AuNPs EMBEDMENT INTO THE INVERSE OPAL PHOTONIC CRYSTALS AND FLUORESCENCE INTENSITY ENHANCEMENT EFFECT

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TÓM TẮT

AuNPs GẮN LÊN VẬT LIỆU QUANG TỬ OPAL DẠNG ĐẢO VÀ HIỆU ỨNG TĂNG CƯỜNG ĐỘ HUỲNH QUANG

Trong nghiên cứu này, việc gắn hạt nano vàng (AuNPs) vào vật liệu tinh thể quang tử opal cấu trúc đảo (IOPC) bằng cách trộn với hạt nano silica trong bước chế tạo mẫu tinh thể quang tử opal để làm tăng cường độ huỳnh quang đã được khảo sát. IOPC thu được bằng việc phủ các khối cầu nano silica cùng với poly (ethylenglycol) diacrylate (PEGDA), sau đó ăn mòn bằng dung dịch đệm ăn mòn. Sự có mặt của AuNPs trong IOPC được nghiên cứu bằng phương pháp chụp ảnh hiển vi điện tử quét (SEM) và phổ tán xạ năng lượng tia X (EDX). Ảnh chụp huỳnh quang cho thấy rõ mức độ phản xạ tăng lên khi có mặt AuNPs trong silica/PEGDA. Với sự có mặt của Alexa Fluor® 594, là thuốc nhuộm huỳnh quang, kết quả đo cường độ hùynh quang đã rõ ràng cho thấy sự tăng của vật liệu IOPC khi có mặt AuNPs.
Từ khóa: *AuNPs, tinh thể quang tử opal dạng đảo, huỳnh quang.*

1. INTRODUCTION

Fluorescent-based detection methods have been widely utilized in various applications such as sensing, imaging and diagnose due to high sensitivity, convenience and low cost. Therefore, the increase in the fluorescence intensity is always required for increasing the sensitivity of the analysis. Among materials used to fabricate devices for fluorescent-based detection, photonic crystals (PC) has attracted enormous interest because of their ability to confine and control the flow of light [1]. PC are periodic structure with a spatial modulation in their dielectric function, with the periodicity being comparable to the wavelength of light in the ultraviolet, visible or infrared region of the electromagnetic spectrum. Thus, the transport of electromagnetic waves in PC is determined by the so-called photonic band gap [2]. Some techniques have been investigated to improve reflective intensity of the PC, such as preparation of 'inverse opals' which are known to exhibit more complete photonic band gap than conventional ones [3], while other is infilling a second material into the interstitial lattice voices between the colloidal sphere of the PC followed by removal of the sphere to create the inverted structure [4,5]. In addition, the use of noble metal nanoparticles such as Au, Ag and Pt has been known to result in localized surface plasmon resonance (LSPR) due to collective ascillation of conduction band electrons induced by interaction with light radiation [6]. The LSPR frequency depends on the size, shape and composition of metal and their surrounding dielectric environment as well as interaction between adjacent metal nanoparticles [7].

In a previous study, we showed that an inverse opal photonic crystals, which was made of polyethylene glycol diacrylate (PEGDA), could enhance the fluorescence intensity over

7.7-fold with the presence of Fluor® 488 dye on the IOPCs sample. This is due to the decrease in pore size when etching silica nanospheres (300 nm) to generate air pores (270 nm), leading to a decrease in the average refractive indexes from 1.4 to 1.12, as well as a remarkable stopband blue shift for the IOPC [8].

In this work, we further develop the obtained IOPC by an embedment of AuNPs to further improve the fluorescence intensity due to the LSPR. With the role of AuNPs in enhancing the fluorescence intensity of the IOPC, this material can be further studied in the field of biological system that might benefit from the added sensitivity afforded by this approach.

2. EXPERIMENTAL

2.1. Chemicals

Non-Functionalized Silica (SiO_2) microspheres with a diameter of 300 nm were purchased from the Polyscience Asia Pacific Inc. Poly (ethylene glycol) diacrylate (PEGDA) (Mn=250), 2-hydroxy-2-methylpropiophenone 97% (*Irgacure 1173)*, buffered oxide etchant (BOE) and ethanol 95% were supplied by Sigma-Aldrich. *Irgacure 1173*, is a photoinitiator, was used in radiation curing in the polymerization of PEGDA. Alexa Fluor® 488 conjugate (A-21206, Invitrogen) were supplied by Sigma-Aldrich.

