on SiO_2 slide was then annealed in air at 450° for 2 hours, during the annealing process, the PS spheres were decomposed and removed in the array. In the meantime, most of the deposited Au layers on them were melted and formed spherical nanoparticles driven by the principle of surface free energy minimum in-situ. 2D periodic Au nanosphere arrays were finally created in-situ on the substrate (Fig. 1d).

2.4 Preparation of 2D Au nanosphere arrays on hydrogel films

Polymerization solution was prepared by mixing 5 ml H_2O, 5 ml AAc, 0.08 g MBAAm and 500 µL Irgacure 2959 (0.33 g Irgacure 2959 in 1 ml DMSO). The polymerization solution was carefully cast onto 2D Au nanosphere array on SiO_2 substrate. Then another glass slide was carefully placed on the top of the polymerization solution on 2D Au nanosphere array. The solution was photopolymerized for 30 min at room temperature by using UV Lamp (365 nm, 16 w) (Fig. 5e). 2D Au nanosphere array/hydrogel composite sensing film could be prepared and it could be peeled off from the substrate to form a free standing film (Fig. 1f).

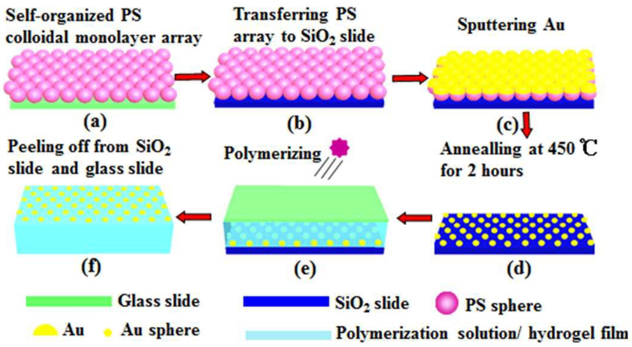

Fig. 1 Preparation of 2D Au nanosphere array/hydrogel composite sensing film: (a) 2D PS monolayer colloidal crystal was fabricated on a cleaned glass slide by an air/water interfacial self-assembly method; (b) The 2D PS microsphere array was transferred onto a SiO_2 substrate; (c) A layer of Au was deposited on the 2D PS colloidal array; (d) The 2D PS colloidal array with Au coating was annealed at 450° for 2 hours, and 2D Au nanosphere array was formed in-situ on the substrate; (e)Polymerization solution was cast on the Au nanosphere array and photopolymerized into hydrogel with irradiation of UV light; (f) A free standing 2D Au nanosphere array/ hydrogel composite film was obtained by peeling it off from the substrate.

2.5 Characterization

The morphologies of as prepared samples were characterized by a field-emission scanning electron microscope (FESEM, Sirion200) after depositing a thin layer of Au for the good electric conductivity. UV-vis absorption spectra were measured on Cary 500 (Varian). The measurements of diffraction spectra were conducted at a fixed angle utilizing an Idea Optics PG2000-Pro-EX Spectrometer, R1-A-UV Support and Halogen & Deuterium Light Source. Diffraction measurements were performed in the Littrow configuration by using two arms at the same direction. One arm excites white light and another arm collects the diffracted light with a semi-transparent mirror. The measurement angle between the probe and the normal direction to the samples is 32°. To characterize the response of the 2D array/hydrogel composite film to pH, the as prepared samples were immersed in Britton-Robinson (B-R) buffer solutions with different pH values. The 2D array/hydrogel composites were equilibrated overnight before diffraction measurements.

