Fluorescence Enhancement with One-Dimensional Photonic Crystals/ Nanoscaled ZnO Composite Thin Films

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ABSTRACT: One-dimensional photonic crystals (1DPCs)/ nanoscaled ZnO particles composite thin films were fabricated with spin-coating technique. Organic dyes, whose emission wavelengths overlap the photonic stopbands of the selected 1DPCs, were deposited on the surface of the 1DPCs films with spin-coating technique. The fluorescence of the organic dyes deposited on 1DPCs/ nanoscaled ZnO composite thin films was obviously enhanced in comparison with that on 1DPCs films or ZnO films. Otherwise, the nanoscaled ZnO particles were modified with Poly (sodium 4-styrenesulfonate) (PSS) and Poly (allylamine hydrochloride) (PAH) by self-assembly, and we found a novel phenomenon was observed that the thickness of PSS and PAH had relationship with the effect of fluorescence enhancement. The results show

that the 1DPCs/ nanoscaled ZnO composite thin films have potential applications in the highly sensitive fluorescence-based detection and optoelectronic devices.

KEYWORDS: nanoscaled ZnO, enhanced fluorescence, 1DPCs, spin-coating, self-assembly

The fluorescence-based detection technique is a central technology in biological research and clinical chemistry. Fluorescent dyes have attracted great attention due to their potential applications in environmental monitoring, medical examination, and disease diagnostics owing to their advantages of high sensitivity, high selectivity, and low-cost.¹⁻⁵ Enhancing fluorescent signal has contributed to advancement of fluorescence technology, as reducing detection limits, enhancing detection sensitivity, increasing signal-to-noise ratio and increasing the specificity. synthesis of amplifying fluorescent conjugated polymers,⁶ metal-enhanced fluorescence,^{7,8} fluorescence resonance energy transfer,^{9,10} and surface plasmon resonance^{11,12} are alternative methods by which to amplify fluorescent signal. However, those above-mentioned approaches need complicated preparatory and experimental processes, and the effect of such enhancement is limited, which will restrict their practical application.

Photonic crystals, which were first defined by Eli Yablonovitch¹³ and Sajeev John¹⁴ in 1987, are a new type of structure material whose dielectric refractive index changes in spatial periodic. Whether or not photons propagate through this structure depends on their wavelength, thus photonic crystals can affect the emission and propagation of light within a certain wavelength by photonic stopbands, therefore, photonic crystals can modify significantly the emission characteristics of embedded optically-active materials.¹³⁻¹⁶ Recently, photonic crystals have been utilized to improve the fluorescence intensity in many optical devices and lower the detection limit in the fluorescence based sensor.^{17,18} The fluorescence enhancement can be achieved at

band-edges of photonic crystals. When the band edge of photonic crystals overlaps the excitation laser, owing to resonant Bragg scattering, photons propagate at reduced group velocity. That will increase the effective optical path length of light, and dye absorption or emission will be enhanced. On the other hand, when the band edge of photonic crystals overlaps the emission of fluorescent dye, the photonic crystals can lead to the band-edge induced fluorescence enhancement, and directionally collect the emission of matching fluorescent dye.¹⁹⁻²⁵

According to the variations of refractive indexes in space, photonic crystals can be classified as one-dimensional, two-dimensional, and three-dimensional photonic crystals. The photonic stop bands of 1DPCs could be estimated from Bragg's Law^{26,27}, according to it, the optical properties of 1DPCs can be tuned by changing periods, and the refractive index.²⁸ Besides, compared with two-dimensional photonic crystals and three-dimensional photonic crystals, 1DPCs are the simplest photonic crystals. In theory, 1DPCs have a simple preparatory process and low cost. One dimensional photonic crystals used as sensors to apply in fluorescence enhancement are very significant.^{43,44,45}

Engineering of advanced substrates is an effective way to improve the fluorescence detection capability and to reduce the cost. Owing to the optical properties of ZnO, which include a wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO nanostructures have received considerable attention. ZnO thin films and micro/nanostructures show the similar capability to improve the fluorescence intensity.²⁹ Xu and co-workers studied the ability of nanoscaled ZnO films to enhance fluorescence. They found that the fluorescence intensities of Cy5, Rhodamine 6G, and fluorescein can be enhanced about 10-fold on nanoscaled ZnO films as compared to that on glass substrates.³⁰ Recently, ZnO nanomaterials have been used in biological testing schemes, as duplex DNA formation^{31,32}, protein determination^{33,34},

cancer diagnosis^{35,36} and so on, to enhance the fluorescence. Punnoose and co-workers designed dye-doped ZnO composite nanostructures and a nearly 90-fold enhanced fluorescence was found.³⁷

