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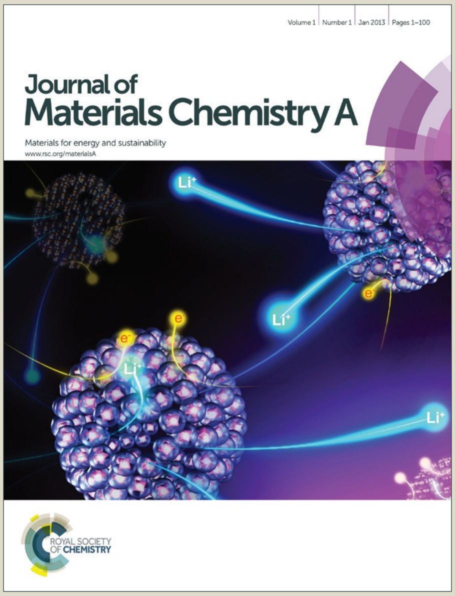

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# Synergetic Enhancement of Photocatalytic Activity with Photonic Crystal Film as Catalyst Support

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**Here we show a photonic crystal (PC) supported photocatalyst prepared by loading meso-$C_3N_4$ nanorods onto polymeric $SiO_2$ colloidal crystals film, and demonstrate the synergetic enhancement of catalytic activity by the PC substrate. Compared to the traditional three dimensional ordered macroporous structure, the current PC with high crystallinity can be prepared in large scale following simplified procedures and its bandgap can be flexibly tuned, which makes the PC supported photocatalyst a practically usable material. It possesses higher activity than that deposited on regular substrate and it also shows longer catalyst life and easier separation features comparing with the dispersed catalyst.**

Photonic crystal (PC) or its composite has emerged as one kind of important smart materials due to its potential applications in photonic sensing[1-5], biochemical detection[6, 7], photonic printing[8-10], solar cell[11, 12] and photocatalysis[13-16]. Among all these applications, the synergetic enhancement to photocatalysis has attracted people's attention because it provides a new path to improve the photocatalytic performance in addition to the traditional bandgap engineering, surface plasmonic absorption enhancement and construction of z-scheme system. It is known that high efficiency of photocatalysis under sunlight irradiation can be achieved when semiconductor catalysts effectively absorb the visible light, and the separated photo-excited electrons/holes migrate to the surface without recombination.[17-19] Three dimensional ordered macroporous (3DOM) structures, as a typical inverse opal photonic crystal, can function as a Bragg mirror, reflect desired visible light with certain wavelength and enhance light harvesting for photocatalyst.

Recently, there have been successful demonstrations that the photocatalytic activity of semiconductor material can be promoted through the incorporation of macroporous photonic structures.[20, 21] For example, Quan et al. have reported a $TiO_2$-Au photocatalyst prepared by depositing Au nanoparticles onto $TiO_2$ 3DOM frameworks, which intensify light harvesting and improve the catalytic performance due to plasmonic absorption of Au and reflection enhancement by photonic structures.[14, 22] Zhou and Lou *et al.* also prepare $BiVO_4$ 3DOM materials with controllable dual porosity and prove that charge migration in these architectures shows strong dependence on the relative size of dual porosity.[23] Up till now, much attention has been paid to the construction of 3DOM structures with various chemical compositions including $TiO_2$[24], $WO_3$[25], ZnO[26], $Fe_2O_3$[13] and β-$Ga_2O_3$[27], which act as both the photocatalysts and the photonic materials. Most of these works prove that matching the photonic band gap (PBG) of 3DOM structures with the electronic band gap (EBG) of photocatalysts results in considerable enhancement of the photocatalytic activity under sunlight irradiation.[24]

Although photonic crystal has been proved to be a useful component in photocatalysis, its practical application is uneasy to be realized due to the lack of effective methods to produce high quality 3DOM structures in large scale. Generally, the production of 3DOM materials includes the preparation of colloidal crystal templates, the formation of inorganic macroporous framework in opal voids and the removal of template through calcination or etching. [28] In addition to very careful control for conversion from opals to 3DOM materials, a much bigger challenge seems to be the lack of adequate template when choosing this conversion route. In the past decade, various methods have been developed to prepare opal structure on different substrates, but the yield and crystallinity of PCs are unsatisfactory because a mass of defects and cracks will form during the conventional synthetic procedures. [28]