3 Results and discussion

3.1 2D Au nanosphere array/hydrogel composites

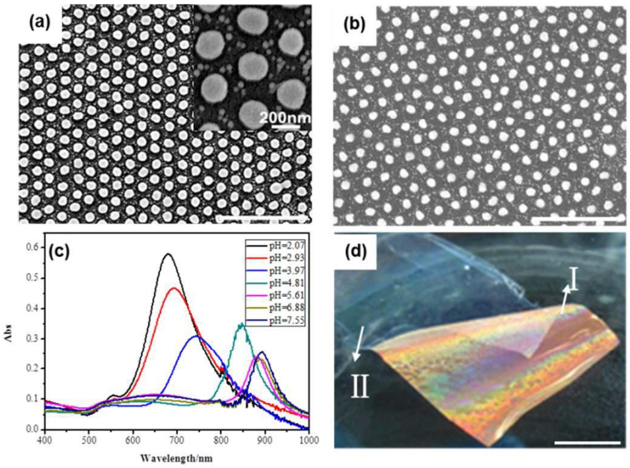

Fig. 2 (a) SEM image of 2D Au nanosphere array templated from the 2D monolayer colloidal crystal with a periodic length of 350 nm (Inset: SEM image with high magnification); (b) SEM image of 2D Au nanosphere array/hydrogel composite film, the scale bars are 2 μm in (a) and (b) ; (c) Absorption spectra of 2D Au nanosphere array/hydrogel composite films at different pH values: 2.07, 2.93, 3.97, 4.81, 5.61, 6.88 and 7.55; (d) Photograph of hydrogel films embedded with 2D Au nanosphere array (Ⅰ) and PS microsphere hncp array (Ⅱ) in water at the same time, the scale bar is 1cm.

Fig. 2a shows 2D Au nanosphere array on a SiO_2 substrate. One can find that Au nanospheres with size of ca. 200 nm demonstrated the hexagonal non-closed-packed (hncp) arrangement and the whole 2D Au nanosphere array kept a good ordering on the substrate. During the annealing process, each PS sphere was decomposed and removed in the array, and most of the Au coating on it was melted and formed a spherical nanoparticle driven by the principle of surface free energy minimum in-situ. Hence the 2D Au nanosphere array was prepared on the substrate, however, please note that there still existed some discrete tiny nanoislands (ca. 20 nm) without ordering distributed among Au nanosphere array on the substrate. Fig. 2b shows 2D Au nanosphere array/hydrogel composite film and it reflects that the 2D periodic Au nanosphere array was successfully transferred onto the hydrogel to form the composite sensing film by the polymerization process. Although these discrete Au nanoislands were also attached on hydrogel film surface, they would make a negligible positive contribution to the diffraction intensity and peak position due to their disordered distribution, which was further confirmed by our results. Fig. 2c displays the absorption spectra of as prepared 2D Au nanosphere array/hydrogel composite sensor at B-R buffer solution with different pH values. Each curve of absorption spectra of the films shows two peaks. The first one (ca. 540 nm) comes from the localized surface plasmon resonance (LSPR) of Au nanosphere and the second one originates from the diffraction of the 2D ordered structures of Au nanosphere array[48]. The LSPR peaks of 2D Au nanosphere array/hydrogel composite film are almost in the same position with increasing of pH value. But the second one, i.e. diffraction peak, is more sensitive to periodic length of Au nanosphere array. When the pH value of the B-R solutions was increased from 2.07 to 7.55, the diffraction peaks were produced and gradually red shifted. At pH value of 2.07, a diffraction peak centered at 679 nm was observed and it shifted to 893 nm when pH value increased to 7.55. The red shift was caused by the increased Au nanosphere interspace due to the swelling of hydrogel caused by ionization of pendant carboxyl groups. Ionization of carboxyl groups immobilized counterions inside the hydrogel. This resulted in an osmotic pressure, which swelled the gel against its restoring elastic constant[9,15]. Thus, an increased pH value increases the ionization, leading to the gel swell, further resulting in the diffraction red-shift. These shifts originated from the swelling of the hydrogel in response to the pH increase, in agreement with previously reported works by Asher[9,15] and Claire Mangeney[49].

As a comparison, hydrogel film embedded with 2D hncp PS sphere array with the similar diameter of particle and periodic length to 2D hncp Au nanosphere array was also prepared, as demonstrated in supporting information (Fig. S1, S2). Fig. S2a shows 2D hncp PS microsphere array obtained by reactive ion etching (RIE) of hexagonal closed-packed (hcp) monolayer colloidal crystal. One can see that the PS spheres had the similar diameter to Au particles and the 2D hncp PS sphere array had the same periodic length as 2D Au nanosphere array. Such 2D hncp PS sphere array was transferred onto the hydrogel film, as displayed in Fig. S2b. It indicated the 2D PS hncp PS spheres embedded in hydrogel film kept well ordering. Fig. S2c demonstrated the absorption spectra of 2D hncp PS microsphere array/hydrogel composite film at B-R buffer solution with different pH values. There were no obvious diffraction peaks and there only existed the peaks of 870 nm originated from absorption of PAAc hydrogel film. Additionally, the hydrogel embedded with 2D Au nanosphere array displayed very strong iridescent color, but the one embedded with 2D hncp PS sphere array showed very weak color (Fig. 2d). The resulting strong iridescent color of the hydrogel embedded with 2D Au nanosphere array makes it may realize diffraction measurement or visual detection without high reflective mirror.

