# Electrochemically prepared black silicon for improved photon-to-electron conversion efficiency

**Xianyu Ao**

*Centre for Optical and Electromagnetic Research, South China Academy of Advanced Optoelectronics, South China Normal University, University City, Guangzhou 510006, China*
*E-mail address: optixy@foxmail.com*

**Abstract:** Black silicon with multiscale texture was prepared by electrochemical etching. To confirm the benefits, we coated it with $TiO_2$ and used it as the photoanode in water splitting, and observed 45% enhancement in photocurrent density.
**OCIS codes:** (220.4000) Microstructure fabrication; (160.6000) Semiconductor materials; (040.5350) Photovoltaic

Texturing the silicon surface can reduce the total reflection (and correspondingly enhance the light absorption) and increase the surface area. For applications in converting photons into electrons, however, an increased surface area also means higher surface recombination rate. A balance must be struck between the enhanced light absorption and the potentially higher surface recombination loss, in order to improve photon-to-electron conversion efficiency. In this paper, we introduce an electrochemical method to produce macroporous black silicon with multiscale texture, where the increase in surface area is much smaller than the case with nano-structured black silicon. To confirm the benefits from the black silicon, we coated our black silicon with $TiO_2$ and used it as the photoanode in water splitting. Our macroporous black silicon increased the photocurrent density by about 45%.

Besides irradiating silicon with femtosecond laser pulses [1], reactive ion etching [2,3] and metal-assisted wet etching [4-7] were previously employed to prepare black silicon, forming random nanospikes or nanoholes. The reflection was reduced by creating an effective index gradient, with a feature size smaller than the wavelength of light. In contrast, macroporous silicon has a much larger feature size, and established technologies to etch straight pores in silicon, with diameters in the range of sub-micrometers up to several micrometers as well as high aspect ratios, have been developed [8]. Moreover, pores having large diameter variations on the length scale of the interpore distance can be achieved [9-11], allowing the fabrication of complex three-dimensional (3D) structures with a sufficient precision even to provide applications as 3D photonic crystals [12]. This 3D etching capability is unique among all the microfabrication techniques. Here we demonstrate that macroporous silicon can also be made black. Figure 1(a) shows a bird's eye view of our black silicon. Moreover, light-trapping structures can be incorporated in a single run. Figure 1(b) shows an example of modulated pores, which can realize the function of light trapping. As shown in Fig. 2, the total reflectance from our black silicon is below 5% over 400 – 1000 nm (the short wavelength part is limited by the light source used for this measurement), and close to zero around 500 nm. Note that the interpore distance (6 μm) is much larger than the optical wavelength concerned.

We coated our black silicon with $TiO_2$ by atomic layer deposition [13] and used it as the photoanode in water splitting. In photocatalytic splitting of water into $H_2$ and $O_2$ [14,15], electrons and holes, generated in semiconductors upon light absorption, drive the reduction and oxidation reactions, respectively. (In Ref. 7, nanostructured p-type black silicon was used as a photocathode to produce $H_2$ from water, and a 20% enhancement relative to a polished sample was observed.) The photocurrent density and onset potential of our samples are comparable to those from n-$TiO_2$ coated n-Si nanowire arrays [16,17]. Increasing the surface area of photoelectrodes can reduce the overpotential for gas evolution [7]. The relative shift of the onset potential after macroporous etching is not so dramatic as the case with silicon nanowire array [16], which reflects that the relative increase of surface area in our case is much smaller (this point should be beneficial for photovoltaic applications which means relatively low surface recombination rate in comparison with nanostructured silicon).

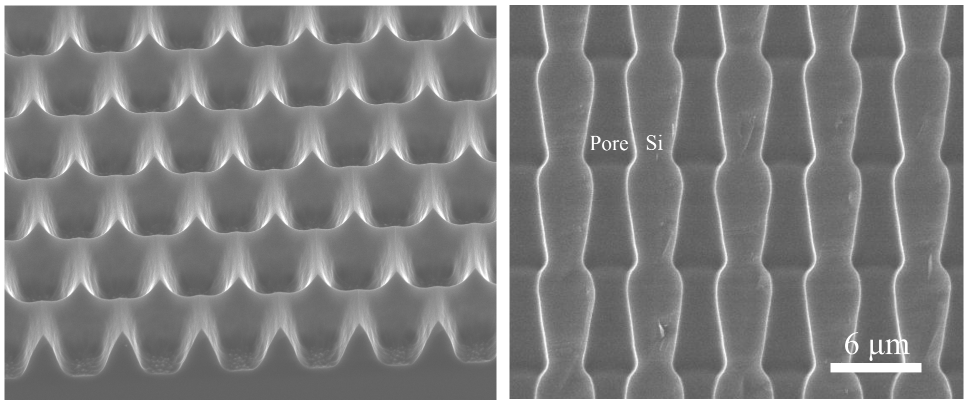


**Fig. 1** SEM images of macroporous silicon. The pores were arranged in a hexagonal pattern with an interpore distance of 6 μm. (a) Tilted top view of the entrance of the etched pores. (b) Cross-sectional view of an array of modulated pores.