In this work, we find a new way to fabricate "photonic crystal based photocatalyst" through the deposition of meso-$C_3N_4$ nanorods on a premade silica/trimethylolpropane ethoxylate triacrylate ($SiO_2$/ETPTA) PC film. The PC film can be conveniently prepared based on the integration of spin coating, assembly of metastable colloidal crystals and photo polymerization reactions. Compared to the traditional 3DOM photocatalyst, the current PC supported photocatalyst has merits in many aspects. For instance,

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† Electronic Supplementary Information (ESI) available: experimental details, photos and reflection spectra of PC film and catatylst loaded PC film, optimized catalyst dosage, catalyst life in continuous reaction and enhancement in photocatalytic water splitting. See DOI: 10.1039/x0xx00000x

the synthetic procedures are greatly simplified and high quality PC film in large scale can be reliably prepared. The bandgap structure of PC film can be flexibly tuned to study and optimize the synergetic effect of photonic structure towards photocatalysis. As the catalyst are deposited on the PC film but not used to form the photonic structure, there will be great flexibility in choosing the catalyst with various chemical constituents.

First of all, the polymeric photonic crystal film is prepared by spinning the $SiO_2$ colloidal particles dispersed in monomer liquid (ETPTA) onto a 9-cm petri dish, followed by fixing the colloidal crystals through photo polymerization. (Fig. 1a) The synthesis is developed from the recent study of metastable colloidal crystals and polymerization induced colloidal assembly, which provides an effective way to obtain large-scale photonic crystal films with superior crystallinity. [29-31] Typically, $SiO_2$ particles dispersed in ethanol are mixed with ETPTA to form a homogeneous solution, which is concentrated by evaporating the ethanol at high temperature. The concentrated $SiO_2$/ETPTA solution is then spun onto the petri dish. The liquid film is kept steady for several minutes until a part of $SiO_2$ particles precipitate to form colloidal microcrystals due to supersaturation, leaving behind the rest of $SiO_2$ particles dispersed in solution disorderly. Since the particles are dispersed in photo-curable monomer, the precursor can be quickly transformed into a photonic crystal film under UV irradiation.

The as-prepared photonic crystal film has good crystallinity, intense reflection signals and uniform photonic structures throughout the film. Typically, the PC film shows a brilliant structural color due to its strong Bragg scattering of incident light projected onto the numerous colloidal microcrystals within the film. (Fig. 1b, d) Corresponding scanning electron microscope (SEM) images prove the ordered arrangement of colloidal particles in these microcrystals. (Fig. 1e) Here, reflection spectra are repeatedly measured in the “inner”, “middle” and “outer” region of the film in order to assess the evenness of PC film and explain the change of reflection signals. (SI Fig. 1) The photonic crystals within the same region have very close photonic structures except that a slight larger difference occurs in the inner region, which might be caused by the inadequate homogenization by spin coating in the center. Among different regions, the photonic structures regularly changed along the radial direction due to spin coating process. The average reflection wavelengths of inner, middle and outer PCs are 417 nm, 424 nm and 432 nm, where the deviation to their average value is smaller than 2.0%. The average reflection intensities for three regions are 46%, 87% and 76%. Since the inner region makes up only 1/9 of the whole film, the deviation of intensity is also acceptable. (Fig. 1c) With the tested position changes from inner to outer region, the reflection wavelength changes from 417 nm to 432 nm, because a larger centrifugal force applied to the outer particles will enlarge the interparticle spacing and thereby increase the reflection wavelength. At the same time, the reflection intensity increases from 46% to 76%, probably because a more effective homogenization of colloidal suspension in outer regions helps to the assembly of colloidal crystals with higher crystallinity. Overall, the PC film has strong, uniform and narrow reflections than most of the reported photonic materials and it can be produced in large scale without sacrificing its high crystallinity.