3.2. Enhanced optical diffraction intensity

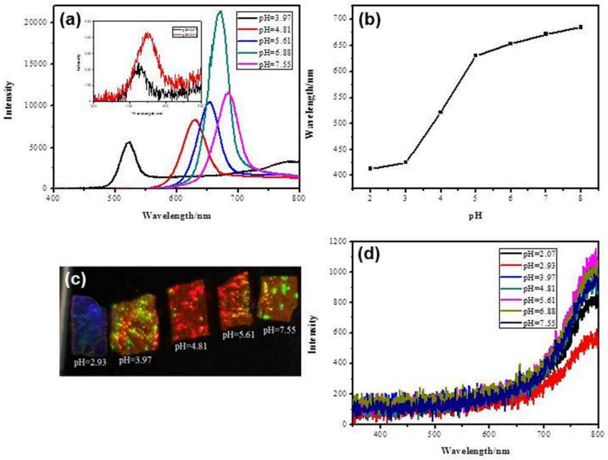

Fig. 3 (a) Diffraction spectra of 2D Au nanosphere array/hydrogel composite films on a quartz slide measured in the Littrow configuration by using two arms at the same direction at pH value: 3.97, 4.81, 5.61, 6.88 and 7.55; The inset in (a) is the diffraction spectra of 2D Au nanosphere array/hydrogel composite films at pH value: 2.07, 2.93; (b) pH dependence of the diffraction wavelength of the 2D Au nanosphere array/hydrogel composite films after equilibration in different pH buffer solutions; (c) photograph of 2D Au nanosphere array/hydrogel composite films at pH: 2.93, 3.97, 4.81, 5.61 and 7.55; (d) Diffraction spectra of 2D hncp PS array/hydrogel composite films on quartz slide at pH value: 2.07, 2.93, 3.97, 4.81, 5.61, 6.88 and 7.55 obtained by the same measurement route as Au nanosphere array/hydrogel composite films.

To obtain more information about the optical diffraction intensity of hydrogel sensing film attached with 2D Au nanosphere array, diffraction spectra of 2D array/hydrogel composites embedded with 2D Au nanosphere array were performed in the Littrow configuration by using two arms at the same direction, as displayed in Fig. 3a. In this measurement, one arm excites white light and another arm collects the diffracted light with a semi-transparent mirror. Bragg diffraction will occur when lights with certain wavelengths illuminate the corresponding matched periodic structure. In this Littrow configuration, the diffraction of the 2D periodic array can be calculated by the following formula, $m\lambda = \sqrt{3}d\sin\theta$, where *m* is the diffraction order, λ is the diffraction wavelength, *d* is the interspacing of neighboring colloidal particles in a periodic array, and ϑ is the angle between the incident light and the normal direction of the periodic array[33]. Hence, the position of the diffraction peak could be largely tuned by changing of the interspace of neighboring particles (i.e. periodicity of array) caused by volume swelling or shrinking of the functional hydrogel carrier[26].

