Supporting Information

Advanced Nanostructuring and Gradient Phosphorus Doping Enhance *p*-Si Photocathode Performance for Photoelectrochemical Water Splitting

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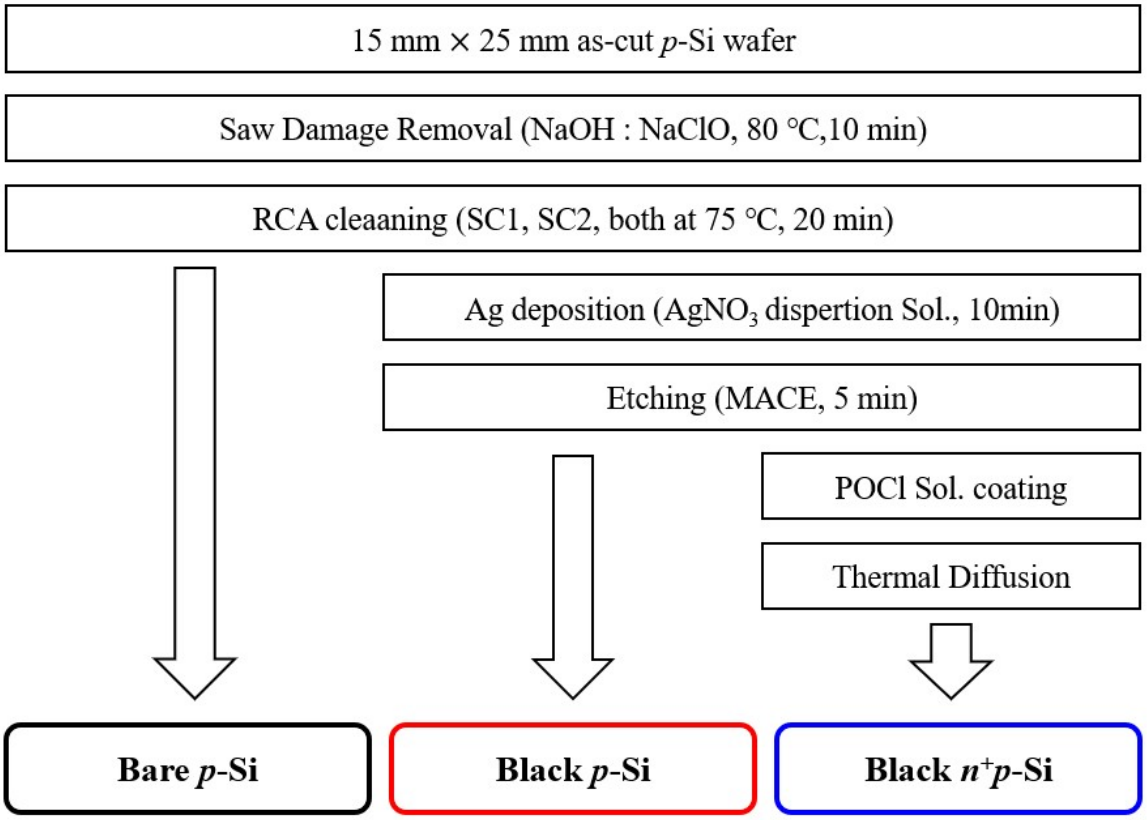


Figure S1 depicts the sequence of the sample fabrication process. We began with a 15 mm × 25 mm commercial *p*-Si wafer. This *p*-Si was subjected to Saw Damage Removal (SDR) followed by a cleaning process, culminating in the production of Bare *p*-Si. To further enhance its properties, we employed the Metal Assisted Chemical Etching (MACE) technique using Ag, resulting in a nanoporous structure known as Black *p*-Si. For doping purposes, a POCl solution was prepared by combining H_3PO_4 and P_2O_5. Finally, the Black *p*-Si was doped with this high-concentration POCl solution through a thermal diffusion method, leading to the creation of Black n^+p-Si.