To the best of our knowledge, no report on the 1DPCs/ nanoscaled ZnO composite thin films has been studied for fluorescence enhancement. Herein we report a new way to enhance fluorescence by 1DPCs/ nanoscaled ZnO composite thin films, rather than single 1DPCs or nanoscaled ZnO films. The nanoscaled ZnO particles were modified with PSS and PAH by self-assembly (Scheme 1a). Then, the modified ZnO and fluorescence molecules were spin-coated onto the surface of the TiO₂/ graphene oxide (GO) 1DPCs, (Scheme 1b). We demonstrate that the composite thin films can serve as excellent signal-intensifying substrates for various fluorescence dyes, and the thickness of PSS and PAH can tune the effect of enhancement. The effect may be caused by scattering effect and dissipation of excitation light. This method of fluorescence enhancement on 1DPCs/ nanoscaled ZnO composite thin films can provide a promising direction for developing the highly sensitive fluorescence-based detection. This method has attracted great attention due to their potential applications in environmental monitoring, medical examination, and disease diagnostics.^{48,49,50}

Scheme 1. a) Schematic representation of the processes used to modify nanoscaled ZnO by self-assembly. b) Structural representation of the formation of 1DPCs/ nanoscaled ZnO composite thin films.

RESULTS AND DISCUSSION

Figure. 1 a) shows the cross-section SEM image of TiO₂/GO 1DPCs with nanoscaled ZnO (2N, N=4, N is the number of TiO₂ layers), which was fully prepared in the light of our current work, where we can see the evident multilayered construction. TiO₂/GO 1DPCs have four layers, that is to say, they include eight layers. We could not see nanoscaled ZnO from the cross-section image of TiO₂/GO 1DPCs, but the surfaces of the TiO₂/GO 1DPCs were full of the homogeneous nanoscaled ZnO, as shown as Figure. 1 b). Looking at these, it was very obvious that the layered structure of the 1DPCs was in accord with the points of the most basic characteristic of 1DPCs. Nanoscaled ZnO were successfully coated on the surface of TiO₂/GO 1DPCs by spin-coating technology.

Figure 1. a) The cross-section SEM of TiO₂/GO 1DPCs. b) The SEM of nanoscaled ZnO coated on 1DPCs.

Photonic stopband is the most basic characteristic of 1DPCs, and it can be evaluated with the sample's reflection spectra. Fig. 2 shows the reflective spectra of two TiO₂/GO 1DPCs, which were adjusted by controlling the rotational speed and the time of spin-coating. The photonic stopbands are at 599 nm and 650 nm, and they just overlap the emission wavelength (594 nm) of Rhodamine B (RhB) and the emission wavelength (652 nm) of meso-Tetrakis-(4-sulfophenyl)-porphine tetrasod (TPPS), respectively.

Figure 2. The reflective spectra of two TiO₂/GO 1DPCs with different periods.

Then, RhB and TPPS were deposited on the outmost layer of the 1DPCs/ nanoscaled ZnO composite films, whose photonic stopbands were 599 nm and 650 nm, respectively, and the ZnO particles weren't modified with PSS and PAH as control. The composite films were fabricated by spin-coating technique,^{38,39} in which the emission wavelengths of RhB and TPPS overlap with the stopbands of the matched 1DPCs. Simultaneously, organic dyes were also deposited on 1DPCs film and ZnO film as the control experiments.

Figure 3. a) The fluorescence spectra of RhB deposited on 1DPC/ nanoscaled ZnO composite film, 1DPC film and ZnO film ($\lambda_{em} = 594$ nm), The stopband of 1DPC is 599 nm; b) The fluorescence spectra of TPPS deposited on 1DPC/ nanoscaled ZnO composite film, 1DPC film and ZnO film ($\lambda_{em} = 652$ nm), The stopband of 1DPC is 650 nm. Here the fluorescence spectra were collected at the stopband direction of 1DPCs.

