



# Excellent mechanical properties of three-dimensionally ordered macroporous nickel photonic crystals

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## ABSTRACT

High quality three-dimensionally ordered macroporous (3DOM) nickel photonic crystals (PCs) are fabricated using the polystyrene template-assisted electrodeposition method on nickel alloy substrate. The Ni<sup>2+</sup> in solution will firstly arrive in the electrode (nickel alloy substrate) and occupy the interstices among the PS template spheres; when enlarge the deposition time to 5 min, 3DOM nickel PCs will be achieved. The 3DOM nickel PCs grow firmly on the substrate due to the similar bounds between the PCs and substrate. Excellent mechanical properties are observed in the 3DOM nickel PCs, which may promote the practical applications of PCs.

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## 1. Introduction

Photonic crystals (PCs) are at the focus of the three-dimensionally ordered macroporous (3DOM) materials. The existence of the photonic band gap in PCs makes them have the large applications in the optical communications, sensors, solar cells, etc. [1–6]. High quality PCs have deep photonic band gaps and steep photonic band edges, which are necessary for the use of PCs in the practical optical applications [7]. Therefore, various attempts have been made to prepare the PCs, such as chemical vapor deposition, electrochemical deposition, sol-gel techniques and atomic layer deposition [8–11]. Especially, the self-assembly method is widely used to synthesize the PCs. A lot of effectively modified self-assembly methods had been developed to achieve the high quality PCs. For example, Jiang et al. and Zheng et al. developed vertical deposition method and pressure controlled vertical deposition method for fabricating PCs, respectively [12–13]. Recently, we fabricated high quality 3DOM germanium PCs using direct template-assisted electrodeposition in ionic liquids, which provided a novel route for the synthesis of 3DOM PCs [14]. Different from other methods that the deposited materials fill from surface of the template spheres, the deposited germanium will firstly arrive

in the electrode (substrate) and occupy the space among the template spheres during the electrodeposition process. So the growth of germanium PCs begins from the surface of electrode (substrate) due to the force of the electric field rather than from the top few layers of template.

It is well known that the porous nickel materials with high surface area have wide applications in the fields of catalysts, high-density data storage, lightweight structure, electrodes, and sensors [15]. Similar with our method for the synthesis of high quality 3DOM germanium PCs, template-assisted electrochemical deposition has been used to prepare the 3DOM nickel structure [16]. However, the 3DOM PCs cannot grow firmly on the substrate yet and usually strip away from the substrate, which restrict the applications of PCs. It is necessary to enhance mechanical properties of 3DOM PCs and substrate. Ma et al. found that the nickel films on carbon steel sheet showed good mechanical properties [17]. Therefore, it is worthwhile to find the optimal condition for achieving high quality nickel PCs on metal substrate because the good mechanical properties is expected.

In this paper, we investigate the mechanical properties of 3DOM nickel PCs, which are prepared using the template-assisted electrodeposition method on nickel alloy substrate. Scanning electron microscopy (SEM) images give clear supporting data that the high quality 3DOM nickel PCs are achieved. The 3DOM nickel PCs, growing on the nickel alloy substrate directly, show an excellent mechanical strength due to the similar bounds between nickel PCs and substrate.

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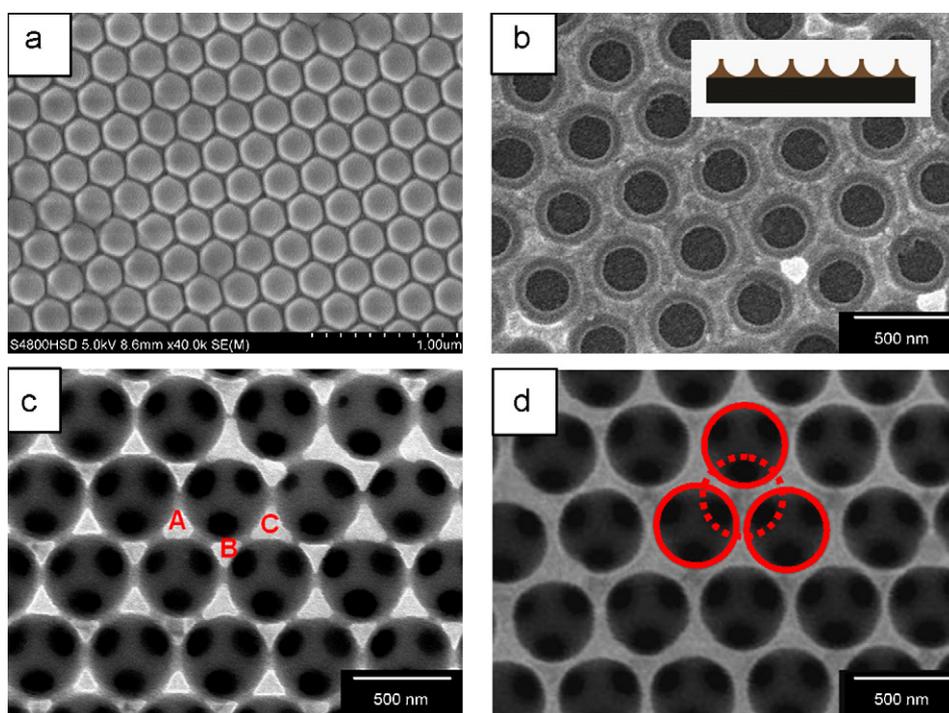