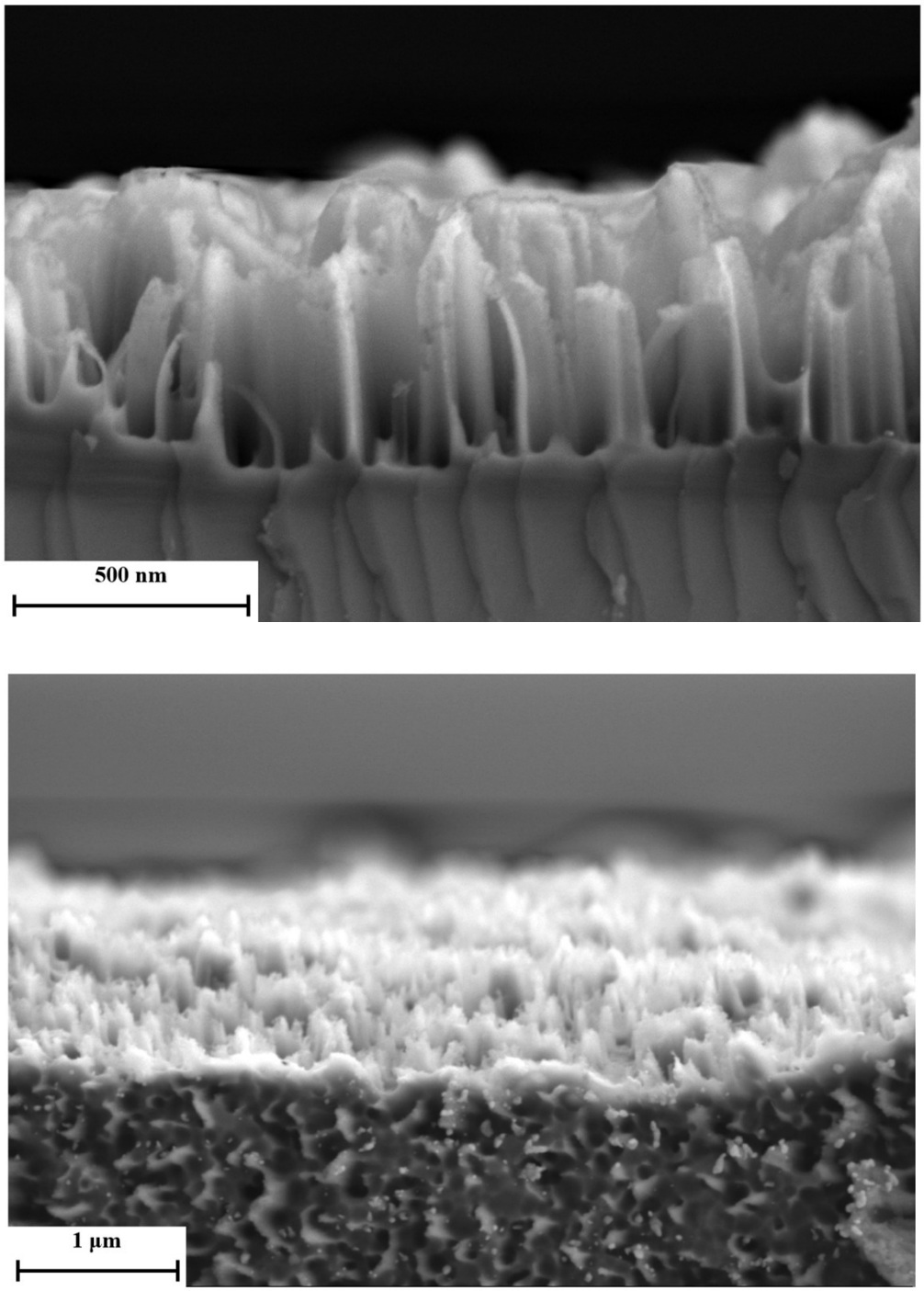