The fluorescence spectra of RhB and TPPS deposited on 1DPCs/ nanoscaled ZnO composite films, 1DPCs films and ZnO films are given in Fig. 3, the stopbands of 1DPCs are 599 nm and 650 nm, respectively. From Fig. 3, it can be observed clearly that there is a fluorescence enhancement on the 1DPCs/ nanoscaled ZnO composite films in comparison with that on 1DPCs films or ZnO films. The fluorescence intensities of different dyes can be greatly enhanced on the 1DPCs/ nanoscaled ZnO composite films as compared to that on the 1DPCs films and ZnO films. 1DPCs/ nanoscaled ZnO composite film is more effective than the 1DPCs film or ZnO film, there are about 1.5-fold enhancement for RhB and 1.3-fold enhancement for TPPS obtained from Fig. 3, which probably results from the combination enhancement effect of 1DPCs and ZnO. When the emission wavelengths of the dyes are in the range of the stopbands of 1DPCs, the 1DPCs surface will act as a Bragg mirror which can effectively increase the fluorescence intensity of the organic dyes. According to the reference,^{34,35,37} ZnO film also has an ability to enhance the fluorescence intensity, the ability of nanoscaled ZnO to enhance the intensity of evanescent field can be explained the fluorescence sensitivity observed in our system.

In order to tune the enhancement, PSS and PAH were employed to modify nanoscaled ZnO particles by layer-by-layer self-assembly, and the nanoscaled ZnO particles modified by PSS and PAH with different layers were successfully prepared. The electrostatic interactions between PSS and PAH by self-assembly modified on the surface of ZnO. PSS and PAH should cross with each other, so there are not structure layers, which are the features of 1D photonic crystals. In addition, PSS and PAH were alternately dropped on the silicon wafer by spin-coating method. We can't see structural color from 1 to 8 periods. Above these, PSS and PAH multilayers are not another photonic crystals.^{46,47} Then the modified nanoscaled ZnO particles were deposited on the surface of the 1DPCs by spin-coating method, in which the emission wavelengths of RhB

overlap the stopbands of the matched 1DPCs, and the RhB was deposited on the modified nanoscaled ZnO by spin-coating method.

Figure 4. a) The fluorescence spectra of RhB deposited on 1DPCs/ nanoscaled ZnO, which was modified by PSS and PAH under different layers (the numbers in parentheses), composite film ($\lambda_{\text{ex}} = \sim 550$ nm). b) Relation between the fluorescence intensity with number of polymer layers.

Here the fluorescence spectra were collected at the stopband direction of 1DPCs. The stopband of 1DPC is 599 nm.

The fluorescence spectra of RhB deposited on the 1DPCs/ nanoscaled ZnO composite film, whose ZnO particles were modified by PSS and PAH with different layers, are shown in Fig. 4a. From Fig. 4a, it can be seen clearly that the number of PSS and PAH layers have relationship to the fluorescence intensity. The relative fluorescence intensities are shown in Fig. 4b, which indicate the number of PSS and PAH layers. The results show that the fluorescence intensity decreases first, and then rises and decreases again with the increase of the layer number. The fluorescence intensity is the weakest when the layer number is 2, and is strongest when the layer number is 8. This phenomenon may be because that the scattering effect and the dissipation of excitation light may take place in our nanoscaled ZnO, and the synergy between them results in the novel phenomenon in Fig. 4b. The fluorescence intensity is the weakest when the layer number is 2, and is strongest when the layer number is 8. This phenomenon may be because that the scattering effect and the dissipation of excitation light may take place in our nanoscaled ZnO, and the synergy between them results in the novel phenomenon in Fig. 3b. There are three where about of the scattered light, the first is absorbed by RhB, the second is scattered to space, and the last incidence to the 1DPC. Due to the stopband of 1DPC is 599 nm, the excitation light, which is transmitted and scattered, cannot be completely reflected, some of the excitation light will be absorbed by 1DPC or penetrate through 1DPC, and these light will dissipate. Therefore, the bigger of gaps, the more excitation light incidence to 1DPC, and the more excitation light dissipate. As the layer number of PSS and PAH increases, the radius of nanoscaled ZnO increases, then the gaps of nanoscaled ZnO increase. In addition, the excitation light can percolate through PSS and PAH, it will result in more dissipation of excitation light. Considering

the above, the phenomenon, the fluorescence intensity decreases.