Fig. 1. (a) SEM images of the PS template. The nickel PCs prepared at 40 °C with different electrodeposition time: (b) 1 min, (c) 3 min and (d) 5 min.

## 2. Experimental details

The three-dimensionally ordered macroporous (3DOM) nickel photonic crystals (PCs) were synthesized by the template-assisted electrodeposition method, which includes three steps as describing in Ref. [14,18]. First, the polystyrene (PS) latex spheres, as shown in Fig. 1(a), were prepared by the self-assembly of polystyrene (PS) latex spheres on nickel alloy substrate that was put into 1 wt% polystyrene spheres latex. After the water evaporating completion, the well-ordered PS templates formed. Second, the nickel alloy substrates with the ordered PS template were immersed into the electrolyte, and the deposition begins at different temperature. Where the nickel alloy substrate is the working electrode and the constant cathode current density is fixed at  $30 \text{ mA cm}^{-2}$ . Third, the PS template was thoroughly removed with toluene for 2 days and the nickel PCs were achieved.

The surface morphology of the samples was obtained using a HITACHI S-4800 field emission scanning electron microscope (SEM). The nanoindentation tests with atomic force microscope (AFM) were conducted using a TriboIndenter from Hysitron with a three-sided pyramidal Berkovich diamond indenter. The values of hardness and Young's modulus were calculated by the Oliver and Pharr method using a tip shape correction [19].

## 3. Results and discussion

Fig. 1(b)–(d) shows the SEM images of nickel PCs formed at different electrodeposition time after removing the PS templates in toluene. It is clear that the porous monolayer nickel two-dimensionally (2D) structure will be achieved when the deposition time is as shorter as 1 min. The holes in Fig. 1 are due to the removed PS spheres, and the cirques are nickel. The porous 2D nickel structure suggests that the  $\text{Ni}^{2+}$  in solution will firstly arrive in the electrode (nickel alloy substrate) and occupy the interstices among the PS template spheres. When enlarge the deposition time to 5 min, 3DOM nickel PCs will be achieved, as shown in Fig. 1(d). Obviously, the holes into the layer below are clearly visible; the average center-to-center distance between the holes is about 500 nm, similar with the PS spheres diameter of 560 nm. These results indicate that high quality 3DOM nickel PCs are fabricated using the PS template-assisted electrodeposition method. Interesting, when the deposition time is about 3 min, the top nickel layer of 3DOM nickel PCs does not continue and the nickel firstly appear in the space among the three PS spheres, as shown in Fig. 1(c).

