Supporting Information

Nanobowtie Arrays with Tunable Materials and Geometries Fabricated by Holographic Lithography

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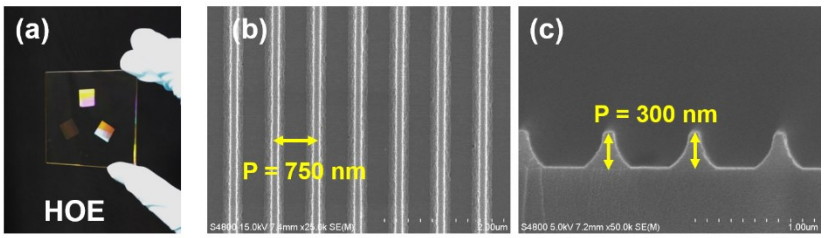

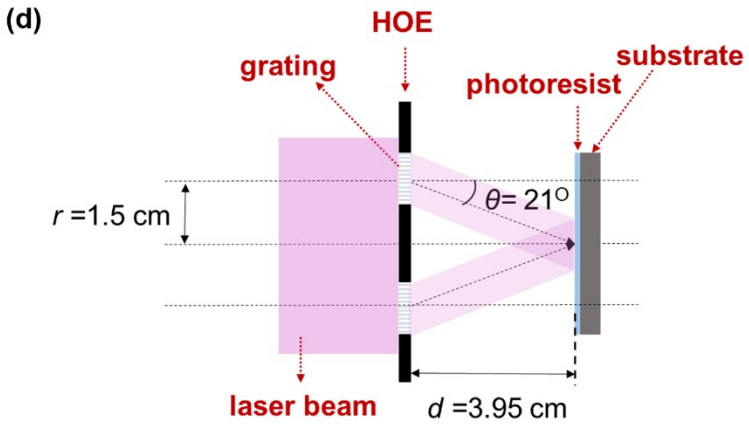

Figure S1. (a) A photograph of a fabricated HOE; (b) and (c) the SEM images of top-view and side-view of the gratings prefabricated on the HOE; (d) a schematic of the holographic lithography employed in this work.

A photo of holographic optical element (HOE) with prefabricated diffractive gratings is shown in the Figure S1(a), where three gratings were fabricated on a square quartz slide. The side length of the quartz slide is 60 mm and the side length of the gratings is 10 mm. From the SEM images shown in Figure S1(b) and (c), the period and depth of the gratings are 750 nm and 300 nm, respectively. A schematic of holographic lithography (HL) is shown in Figure S1(d) in a cross-section view. When the HOE is uniformly illuminated with a single expanded 266 nm laser beam, the interference of the first-order laser beams of gratings produces the designed periodic pattern. The distance between the center of the square quartz slide and the center of the grating (r) is 1.5 cm. The distance between the HOE and photoresist surface (d) is calculated to be 3.95 cm following $d = \frac{r}{\tan\theta}$, where θ is the diffractive angle. This angle can be obtained from the grating diffractive equation: $p\sin\theta = m\lambda$, where p is the period of the gratings (750 nm), m is the diffractive order (1), and λ is the incident wavelength (266 nm).

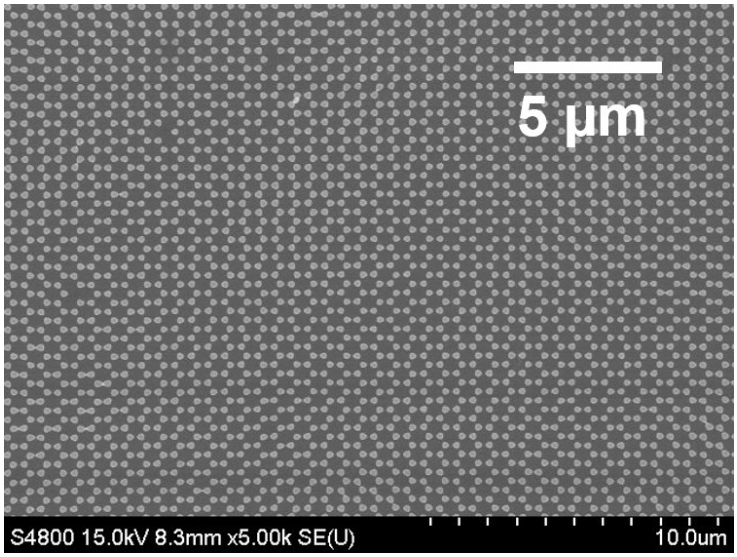

Figure S2. The SEM image of the nanobowtie array over a large area.

The gap size between the two arms of a nanobowtie unit can be tuned by changing the ridge widths between two nanopillars of the templates during the holographic lithography process. By decreasing the exposure time from 20 to 13 to 5 s, the ridge widths were narrowed. We fabricated five parallel samples under three different exposure time. The gap size of nanobowtie was carefully measured for the fifteen samples. The mean value and standard deviation (SD) of gap sizes for the different exposure time (different color) are shown in Figure S3 (same color indicates same exposure time). Indeed, from this result we can conclude that our fabrication method can efficiently and reproducibly control the gap size. When the exposure time is 20 s, 13s and 5s, the mean values of gap sizes are 112 nm, 62 nm and 13 nm, respectively.