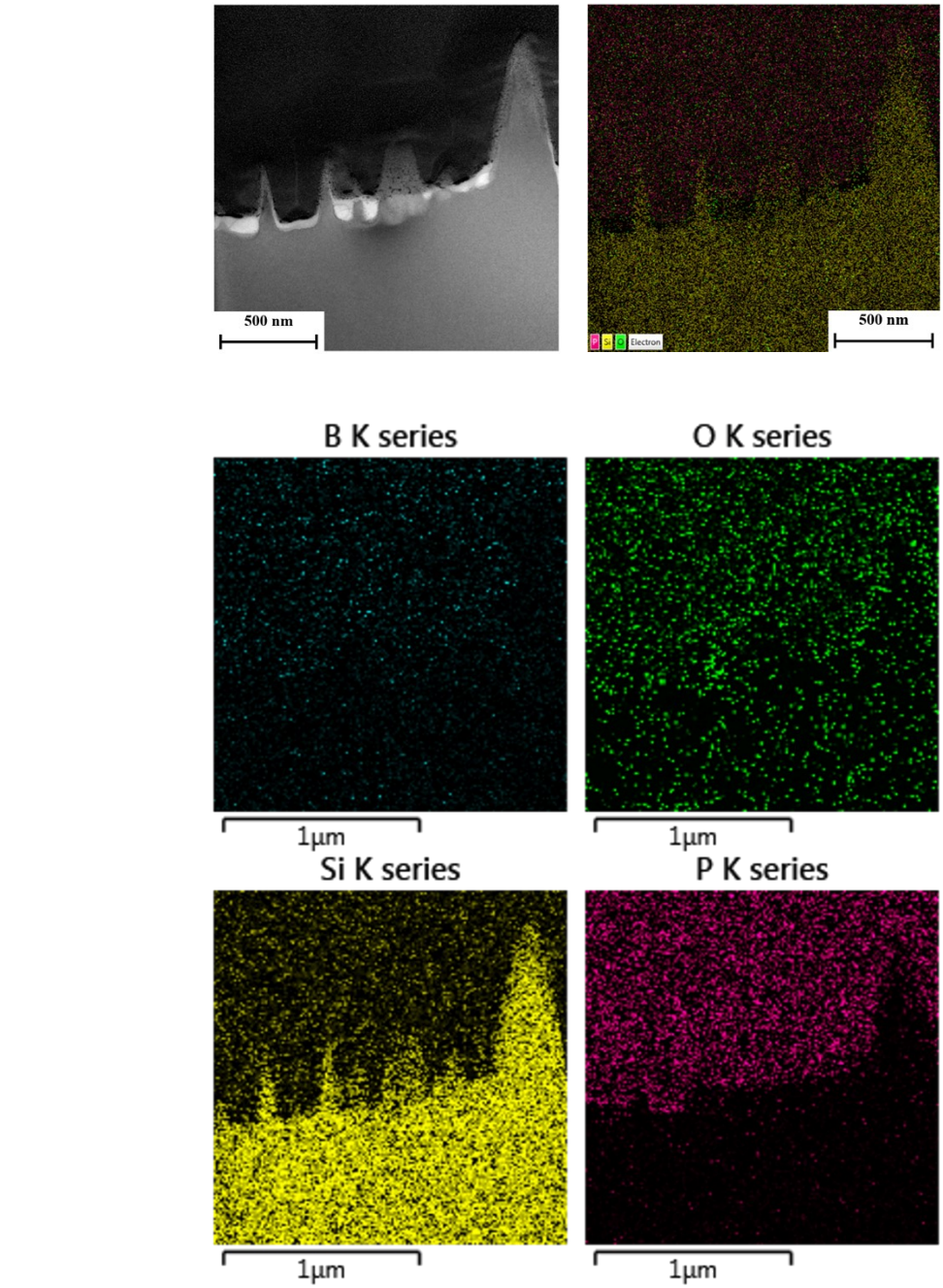