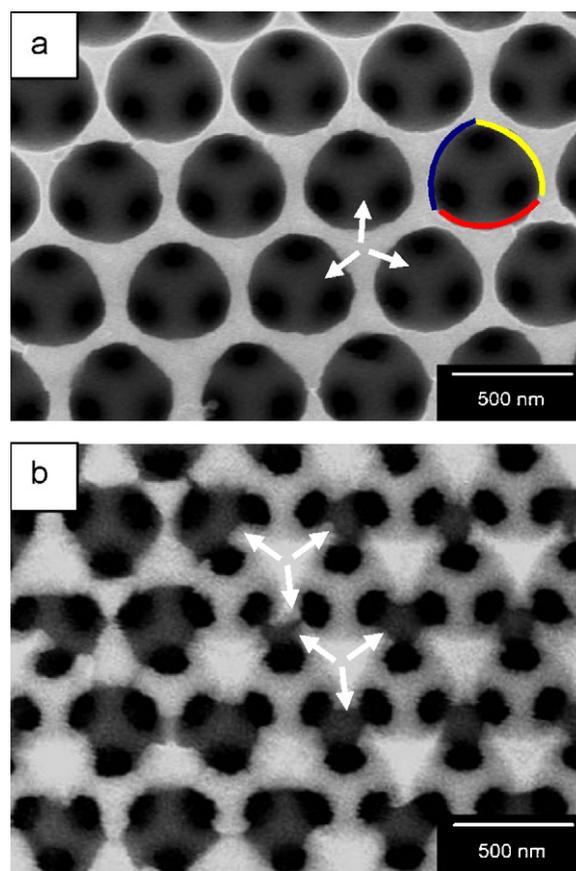


Fig. 2. SEM images of nickel PCs prepared at different deposition temperature for 5 min: (a) 50 °C and (b) 60 °C.

It is well known that the deposition condition play (such as the temperature and pressure) an important role in the quality of PCs [13]. Optimal condition is necessary for achieving high quality 3DOM PCs in application. So, we change the deposition temperature from 40 to 60 °C at a constant cathode current density of 30 mA cm<sup>-2</sup>. Figs. 1(d) and 2 show the SEM images of nickel PCs formed at different deposition temperature. Perfect circular holes are observed in the high quality sample prepared at 40 °C. The holes and the width of nickel cirques are uniformed. However, the width of the nickel cirques increase with increasing deposition temperature and the circular holes become unequal with increasing the temperature. We can't find circular holes at the top layer of the sample prepared at 60 °C. The PS template quality and deposition rate are the key issues in the formation of the high quality 3DOM PCs. On the one hand, the self-assembled PS template will become coarse at high temperature, which can influence the quality of the PCs. On the other hand, the metal ion deposition rate increases with increasing temperature due to the higher diffused rate at high temperature. The higher deposition rate results in the metal accumulation at the space where the deposited metal firstly appears. Therefore a lot of the nickels accumulate at the border of the nickel cirques, and the quality of the PCs decreases with increasing deposition temperature. The SEM patterns give clear supporting data that we can prepare high quality 3DOM nickel PCs using the PS template-assisted electrodeposition method, and that the optimal position temperature is at 40 °C. We investigate the mechanical properties of 3DOM nickel PCs prepared at 40 °C on nickel alloy substrate; the deposition time is 5 min and the thickness of nickel PCs is about 2 μm. We measured the load-displacement curve of 3DOM nickel photonic crystal and the 3DOM nickel PCs will be broken when the tensile strain is about 31%, as shown in Fig. 3. Fig. 4(a) and (b) shows the SEM images of nickel PCs under 0% and 10% ten-

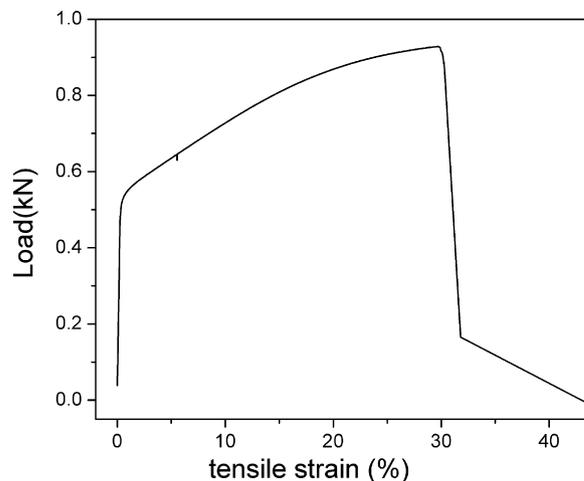


Fig. 3. The load-displacement curve of nickel PCs.

sile strains, where the load is about 2000 μN and the indentation depths are about 0.32–0.35 μm. After 10% tensile strain, the holes of nickel PCs change a little and the nickel PCs still grow firmly on the substrate. Fig. 4(c) shows the load-displacement curves of nickel PCs under 0 and 10% tensile strains. The penetration depth is larger for the PCs under 10% tensile strain than that of PCs without strain, suggesting that the tensile deformation lowers the hardness of the nickel PCs. The hardness and Young's modulus of PCs without strain are 0.98 GPa and 23.5 GPa, respectively. Although this hardness and Young's modulus data of nickel PCs are smaller than that of nickel films with 3.0 μm thickness on carbon steel sheet [17],

