GRAPHENE NANOSIEVE USING BLOCK COPOLYMER LITHOGRAPHY AND ITS APPLICATION TO SEPARATION OF HEMOGLOBIN PROTEIN AND IMMUNOGLOBLIN G

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ABSTRACT

This paper reports a graphene nanosieve using a unique block copolymer lithography method and its application to separation of hemoglobin (Hb) and human immunoglobulin G (IgG) proteins. The preliminary fabrication process for the nanopores using universal block copolymer lithography was reported in Advanced Materials. [1] Our method differs from that of group C. Dekker [2] in the specific method of grapheme nanopores fabrication and its targeting application of the DNA translocation.

KEYWORDS

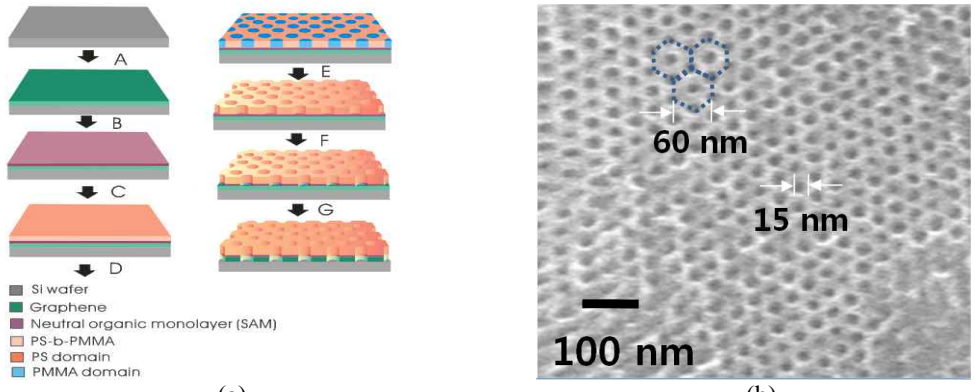
Proteins separations, Nano sieve, Graphene, Block copolymer lithography

INTRODUCTION

Ultrathin nanosieves with nanopores are highly being important for their versatility and outstanding performance comparing to a commercialized nanoporous membrane.[3] Even though numerous methods have been reported, they are still very expensive and cannot be realized in a large scale,[4] or need a complicated processing technique. Here, we propose a unique and handy method for fabricating a nanosieve. Without any specialized photolithography, processes or equipment, general block copolymer spin coating and reactive ion etching (RIE) were only used. Spin coating and RIE are well-known and very reliably mass-producible processes. Thus, the proposed method has great advantages of low cost, reproducibility and high throughput. In this work 3~4 nm-thick graphene nanosieve was successfully manufactured, and the pores size could be controlled from several nanometer to several tens of nanometer, by controlling the mixing ratio of polymers and annealing temperatures.

EXPERIMENT

Figure 1 shows schematic diagram of the grapheme nanosieve fabrication using lithography process based on polystyrene (PS) - polymethyl metacrylate (PMMA) block copolymer. A nano-template of surface perpendicular PMMA cylinders in a PS matrix assembled on a graphene film (average diameter of PMMA cylinders: 15 nm, center-to-center distance between neighboring cylinders: 45 nm) was utilized and etched using RIE as shown in Fig. 1(b).



(a) (b)

Figure 1. Schematic diagram of the grapheme nanosieve using block copolymer lithography process (a), and the SEM photograph of grapheme sieve with nanopores of a diameter of 15 nm (b) .

The etching grapheme nanofilm is transferred successfully to the 1.5 cm x 1.5 cm silicon device, which has low stresses SiN membrane with one micrometer-wide micropores (Figure 2). In order to investigate the separation ability of the grapheme nanopores, we did a separation test between the haemoglobin with a diameter of around 7 nm and the IgG with a diameter of above 15 nm.

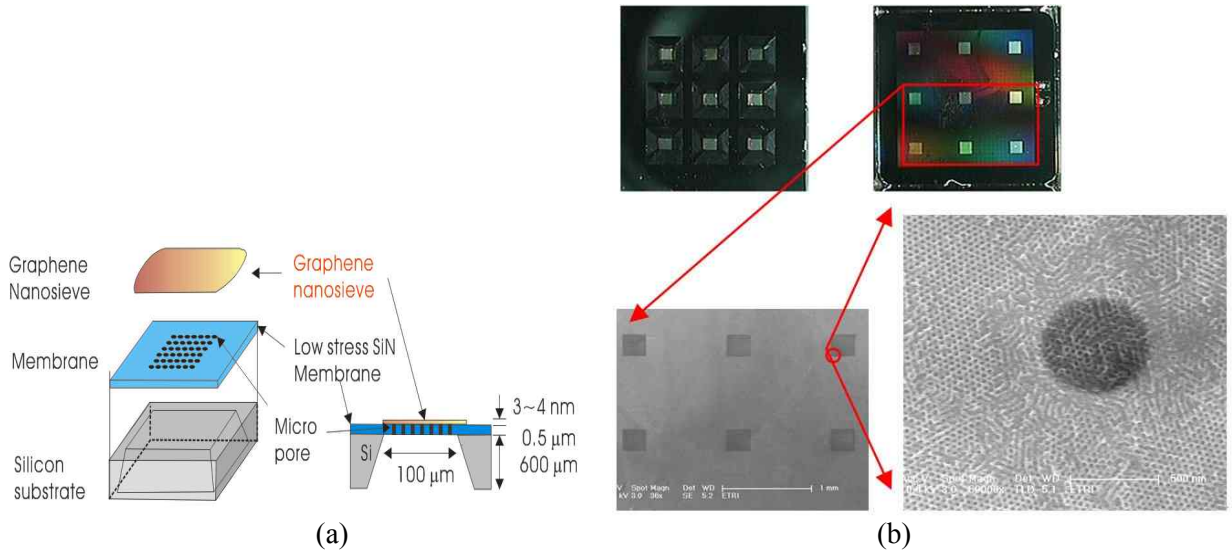


Figure 2. Cross-sectional view of the nano-sieve devices; top and bottom photographs(a) and top SEM photographs of them (b).