Figure S2 shows the cross-sectional SEM image of Black *p*-Si with nanoporous structure. The porous morphology covers the entire surface with a pore depth of ~1 µm, contributing to reducing the high light reflection properties of crystalline silicon.



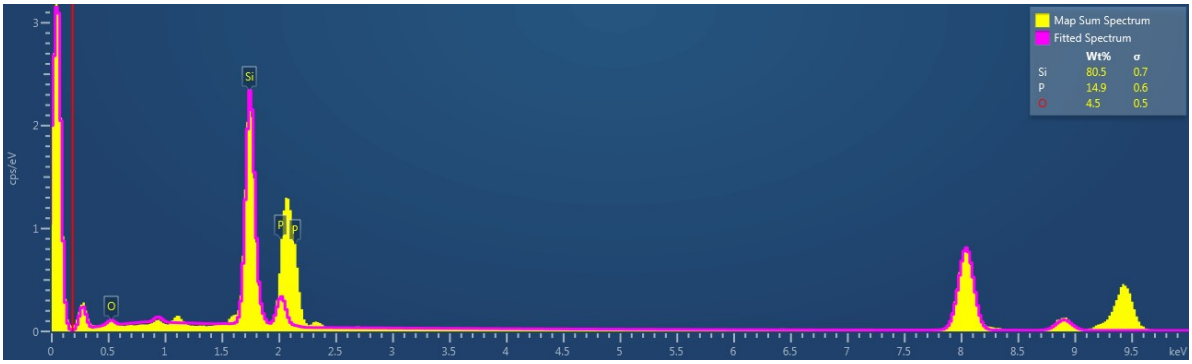


Figure S3 presents the cross-sectional TEM-EDS image of Black $n^{+}p$-Si. Phosphorus diffuses along the nanostructure interfaces to the Si substrate, as evident in the indistinct nanoporous boundaries in the P K series image.

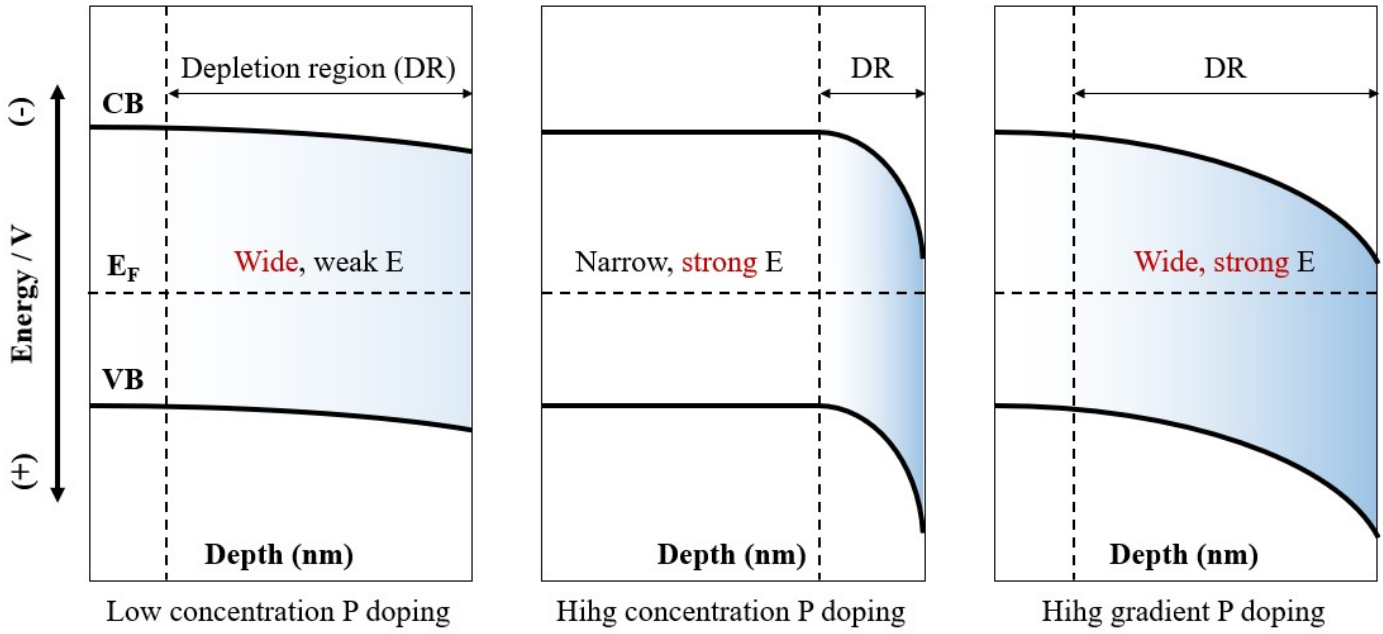


Figure S4 shows the relationship between doping depth and electric field. Low-concentration doping allows the dopant to diffuse deeper, whereas high-concentration doping limits dopant diffusion due to surface concentration. The electric field strength is directly proportional to the dopant concentration. Low concentration doping creates a large depletion region where the electric field strength is relatively weak. In contrast, high doping produces stronger electric fields but does not extend to depth. To take advantage of both dopant concentrations, we used gradient doping, which combines a highly concentrated doping solution with deep dopant diffusion promoted by the nanoporous structure. This approach enhances the photoelectrochemical occurs.