The scattering effect of ZnO will affect the absorption efficiency of the fluorescence molecules. In theory, the stronger scattering effect, the more excitation light will be absorbed by fluorescence molecules, and the more absorption efficiency of the fluorescence molecules. As the increase of the absorption efficiency of fluorescence molecule, the fluorescence intensity will increase, too. Besides, nanoparticles also can scatter emission light of fluorescence molecules, and the scattering effect can improve the collected fluorescence signals. The scattering of the light by sub-wavelength-sized particles is well described by the Rayleigh theory.³⁷ For the incident light is polarized and observed in the same plane, the intensity of the light scattered, I , in the direction θ by a homogeneous spherical particle with radius r , given that this particle is much smaller than the wavelength of the incident beam, λ , is described by the Rayleigh expression.⁴⁰

$$I = \frac{16\pi^4 r^6 m^4 I_0}{d^2 \lambda^4} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \cos^2 \theta \quad (1)$$

Where I_0 is the incident intensity of monochromatic light, m is the refractive index surrounding the particle, n is the refractive index of the bulk particle material, and d is the distance between the particle and the location of scattered light detection. As the layer number of PSS and PAH increases, the radius of nanoscaled ZnO will increase. Besides that, from the above equation, we can conclude that the scattering effect can be enhanced by increasing the radius of nanoscaled ZnO, and that result in increase of efficiency of the fluorescence molecules and improvement of the collected fluorescence signals. Subsequently, the fluorescence intensity will be enhanced.

Scheme 2. Schematic of excitation light falling on 1DPCs/ nanoscaled ZnO, which isn't modified by PSS/PAH, composite thin films (left) and 1DPCs/ nanoscaled ZnO, which is modified by PSS/PAH, composite thin films (right).

Besides, the dissipation of the excitation light may be used to explain the phenomenon in Fig. 3b and the remarkable fluorescence sensitivity can be observed during the experiment. As shown in Scheme 2, when the excitation light, whose wavelength is about 550 nm, incidence to the RhB layer, a portion is absorbed by RhB directly, and the others will pass through the composite thin film and RhB layer. Within the film, Part of the transmission light is scattered by nanoscaled ZnO, and the others will incidence to the 1DPC, whose stopband is 599 nm, from the gaps among nanoscaled ZnO. Then there are three where about of the scattered light, the first is absorbed by RhB, the second is scattered to space, and the last incidence to the 1DPC. Due to the stopband of 1DPC is 599 nm, the excitation light, which is transmitted and scattered, cannot be completely reflected, some of the excitation light will be absorbed by 1DPC or penetrate through 1DPC, and these light will dissipate. Therefore, the bigger of gaps, the more excitation light incidence to 1DPC, and the more excitation light dissipate. As the layer number of PSS and PAH increases, the radius of nanoscaled ZnO increases, then the gaps of nanoscaled ZnO increase. In addition, the excitation light can percolate through PSS and PAH, it will result in more dissipation of excitation light.

Considering the above, the phenomenon, the fluorescence intensity decreases first, and then rises and decreases again with the increase of the layer number, may be caused by the synergy between scattering effect, which will be enhanced, and dissipation of excitation light, which will weaken fluorescence, with the increase of the layer number.

CONCLUSION

In conclusion, the nanoscaled ZnO modified with different layers PSS and PAH were successfully prepared by layer-by-layer technique. The matched TiO_2/GO 1DPCs and 1DPCs/nanoscaled ZnO composite thin films are prepared by spin-coating technique. The optical properties of 1DPCs can be tuned by period. Our results show that fluorescence of organic dyes has been enhanced drastically by 1DPCs/nanoscaled ZnO composite thin films as the emission wavelengths of the organic dyes are in the range of the photonic stopbands of the matched 1DPCs, which demonstrates that the 1DPCs/nanoscaled ZnO composite thin films will be more efficient and selective reflection mirrors than single 1DPCs films or ZnO films. The thickness of PSS and PAH can tune the effect of fluorescence enhancement, and it is may because of the synergy between scattering effect and dissipation of excitation light. The approach will be of great significance for building a multilayer thin film with a simple way, which provides a promising strategy for developing the highly sensitive fluorescence-based detection.