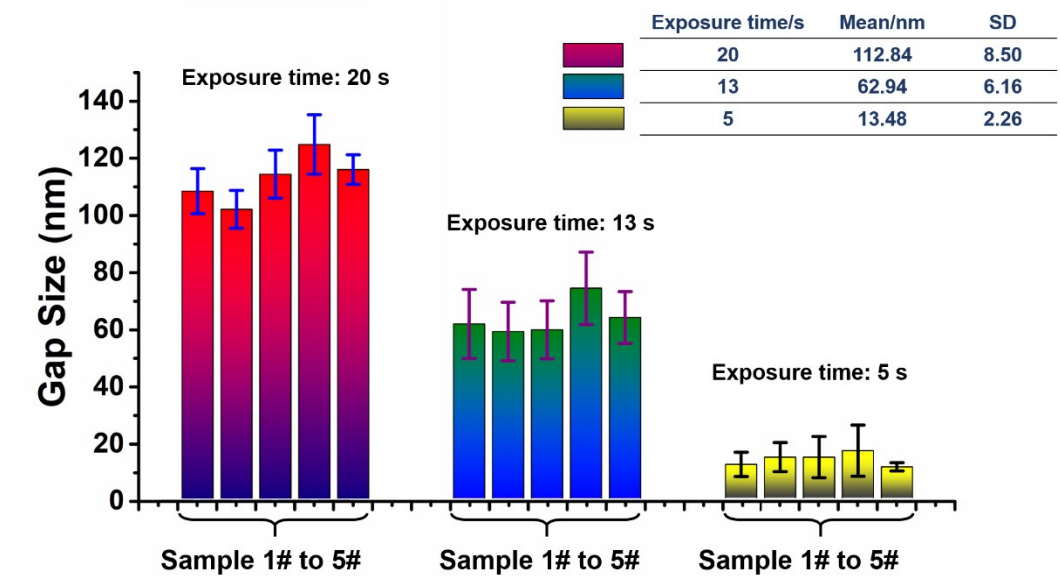

Figure S3. The distribution of the gap sizes for different exposure time.

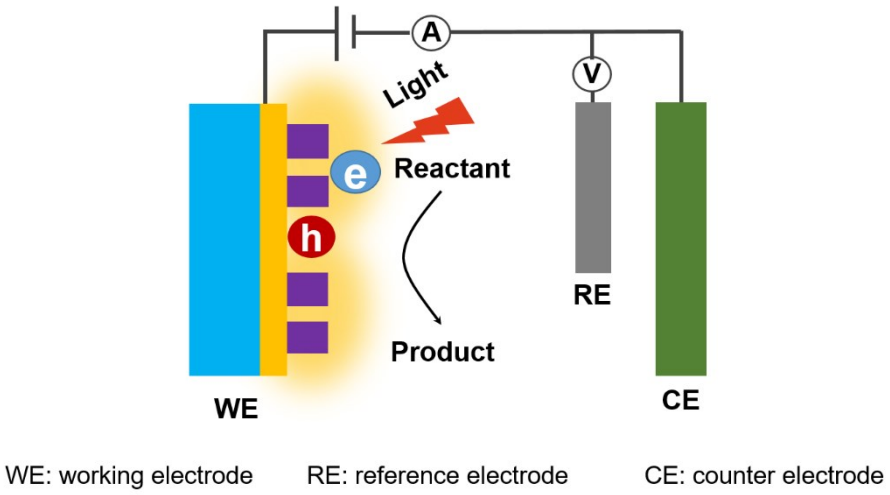

Figure S4. The setup for the photoelectrochemistry experiment.

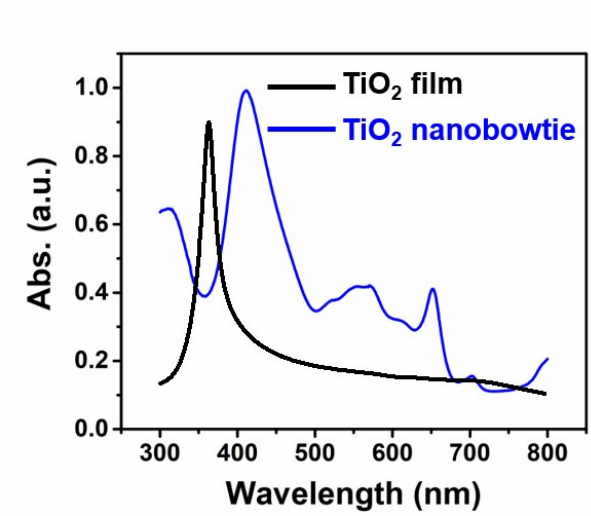

Figure S5. The UV-Vis absorption spectrum of the TiO_2 bowtie array (blue)and TiO_2 film (black).