Fluorescent Photonic Crystal (FPC) Films for Higher Dye-Sensitized Solar Cells (DSSCs)

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Abstract. A novel kind of fluorescent photonic crystal (FPC) films were prepared by co-assembly of monodispersed silica colloids and carbon dots (CDs), exhibiting brilliant structural color and excellent fluorescence simultaneously. The fluorescence spectra of FPC films have been showing a peak at 486 nm. By comparison, the dye-sensitized solar cells (DSSCs) with FPC film show higher power conversion efficiency (PCE) (4.28%) than those of DSSCs without PC film (4.08%). A relative efficiency enhancement of 4.9% was achieved, indicating that the carbon-based fluorescent photonic crystal film can be applied to enhance the efficiency of the dye-sensitized solar cell.

Key words: Silica colloids; Carbon dots; Photonic crystals; Back-reflecting layers.

1. Introduction

Multifunctional photonic crystals, especially fluorescent photonic crystals, have attracted the interest of a wide range of scholars over the past decade due to their unique properties, such as photonic band gaps and fluorescence [1]. In general, there are two methods to prepare a fluorescent photonic crystal film: one is to directly fill a fluorescent substance such as using an organic dye or a quantum dot into the gap of a photonic crystal to form a composite fluorescent photonic crystal structure [2-9]; Another method is to directly assemble fluorescent photonic crystal microspheres to form a fluorescent photonic crystal film [10-19]. Generally speaking, each method has its shortcomings. For the first method, the introduction of fluorescent substances affects the reflection intensity and structural color of the film; the second method is subject to monodisperse fluorescent composite colloidal microspheres. At present, fluorescent substances such as organic dyes and inorganic nanocrystal quantum dots have been applied to the preparation of fluorescent photonic crystal films, but this method has disadvantages such as complicated preparation and toxicity, and thus limit its further application. Recently, a new type of organic fluorescent substance, carbon dots, has been introduced into this method, and the carbon dots exhibit excellent fluorescence stability, biocompatibility, easy synthesis, and non-toxicity. However, there have been few reports on carbon-based fluorescent photonic crystal films, especially in the case of dye-sensitized solar cell back reflectors.

In this paper, we have prepared a novel fluorescent photonic crystal film by co-assembly of monodisperse silica colloid and carbon dots. Fluorescent photonic crystal films prepared by the vertical deposition method exhibit many advantages, such as simple operation, short cycle for preparing carbon
dots, and good crystallinity of fluorescent photonic crystals. The prepared fluorescent photonic crystal not only exhibits a bright structural color, but also has excellent fluorescence properties. Therefore, the carbon-based fluorescent photonic crystal film can be applied to enhance the efficiency of the dye-sensitized solar cell, and opens up a new road for the advanced optical materials.

2. Experimental
The carbon dots were synthesized by hydrothermal method [17]. The Stöber method was used to prepare a monodisperse silica colloid [20]. The carbon dots emit blue fluorescence under the excitation of ultraviolet light, and the photonic crystal enhances the light at the matched frequency. Therefore, the blue photonic crystal enhanced the fluorescence of the carbon dots. The silica microspheres herein are prepared, whose diameter was controlled at about 180 nm, so that a blue photonic crystal film can be obtained. A certain amount of silica colloid was mixed with the prepared carbon dot solution, and after centrifugation, composite microspheres were obtained and washed three times with alcohol. The silica dispersed microspheres were ultrasonically dispersed, and the uniform dispersion of the composite microspheres was transferred to a 5 mL glass bottle. The aqua regia treated glass piece was vertically inserted into a vial and placed in an oven at 45 °C. After the ethanol was completely evaporated, a carbon dot-based fluorescent photonic crystal film could be prepared.

The morphology of the carbon dots and silica can be characterized by transmission electron microscopy (FEI TECNAI G20, USA). The microstructure of the carbon dot-based photonic crystal film can be measured by a scanning electron microscope (JSM7100F Japan). The fluorescence spectra of the carbon dot solution and the carbon dot-based fluorescent photonic crystal film can be measured by a fluorescence spectrometer (PE LS-55 USA). The transmission spectrum of the dye-sensitized solar cell (preferably China) was measured by an ultraviolet-visible spectrophotometer (UV3600, Shimadzu Company, Japan). The conversion efficiency of the dye-sensitized solar cell was measured solar simulator (Oriel, model 91192-1000) at 1.5 M with a light intensity of 100 mW/cm², and IM6 electrochemical workstation (ZAHNER, Germany).