The hydrogel films embedded with 2D Au nanosphere array or 2D hncp PS sphere array were both placed on quartz slides for the optical measurement. 2D Au nanosphere array/hydrogel composite films demonstrated strong diffraction peaks, which had a similar trend as their absorption spectra. The diffraction wavelength red-shifted with increasing pH value as the carboxyl groups in PAAc gradually became ionized. For example, the diffraction peak monotonically red-shifted about 271 nm owing to the increased interspacing between two adjacent Au nanosphere induced by the rising swelling degree as the pH values increased from 2.07 to 7.55. Additionally, there are no other peaks in diffraction spectra of 2D Au nanosphere array/hydrogel composite films, indicating that the existed discrete Au tiny nanoislands with random distribution among Au nanosphere array made a negligible influence to the diffraction intensity and peak position according the measurement results. Fig. 3b shows the pH dependence of the diffraction peak positions of 2D Au nanosphere array/hydrogel composite films at B-R buffer solution with different pH values. It indicated that the diffraction wavelength increased significantly with increase of pH value. Additionally, we could calculated the corresponding interspacings (d: 450 nm, 463 nm, 568 nm, 686 nm, 710 nm, 730 nm, 745 nm) by using the diffraction peak position (413 nm, 425 nm, 522 nm, 630 nm, 652 nm, 670 nm, 684 nm, respectively) in Fig. 3a by the Bragg diffraction formula. Furthermore, an obvious color change of 2D Au nanosphere array embedded in hydrogel films could be clearly observed by naked eyes under different pH values, as demonstrated in Fig. 3c. One can find it changed from purple to olivine, to red, then to bright red, finally to iron oxide red with increase of pH value. These hydrogel films were also placed on quartz substrates when they were observed by naked eyes. The observed color can be used to visually determine the pH value. Additionally, the diffraction spectra of hydrogel films embedded with 2D hncp PS microsphere arrays on quartz substrates were also measured in the Littrow configuration as a comparison, as displayed in Fig. 3d. One can find that there were no obvious diffraction signals in the diffraction spectra of such 2D hncp PS microsphere arrays/hydrogel composite films on quartz slide. Above results indicated that, for the hydrogel films embedded with 2D hncp PS microsphere arrays on quartz substrates, it was difficult to obtain the diffraction signals due to the low reflectance of PS and quartz substrate. However, if such 2D hncp PS microsphere arrays/hydrogel composite films were placed on a high reflective mirror, i.e. Al mirror, the weak diffraction peak could be found, as shown in inset in Fig. 4. The diffraction intensity of 2D Au nanosphere array/hydrogel composite film on quartz slide was slightly decreased compared with that of one on Al mirror, however, it was still strong enough to be detected and the intensity was much stronger and increased by more than one order of magnitude (88 times) than that of 2D hncp PS microsphere array/hydrogel composite film on Al mirror, as shown in Fig. 4.

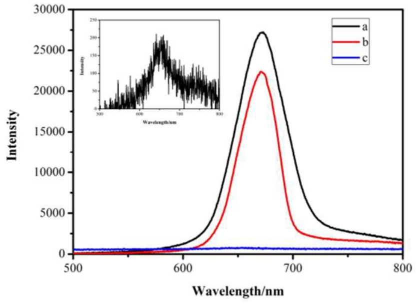

Fig. 4 Comparison of diffraction intensity: a. 2D Au nanosphere array/hydrogel composite film on Al mirror; b. 2D nanosphere Au array/hydrogel composite film on quartz slide; c. 2D hncp PS sphere array/hydrogel composite film on Al mirror. The inset displays diffraction spectrum of 2D hncp PS sphere array/hydrogel composite film on Al mirror.

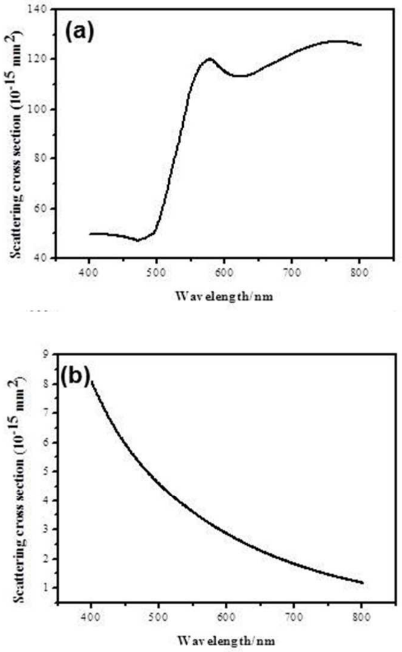

Fig. 5 Scattering cross section of the Au sphere (a) and PS sphere (b) with the same diameter of 200 nm calculated by Mie theory.

A mechanism is proposed to explain this enhanced diffraction intensity of 2D Au nanosphere array/hydrogel composite film on ordinary substrates. We calculated the scattering cross section of the Au sphere and the PS sphere with the same diameter of 200 nm by Mie theory, as shown in Fig. 5. On the whole, the scattering cross section of Au nanosphere is much higher than that of PS sphere. For the Au nanosphere, when the wavelength of incident light is larger than 500 nm, the scattering cross section dramatically increases and it keeps a high value after 550 nm (Fig. 5a), but for PS nanosphere, with increase of the wavelength of incident light, its scattering cross section rapid declines (Fig. 5b). The results show that the scattering cross section of Au sphere is about 10-100 times larger than PS sphere for wavelengths in the range between 500 nm to 800 nm. The diffraction intensity of nanosphere mainly depends on its scattering cross section and the diffraction intensity will increase with increase the scattering cross section of materials[50].Therefore, the higher diffraction intensity of Au nanosphere than PS sphere originates from its larger scattering cross-section. Additionally, the enhancement ratio of scattering cross section was higher with wavelength increasing. For the diffraction peak of 670 nm, the calculated scattering cross section of Au nanosphere was 60-fold increase than that of PS sphere, well explaining the corresponding 88-fold increase of diffraction intensity.