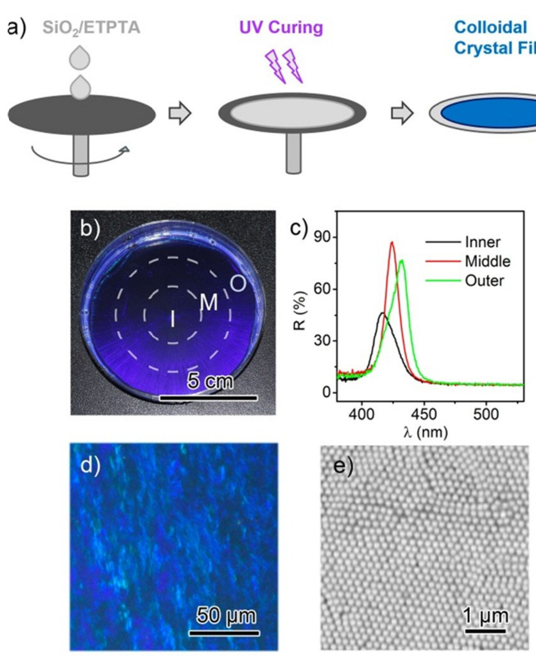

**Figure 1.** a) Fabrication of $SiO_2$/ETPTA PC film. b) Digital photo of PC film spread in petri-dish. c) Average reflection spectra measured at three regions of the PC film. d) Optical microscope and e) SEM image of PC film.

In order to investigate the influence of photonic structures upon the catalytic activity, mesoporous $C_3N_4$ nanorods are deposited on the PC film to form a supported photocatalyst for dye degradation and water splitting. (SI Fig. 2) It should be noted that the loading of photocatalysts won’t change the structure of photonic crystals. (SI Fig. 3) As a recently developed metal-free polymeric photocatalyst with appreciable performance under visible light irradiation, $C_3N_4$ is selected as the photocatalyst to combine with the PC support. The meso-$C_3N_4$ nanorods are prepared through high temperature polymerization of cyanamide inside $SiO_2$ nanotubes, which have average length of 650 nm and diameter of 130 nm. Since the PC supported photocatalyst shows a synchronized enhancement of activity in degradation and water splitting, we majorly use the degradation results to characterize the catalysts in this work.

The photocatalytic degradation proves that the introduction of photonic structure as catalyst support does enhance the catalytic activity and the photonic support with stronger reflections leads to better enhancement. Here, four samples including a pure ETPTA film and three $SiO_2$/ETPTA PC films with different reflection intensity are used as support in photo-degradation of aqueous solution of rhodamine B (RhB). (Fig. 2a, b) The reflection intensity is controlled by the addition of different amount of photo initiator during the synthesis. Since $-\ln(C/C_0)$ varies linearly with the reaction time, the photo-degradation can be regarded as a pseudo-first-order reaction and therefore the reaction rate constant ($k$) can be used to characterize the catalyst activity. When the reflection intensity increases from 13%, 48% to 93%, the rate constant increases from 0.0368, 0.0424 to 0.0481 $min^{-1}$ accordingly, all of which are higher than the rate constant with photocatalyst deposited on pure ETPTA film (0.0274 $min^{-1}$). For the transparent and pure ETPTA film, as the simulated solar light illuminates and goes through the meso-$C_3N_4$ layer, there is no reflected light being absorbed by the photocatalyst. However, for PC support, the reflected light will illuminate the photocatalyst again so that the extra light harvesting will further promote the yielding of photo electrons and thereby the photocatalytic activity. Due to this reason, one can expect an optimal dosage of catalysts loading on the PC support, as excessive catalyst will absorb too much incident light for PC film and decrease the secondary light harvesting by reflection so that the enhancement by PC substrate for photocatalysis will be weakened. In order to realize the best enhancement, the optimal catalyst loading on a circular PC film with diameter of 9 cm is determined to be 5 mg according to the experiments. (SI Fig. 4)