3. Results and Discussions
Here, we used a co-assembly method to prepare a carbon-based fluorescent photonic crystal, and a fluorescent carbon dot and a monodisperse silica colloid were first synthesized. The carbon point was synthesized by hydrothermal method, and citric acid and ethylenediamine were used as precursors for the synthesis of carbon dots. As shown in Fig. 1 (a), the particle size of the carbon dots was about 1 to 2 nm. As shown in Fig. 1 (b), the fluorescence spectrum of the carbon dots was significantly higher at 440 nm when the carbon dots were irradiated with different excitation light of 300-400 nm. These results are consistent with the results measured by Yang et al. [17].

![Figure 1. (a) TEM image of the carbon dots, (b) fluorescence spectrum of carbon dot solution under different excitation lights.](image-url)
Monodisperse silica colloids with a particle size of around 180 nm can be obtained by the classical Stöber method. As shown in Fig. 2(a), the silica colloid show a good monodispersity, and thus the prepared photonic crystal film has excellent optical properties. As shown in Fig. 2(b), the SEM image of the monodisperse silica colloid and the carbon dot co-assembled photonic crystal film showed that they were closely arranged on the (111) face of the face-centered cubic.

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Figure. 2 (a) SEM image of the fluorescent photonic crystal film. (b) TEM image of a monodisperse silica colloid with a particle diameter of 180 nm.
As shown in the inset of Fig. 3(a), the carbon dot-based fluorescent photonic crystal film exhibited a blue color under ultraviolet light due to the fluorescence of the carbon dots. Conversely, a photonic crystal without a carbon spot reflects only the light of the ultraviolet lamp and is purple. The fluorescence spectrum of the fluorescent photonic crystal showed a distinct fluorescent peak at around 486 nm. In order to prove that the fluorescent photonic crystal can be used as the back reflection layer of the dye-sensitized solar cell, Fig. 3(b) shows that the dye-sensitized solar cell used in our UV transmittance is 5%, indicating that some of the ultraviolet light will pass through the solar cell.

Figure 3. (a) Excitation spectrum of a carbon-based fluorescent photonic crystal at an excitation wavelength of 365 nm. Inset: The left side is an optical photograph of a carbon-based fluorescent photonic crystal film under a 365 nm UV lamp, and the right is an optical photograph of a carbon-free photonic crystal film under a 365 nm UV lamp. (b) Transmission spectrum of a dye-sensitized solar cell.
As shown in Fig. 4, a carbon dot-based fluorescent photonic crystal was used as a back reflection layer of a dye-sensitized solar cell having an area of 0.16 cm$^2$. The power conversion efficiency of the dye-sensitized solar cell (control) without the back reflection layer is 4.08%, the open circuit voltage is 0.75V, the short circuit current is 7.64, and the open circuit voltage ($V_{oc}$) the short circuit current ($J_{sc}$) and fill factor (FF) were 0.75 V, and 8.00 mA/cm$^2$ and 69.17%, respectively. In contrast, the efficiency of the DSSCs solar cells was 4.28% with fluorescent photonic crystal (FPC) films as back reflector, which was improved by 4.9%. The $J_{sc}$ was increased from 7.64 to 8.0 mA/cm$^2$. These results indicate that the combination of photonic crystal bandgap effect and fluorescence performance of carbon dots can improve the photoelectric conversion efficiency of dye-sensitized solar cells, opening up a new direction for the preparation and design of advanced solar cell back reflectors.

![Figure 4. JV curves of dye-sensitized solar cell (control) and dye-sensitized solar cell with fluorescent photonic crystal (FPC) films as back reflector.](image)

| Current density, J/(mA·cm$^{-2}$) | Control | FPC film |
|-----------------------------------|---------|----------|
| $V_{oc}$ (V)                      | 0.75    | 0.774    |
| $J_{sc}$ (mA/cm$^2$)              | 7.64    | 8.00     |
| FF (%)                            | 71.2    | 69.17    |
| Efficiency (%)                    | 4.08    | 4.28 (+4.9) |

4. Conclusion
A novel carbon-based photonic crystal film was prepared by the method of co-assembly and vertical deposition. The method can rapidly prepare a large-area and crystallized fluorescent photonic crystal film, and does not require complicated post-processing in the preparation process. In addition, the carbon dots do not affect the self-assembly and structural color. Fluorescent photonic crystals not only have a bright structural color, but also exhibit good fluorescence properties, thus enabling the preparation of multifunctional optical materials. More importantly, in contrast to the DSSCs solar cell without a back reflection layer, the $J_{sc}$ and efficiency of the one with the fluorescent photonic crystal film as a back reflection layer were improved. These results indicate that the combination of photonic crystal bandgap effect and fluorescence performance of carbon dots can improve the photoelectric conversion efficiency of dye-sensitized solar cells, opening up a new direction for the preparation and design of advanced solar cell back reflectors.
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