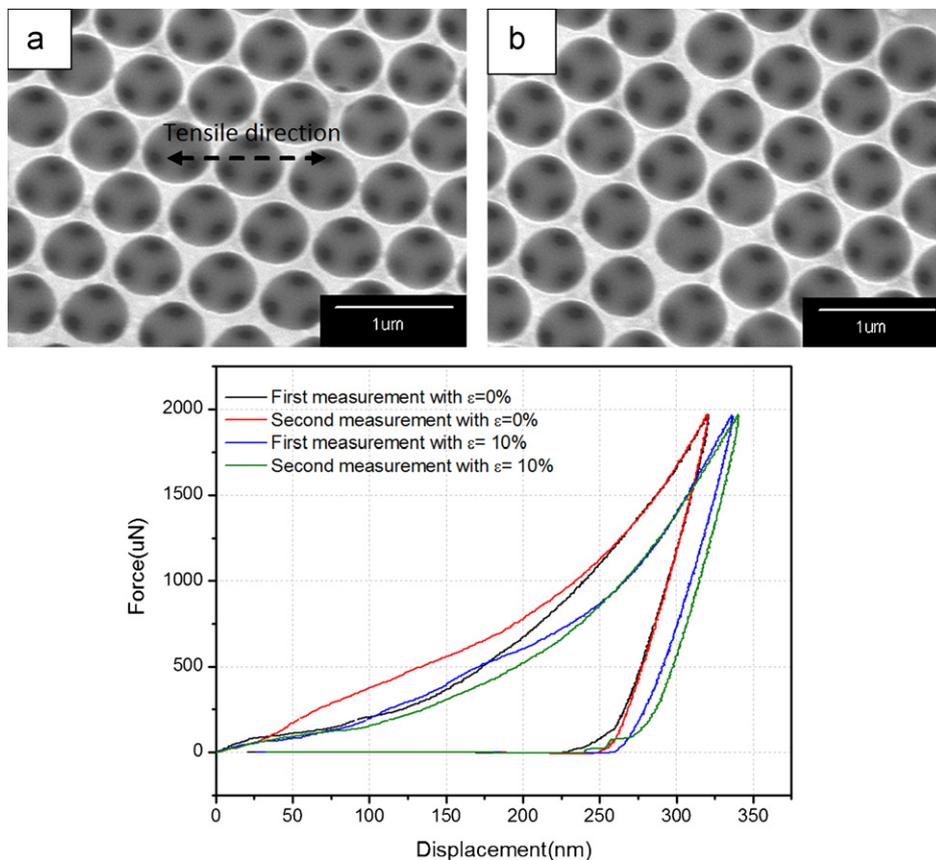


Fig. 4. The SEM images of nickel PCs under (a) 0% and (b) 10% tensile strains. (c) The load-displacement curves of nickel PCs under 0 and 10% tensile strains.

but these data are very wonderful for the 3DOM PCs. Similar with that of thick nickel films, the hardness (0.88 GPa) and Young's modulus (22.6 GPa) of 3DOM nickel PCs with 10% strain are also little smaller than that of PCs without strain. Furthermore, after releasing the 10% tensile strains, the holes and the width of nickel cirques in 3DOM nickel PCs are still uniformed, and the holes into the layer below are clearly visible. These results imply that the 3DOM nickel PCs on nickel alloy substrate have good mechanical properties. The firm growth of nickel PCs on the nickel alloy substrate is due to the similar bounds between the PCs and substrate, which contribute intrinsically to the excellent mechanical properties of 3DOM nickel PCs on nickel alloy substrate.

#### 4. Conclusion

In summary, we prepared high quality 3DOM nickel PCs using the template-assisted electrodeposition method on nickel alloy substrate. The optimal synthesis temperature of high quality 3DOM nickel PCs is about 40 °C. The similar bounds between the nickel PCs and nickel alloy substrate contribute intrinsically to the firm growth of nickel PCs on substrate, which results in the excellent mechanical properties of 3DOM nickel PCs.

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