EXPERIMENTAL SECTION

Materials Preparation. GO was bought from Nanjing XFNano Materials Tech Co., Ltd., (Nanjing, China). Tetrabutyl titanate was obtained from Shanghai Ling Feng Chemical Reagent Co., Ltd.. Poly (sodium 4-styrenesulfonate) (PSS) ($M_w = 70\ 000$), Poly (allylamine hydrochloride) (PAH) ($M_w = 70\ 000$) and Poly (vinyl alcohol) (PVA) (low molecular weight) were obtained from Sigma–Aldrich (Shanghai, China). Rhodamine B, sodium chloride, zinc acetate and lithium

hydroxide monohydrate were obtained from Sinopharm Chemical Reagent Shanghai Co., Ltd.. Meso-Tetrakis-(4-sulfophenyl)-porphine tetrasod was obtained from Changzhou Huanling Chemical Co., Ltd.. All other reagents were used as received.

Preparation and Modification of ZnO. ZnO quantum dots were synthesized by sol-gel method.⁴¹ First the 0.05 M $\text{Zn}(\text{CH}_3\text{COO})_2$ in ethanol solution (20 mL) was boiled and stirred vigorously at 80 °C for 1 h. At the same time, the 0.05 M $\text{LiOH} \cdot \text{H}_2\text{O}$ in ethanol solution (20 mL) was placed into an ultrasonic bath. Then the LiOH solution was added into the $\text{Zn}(\text{CH}_3\text{COO})_2$ solution under vigorous stirring at 0 °C for 1 h.

Multilayer assembly was accomplished by the adsorption of polyelectrolytes (PSS and PAH) at a concentration of 1 mg/ml, 0.5M NaCl aqueous solutions. Oppositely charged polyelectrolyte species were subsequently added to the ZnO followed by repeated centrifugation cycles.

Preparation of 1DPCs/ Nanoscaled ZnO Composite Thin Films. The titania sol was prepared according to ref. 42. Briefly, 4 ml tetrabutyl titanate and 2 ml acetic acid were dissolved into 42 ml ethanol, then dipping the above mixture into the above conical flask, and then stirring 5 h at room temperature. In order to get different thicknesses of the film, the titania sol was diluted with different volumes of ethanol before use. The concentration of the GO solution was 1 mg/mL. Besides, RhB and TPPS were dissolved in 2% PVA solution, and the concentration of RhB and TPPS were 10mg/mL. The silicon wafers were soaked in the mixture of 98% H_2SO_4 /30% H_2O_2 (volumetric ratio 3:1) for 24 h, then rinsed with deionized water several times, and finally were dried with N_2 stream. The 1DPCs were fabricated by spin-coating the titania sol and the GO solution alternatively. Different thicknesses of films were achieved by changing the concentration of the solutions, the time of spin-coating and the spin-coating rate. Both of titania sol and the GO solution were spin-coated onto a silicon wafer. Every layer was baked at 60 °C

for 10 min. The first layer was GO layer and the last layer was titania layer in all our experiments. The number of the total layers of the film materials was 2N (N is the number of TiO₂ layers). Then, nanoscaled ZnO and organic dyes were spin-coated onto the 1DPCs in sequence.

Characterization. The spectra of the 1DPCs at normal incidence were recorded by using a microscope (OLYMPUS BX51) equipped with a fiber optic spectrometer (Ocean Optics, QE65000) at an incidence angle of 0°. Fluorescence spectra were measured by using a fluorescent Inverted microscope (OLYMPUS IX71) equipped with a fiber optic spectrometer (Ocean Optics, QE65000).

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Herein we report a new way to enhance fluorescence by 1DPCs/ nanoscaled ZnO composite thin films, rather than single 1DPCs or nanoscaled ZnO films. The nanoscaled ZnO particles were modified with PSS and PAH by self-assembly. Then, the modified ZnO and fluorescence molecules were spin-coated onto the surface of the TiO_2 / graphene oxide (GO) 1DPCs. the 1DPCs/ nanoscaled ZnO composite thin films have potential applications in the highly sensitive fluorescence-based detection and optoelectronic devices.