In order to observe their performances, first, we had tagged Hb with Alexa fluor 488 nm beads and IgG with Alexa fluor 350 nm beads, respectively. Two proteins are diluted to be a concentration of 100 mg/mL and mixed together, and put on the nanosieves. One mole Hb was labelled with 2 mole dyes and one mole IgG labelled with 6 moles dyes. The fluorescence photographs when starting and after 10 min according to the light-emitting frequencies are shown in Figure 3. The fluorescence intensity in case of Hb is increased but, the intensity in case of IgG is decreased after 10 min reaction. It shows that the separation of two kinds of proteins can be separated using the grapheme-based nanosieve device, in which the diameter of the pores are controlled to be about 15 nm, simply and clearly.

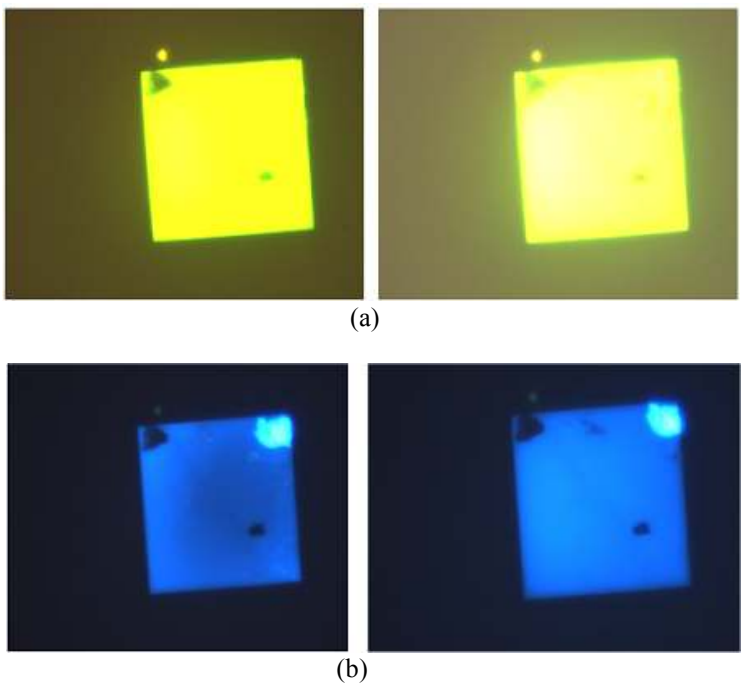


Figure 3. Fluorescene photographs showing selective penetration of mixture of two proteins (Hb) (a) and Immunoglobulin G (IgG)) (b) at separation-starting time and after 10 min. IgG is tagged with 350 nm-fluorescence dyes and Hb with 480 nm-fluorescence dye.

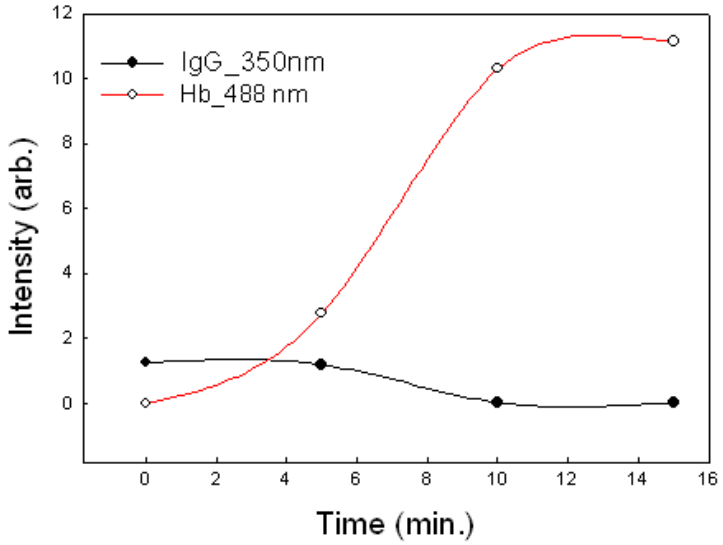


Figure 4. Fluorescence intensity as a function of penetration time using a mixture of Hb and IgG proteins. The signals were measured at a 50 μm-away from the edge of the supporting membrane (200x200 μm^2).

From the edge of the membrane, the diffusion signalling intensity of Hb increases and the intensity of IgG decreases as a function of the operation time (Figure 4). By controlling the diameter of the pores to about 15 nm, it could separate two kinds of proteins easily and rapidly.

We conformed that the separation process is saturated within ten minutes. Since the fabrication of the grapheme nanosieves is so simple and easy to use and the separation of proteins works reasonably, the method can be applicable to the various medical devices, a fuel cell, and water purification.

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