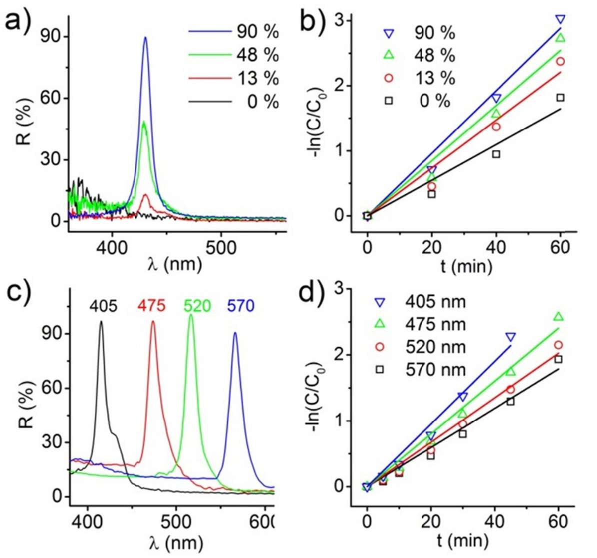

**Figure 2.** Reflection spectra of PC films with different a) intensity and c) wavelength. b, d) Corresponding kinetic curves of RhB degradation for catalysts loaded on these PC films.

Among all the photonic crystal film supports with different reflection wavelengths, the film with a photonic bandgap close to the absorption edge of photocatalyst has the best enhancement to the catalytic activity. Here, $SiO_2$ spheres with different diameters are used to prepare PC films with different PBGs but similar reflection intensity (90 ~ 100%). (Fig. 2c, d) The degradation results indicate that the rate constant (*k*) increases from 0.0296, 0.0338, 0.0401 to 0.0476 $min^{-1}$ as the wavelength blue shifts from 570 to 405 nm, accordingly. The UV-Vis diffuse reflectance spectrum (SI Fig. 2d) shows that the meso-$C_3N_4$ has an absorption edge at 470 nm. It absorbs visible light between 450 to 600 nm and more light with wavelength shorter than 450 nm. The degradation results together with the absorption of $C_3N_4$ suggest that the matching of PBG of supporting material with the EBG of semiconductor catalyst will promote the yielding of photo electrons and thereby enhance the catalytic activity for degradation, which are consistent with previous reports of photonic crystal enhanced photocatalysis.[14, 22]

When meso-$C_3N_4$ nanorods are loaded on multi-layer PC film, their activity can be further improved due to the multiple light harvestings within a broader range of wavelength. (Fig. 3) Thanks to the recent developed metastable colloidal crystal and its fixing techniques, multilayer PC films with narrow, strong and separate reflections at different wavelengths can be prepared following a layer-by-layer process. When the catalysts are deposited on a PC film with single reflection at 450 nm, a low activity with rate constant of 0.0412 $min^{-1}$ can be determined from the dynamic curves. As the same amount of catalysts are loaded on a bilayer PC film with reflections at 440 and 480 nm, its activity is improved and the rate constant reaches 0.0514 $min^{-1}$. Replacing the support with a triple-layer PC film with reflections at 405, 440 and 480 nm will lead to an even larger rate constant of 0.0783 $min^{-1}$, which is 1.9 times as the one in the single-layer case. The narrow and strong reflections of PC multilayers is the key to realize the enhancement of photocatalysis, because the top layer PC film will slightly absorb the incident light for the bottom layer or block the reflected light from the bottom layer at the latter's PBG wavelength. This "near-transparent" characteristic makes it possible to integrate the single-PBG PC film into a dimensionally confined form without sacrificing own enhancing effects. The increased light harvest from multilayer support will certainly enhance the production of photo electrons/holes, so that a higher photocatalytic activity will be achieved. PC substrate composed of even more layers will theoretically lead to more absorption and further enhancement of photocatalytic activity. However, as the layer number gradually increases, the incident light for the bottom layers as well as the reflected light will eventually be blocked by the top layers, so that the enhancement effect will be gradually weakened.