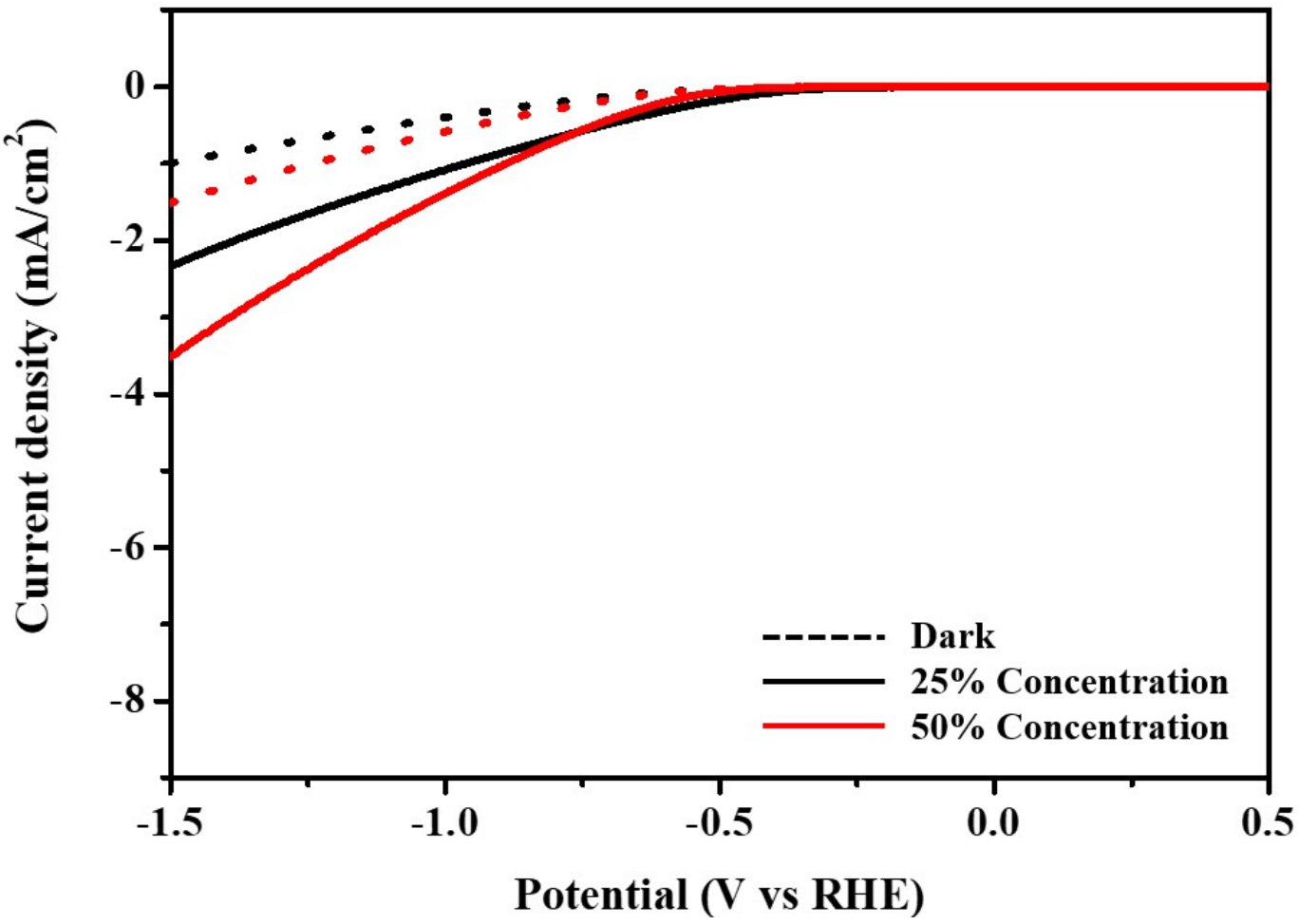


Figure S5 represents a comparison of LSV curves according to doping concentration. Generally, the doping concentration is proportional to the concentration of the doping solution and is inversely proportional to the rpm during spin coating. Furthermore, the dopant diffusion temperature and diffusion time are involved in the diffusion depth of the dopant. Therefore, it is necessary to find the optimal doping condition through the control of various doping conditions. As we reduced the concentration of the prepared POCl doping solution to 50% and 25%, both the dark current and photocurrent decreased. However, contrary research has been conducted stating that an unconditional increase in the concentration of the doping solution provides a more metallic surface, which in turn decreases the efficiency of water splitting.

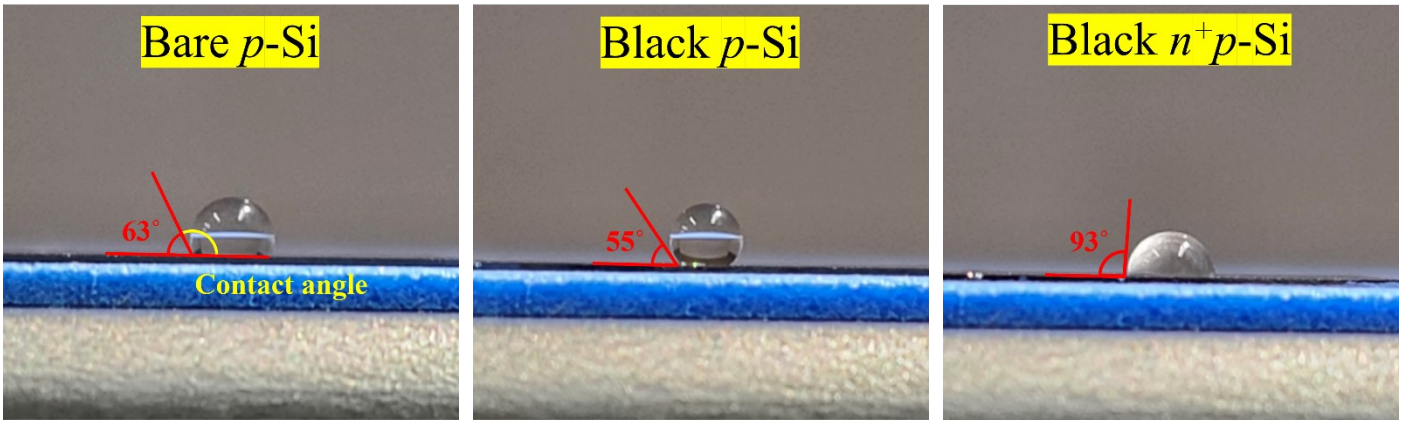


Figure S6 presents the results of contact angle measurements for Bare *p*-Si, Black *p*-Si, and Black n^+p-Si. Contact angles exceeding 90° in relation to D.I. water are indicative of hydrophobic surfaces. Generally, hydrophilic electrodes contribute to stable electrochemical behavior. This is achieved by reducing the size of bubbles on the surface and facilitating their rapid separation, ensuring ongoing electrode participation in the reaction process.[1] Contrarily, the introduction of a nanoporous structure results in hydrophobic surface properties [2], representing a trade-off associated with increasing light absorption. Notably, the contact angle for Bare *p*-Si, initially measured at 117°, rises to 125° in Black *p*-Si upon the introduction of a nanoporous structure. Post-phosphorus doping, however, the contact angle in Black n^+p-Si decreases to 87°, signifying a shift to hydrophilic surface characteristics. This transformation is attributed to the stabilization of the previously unstable porous structure during the thermal dopant diffusion process at 930 °C, which is also likely influenced by high surface concentrations of phosphorus. The observed decrease in contact angle for Black n^+p-Si is a contributing factor to the enhanced PEC efficiency.

Reference

1. B. K. Kim, M. J. Kim and J. J. Kim, *ACS applied materials & interfaces*, 2021, **13**, 11940-11947.
2. L. Schneider, M. Laustsen, N. Mandsberg and R. Taboryski, *Scientific Reports*, 2016, **6**, 21400.