2.2. Protocol for IOPC fabrication with AuNPs embedment

The fabrication of inverse opal photonic crystals (IOPCs) was performed as following. A volume of 0.5 mL microcentrifuge tube including mixture of silica sol suspension and solution of AuNPs, which was prepared from a solution of $HAuCl_4$ 0.1 M to obtain the particle size of 30 nm as described in elsewhere [9], with a desired volume ratio was dropped onto a microscope slide after covering with a hydrophobic thin layer and dried in air for 1 day at room temperature. The mixture of 99 wt% PEGDA and 1 wt% 2-Hydroxy-2-methylpropiophenone was then added into the dried SiO_2 for 5 minutes and exposed under the UV light (312 nm) during 5 minutes for polymeration process. Finally, the chip was etched by BOE for few hours to obtain the IOPCs before being washed by pure water for several times.

2.3. Instruments

Scanning electron microscopy (SEM, Hitachi S-4800, acceleration of 15-20 kV, working electrode distance of 4-5 mm) was used to characterize the surface morphology. X-ray diffraction data were collected using Bruker D8 (20 kV, 5 mA) equipped with a LynxEye detector and a conventional Cu anode. Diffactograms were collected at step of 0.25 s. The spectrometer processor (Ocean Optics QE Pro-FL), which has a wavelength range of 350 nm ÷ 1100 nm, in conjunction with a halogen light source (Ocean Optics HL-2000) was used to determine the reflected spectra. The fluorescent images of the samples were measured using a fluorescent microscope (BX51, Olympus), whereas the fluorescence intensity was analysed by the Image J software.

3. RESULTS AND DISCUSSION

3.1. Characterization of the synthesized materials

The morphologies of the silica/PEGDA before and after embedding AuNPs is shown in Figure 1. As seen in these SEM top view images, silica nanoparticles with diameter of about 300 nm can be clearly observed. The diameter of silica spheres after embedding AuNPs is almost identical to that before embedment. In addition, some white spots on the surface of silica nanoparticles can also be observed in the image (b), indicating to the presence of AuNPs on the surface of nano silica particles. The diameter of these AuNPs on these nano silica particles was estimated to be about 30 nm.

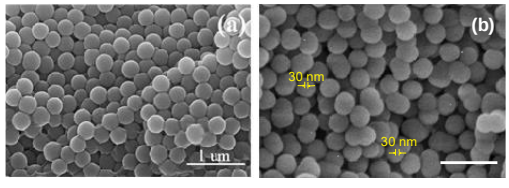

Figure 1. SEM images of silica/PEGDA before (a) and after (b) embedding AuNPs

In addition, the presence of AuNPs on the surface of nano silica particles is also examined by EDX technique as shown in Figure 2.

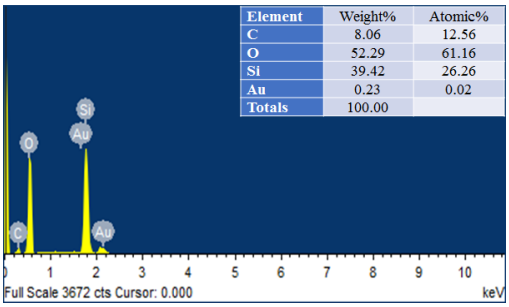

Figure 2. EDX spectra of Silica/PEGDA/AuNPs

As seen, among peaks corresponding to the presence of elements of C, O, Si, the peak of Au appears at 2.149 keV, occupying 0.23 % (weight) as shown in the inset, and the peak at 1.87 keV which corresponds to the Si-Au bonding, indicating the presence of AuNPs on top of the nano silica particles. This result is consistent with that reported by S. Yochlis et al. when authors studied the Au-Si formation with various techniques [10].