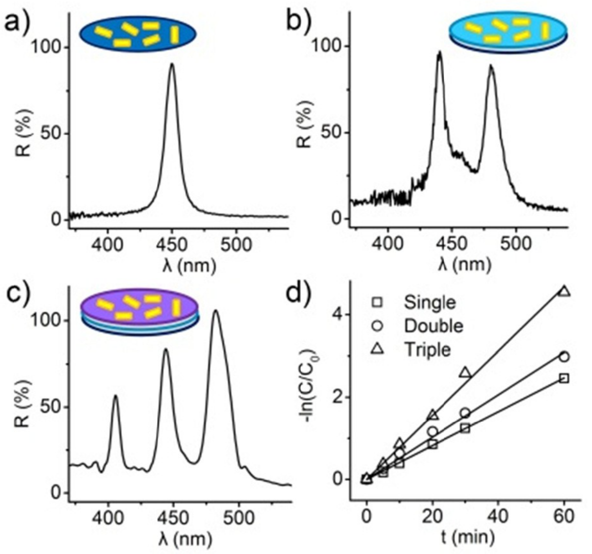

**Figure 3.** Reflection spectra of a) single-layer, b) double-layer and c) triple-layer PC film, and d) the kinetic curve of RhB degradation for catalysts loaded on these substrates.

In addition to the enhancement of catalytic activity, the PC supported nanocatalyst also has intrinsic advantages in separation and recycling utilization compared to the dispersed nanocatalyst. Same amount of meso-$C_3N_4$ nanorods are deposited on PC film and directly dispersed in solution, which are then used in 5 continuous degradation of RhB to evaluate the catalyst life and stability in practical reaction. (SI Fig. 5) The dispersed meso-$C_3N_4$ photocatalyst has high conversion around 97.9% in the first round, which gradually decreases to 65.6% in the following degradation. (Red bars) The decrease in activity might be caused by the aggregation of nanorods during reaction or the inevitable mass loss during centrifugation. When the meso-$C_3N_4$ nanorods are deposited on the PC film, their activity has no significant reduction and the conversion slightly decreases from 89.2% to 87.9% in the same case. (Black bars) At the beginning, the immobilized photocatalyst has a relatively low activity than the dispersed one because the active sites of the dispersed catalyst can contact with substrate molecules better in liquid-phase reaction. However, after three cycles, the activity of immobilized catalysts becomes higher than that of the dispersed ones because they won't suffer from the aggregation or mass loss in the continuous reactions. Furthermore, the immobilized catalyst brings much convenience in the practical photocatalytic reactions, since it can be easily separated from the solution and it requires neither regeneration nor recovery procedures. The excellent catalytic stability as well as the high separation efficiency will render the current photocatalyst more advantages in practical applications.

In summary, meso-$C_3N_4$ nanorods are deposited on $SiO_2$/ETPTA PC film to form a supported photocatalyst, which is used to demonstrate the effective enhancement of catalytic activity by photonic structures. Circular PC film with narrow, intense and uniform reflection signals can be conveniently prepared based on the integration of spin coating techniques, the assembly of metastable $SiO_2$ colloidal crystals and the polymerization process. Compared to the synthesis of 3DOM photocatalysts, the current composite material has intrinsic advantages in not only the large scale production of photonic crystal but also the flexible choosing of catalysts with different chemical constituents. The degradation experiments show that the PC film with intense reflection and reflection wavelength close to the EBG of photocatalyst has better enhancement to the catalytic activity. Meanwhile, the activity can be further improved when the photocatalysts are loaded on multi-layer PC film. All these results proves that the introduction of matched photonic structure will provide extra reflected light to the photocatalysts, which will promote the yield of photo electrons and thereby enhance the activity. Such enhancement is also observed in the splitting of water under visible light irradiation. (SI Fig. 6) Since the PC supported photocatalysts also has good stability, long catalyst life and low loss in the recycling catalysis, it will have great potential in many green chemical processes.

## Acknowledgements

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## Table of Content

# Synergetic Enhancement of Photocatalytic Activity with Photonic Crystal Film as Catalyst Support

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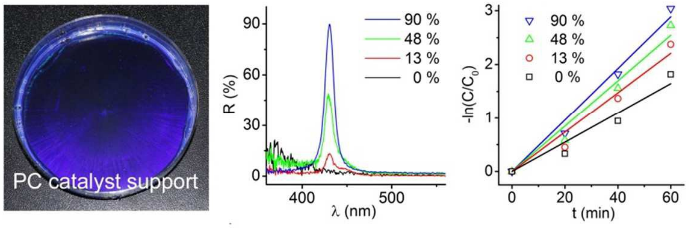

Photonic crystal can be used as support of photocatalyst, which synergistically enhance the photocatalytic activity due to extra light harvesting.