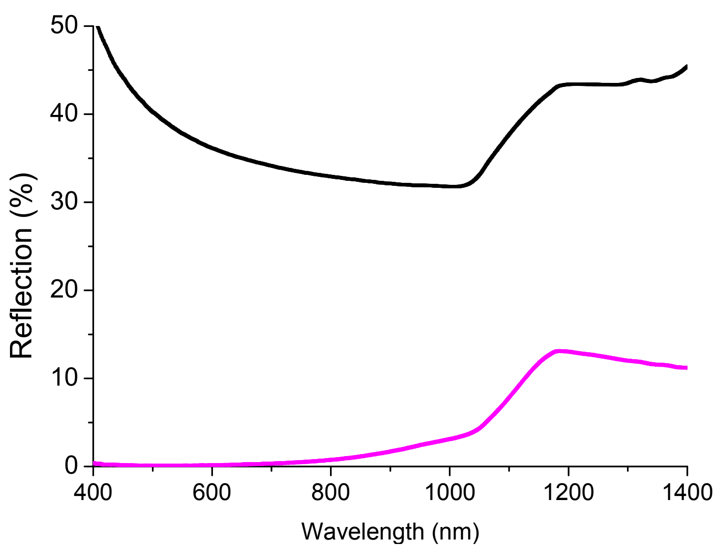


**Fig. 2** Measured total reflectance spectra from bare silicon (upper curve) and our black silicon (lower curve).

In summary, we demonstrated that black silicon with a modulated macropore array can achieve great light absorption enhancement. We observed a 45% enhancement in photocurrent density in photocatalytic water splitting by our black silicon coated with $TiO_2$, in comparison with the reference sample. In contrast to previous nanostructured black silicon, the etching process here has neither metal contamination nor requirement of vacuum facilities, and additionally, the increase in surface area (thus the surface recombination loss) is relatively small.

**References**

[1] T.-H. Her, R. J. Finlay, C. Wu, S. Deliwala, and E. Mazur, Appl. Phys. Lett. **73**, 1673 (1998).
[2] M. Otto, M. Kroll, T. Käsebier, S.-M. Lee, M. Putkonen, R. Salzer, P. T. Miclea and R. B. Wehrspohn, Adv. Mater. **22**, 5035 (2010).
[3] L. Sainiemi, V. Jokinen, A. Shah, M. Shpak, S. Aura, P. Suvanto and S. Franssila, Adv. Mater. **23**, 122 (2011).
[4] S. Koynov, M. S. Brandt and M. Stutzmann, Appl. Phys. Lett. **88**, 203107 (2006).
[5] H. M. Branz, V. E. Yost, S. Ward, K. M. Jones, B. To, and P. Stradins, Appl. Phys. Lett. **94**, 231121 (2009).
[6] F. Toor, H. M. Branz, M. R. Page, K. M. Jones, and H.-C. Yuan, Appl. Phys. Lett. **99**, 103501 (2011).
[7] J. Oh, T. G. Deutsch, H.-C. Yuan and H. M. Branz, Energy Environ. Sci. **4**, 1690 (2011).
[8] V. Lehmann, Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications (Wiley, Weinheim, 2002).
[9] F. Müller, A. Birner, J. Schilling and U. Gösele, C. Kettner, P. Hänggi, physica status solidi (a) **182**, 585 (2000).
[10] S. Matthias, F. Müller, J. Schilling and U. Gösele, Appl. Phys. A **80**, 1391 (2005).
[11] A. Langner, M. Knez, F. Müller and U. Gösele, Appl. Phys. A **93**, 399 (2008).
[12] S. Matthias, F. Müller, C. Jamois, R. B. Wehrspohn and U. Gösele, Adv. Matter. **16**, 2166 (2004).
[13] M. Knez, K. Nielsch and L. Niinistö, Adv. Mater., **19**, 3425 (2007).
[14] A. Fujishima and K. Honda, Nature **238**, 37 (1972).
[15] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, Chem. Rev. **110**, 6446 (2010).
[16] Y. J. Hwang, A. Boukai and P. D. Yang, Nano Lett. **9**, 410 (2009).
[17] J. Shi, Y. Hara, C. Sun, M. A. Anderson and X. Wang, Nano Lett. **11**, 3413 (2011).