3.2. Fluorescence effect of the synthesized materials

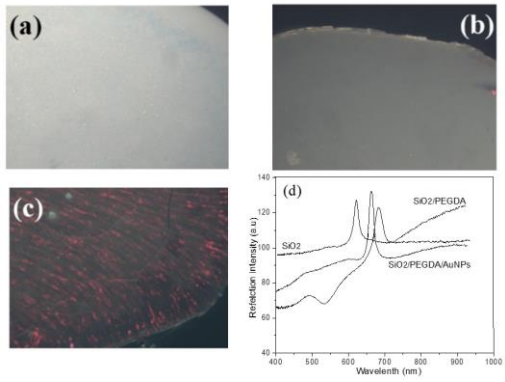

Figure 3. Photos of silica (a), silica/PEGDA (b), Silica/PEGDA/AuNPs (c) and reflected intensity of these samples (d)

Figures 3a ÷ 3c show photographs of silica particles self-assembly, silica particles with PEG-DA and silica/PEGDA/AuNPs, respectively, taken by fluorescence microscopy. It is obvious that the reflectivity of silica/PEGDA is similar with that observed on silica surface. But when AuNPs is embedded into silica (silica/PEGDA/AuNPs), the reflectivity becomes significantly higher than that of two previous materials, as seen in figure 3d. This is again clear evidence for the presence of AuNPs in the IOPC. In fact, when PEGDA formed on the silica, the refractive index of the material is changed, leading to the variation of Bragg diffraction and causing a blueshift of wavelength as obtained. When AuNPs are embedded into silica, the formation of AuNPs causes a LSPR as reported in literature [6].

To investigate the effect of opal photonic structure and AuNPs on fluorescence intensity, a volume of 0.5 µL Alexa Fluor® 594 was added on the surface of PEGDA (control samples), Silica/PEGDA and Silica/PEGDA/AuNPs, respectively. Alexa Fluor® 594 is used in this study because it is well known as a red-fluorescent dye and can be attached to proteins at high molar ratio without significant self-quenching. Since, it can be helpful for fabrication of biosensors having potential application in diagnose and food safety. Figures 4a ÷ 4c present fluorescent photographs of the materials, while their corresponding fluorescence intensities are presented in Figure 4d. Results in this figure reveal that the fluorescence intensity of silica/PEGDA is nearly triple more than PEGDA. Comparison of the fluorescence intensity of the IOPC before embedding AuNPs, the fluorescence intensity of the IOPC embedded with AuNPs also enhances though that is not much significant. However, the obtained results clearly indicate the role of AuNP in improving the fluorescence intensity of the IOPC. The enhancement of fluorescence intensity of IOPC can be controlled by the density of AuNPs on IOPC as suggested by results shown SEM top view image and EDX analysis.

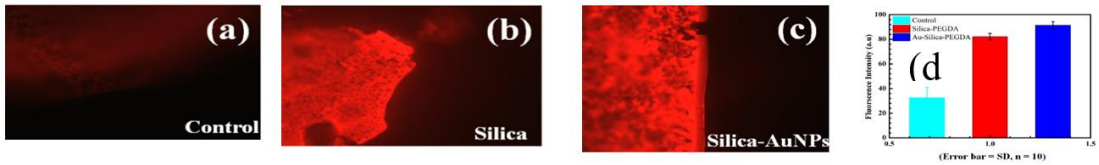

Figure 4. Photographs of control (a), Silica/PEGDA (b), Silica/PEGDA/AuNPs (c) and Fluorescence intensity of these amples (d)

4. CONCLUSION

The embedment of AuNPs into silica to fabricate the inverse opal photonic crystals (IOPC) for enhancing the fluorescence intensity has been studied. A simple embedment of AuNPs has been investigated by mixing with silica sol suspension to create spots in the IOPC. The presence of AuNPs induces the localized surface Plasmon resonance in IOPC, leading to the enhancement of fluorescence intensity. Although the dependence of fluorescence intensity on the density of AuNPs in IOPC has not been approached, but the obtained results are evidences showing that the embedment of AuNPs into the IOPC can be used for enhancing the fluorescence intensity.

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