In previous studies, the materials with low scattering cross section (i.e. PS or SiO_2) could be easily prepared to monodispersed microspheres and 2D microsphere array, therefore such 2D microsphere arrays could be used to prepare the 2D particle arrays/hydrogel composite sensing films, leading to a quite weak diffraction intensity[15,51]. The diffraction peaks must be measured with the help of a high reflective mirror, further limiting their practical application as sensors. Based on successful preparation of Au (a kind of high scattering cross section) nanosphere array, we develop a route to create the 2D Au nanosphere array/hydrogel composite film, the diffracted intensity could be largely enhanced and it is strong enough to be detected without high reflective mirror due to large scattering cross section of Au particles and periodicity of an array. This is helpful for visual observation by naked eyes and further optical characterization. The 2D Au nanosphere array/hydrogel composite films with strong iridescent color have important applications in visual detection of the species in aqueous environments as sensors.

4 Conclusions

In summary, an interesting route to prepare free standing 2D Au nanosphere array/hydrogel composite film is developed. Such hydrogel systems attached with 2D Au nanosphere array could be used as visualized sensors with ultrahigh diffraction intensity. 2D Au nanosphere array/hydrogel composite film on ordinary quartz substrate demonstrated strong diffraction signal, without using high reflective mirror as a substrate. The diffraction intensity of Au nanosphere array/hydrogel composite film was increased by more than one order of magnitude (88 times) than that of 2D PS sphere array/hydrogel composite film to external stimuli because of large scattering cross section of Au sphere. Thus the intense optical diffraction intensity of 2D Au array/hydrogel composite film could make the diffraction measurement and color identification on any ordinary substrates, which is helpful for their practical applications in visual detection and quantitative detection by monitoring the diffraction peak position and intensity. Additionally, this presented strategy is universal and could be suitable for various functional hydrogel to further develop sensors.

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Functional Hydrogel Film Attached with 2D Au Nanosphere Array and Its High Optical Diffraction Intensity as a Sensor

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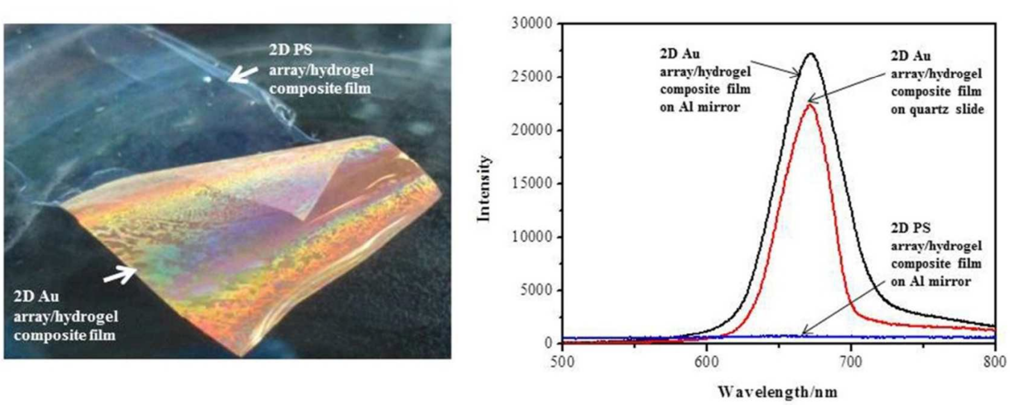

The free standing 2D Au nanosphere array/hydrogel composite films on ordinary quartz substrate demonstrate strong diffraction signal, without using high reflective mirror as a substrate. The high diffraction intensity of 2D Au nanosphere array/hydrogel composite films could improve their practical applications in visual detection by monitoring the diffraction peak position and intensity.