Electronic Supplementary Information

Preparation of porous Au

Porous Au nanonetworks were synthesized by a dealloying method.[1] Commercially available 12 carat white-gold decorative leaf (Ag/Au, 51:49 ratio by weight) was floated on concentrated nitric acid (70%) for 1h, and then transferred to the Si (100) substrate.

Effective surface area calculation

(1) ZnO nanowire arrays:

Fig. S2: in an area of 1 μm^2, there are 36 nanowires. If we assume each nanowire is a cylinder, the total surface area for a nanowire on Si substrate is $S=\pi r^2+2\pi rL$. Here, r and L represent the radius and length of a nanowire which are 32.5 nm and 520 nm, respectively. So the total effective surface area of ZnO in an area of 1μm^2 is 3.94 μm^2.

(2) ZnO NSSs

Fig. 4: in an area of 1 μm^2, 85 ZnO branches were estimated to grow on the nanoporous Au catalyst, the total surface area of which is $85\times(\pi r^2+2\pi rL)$= 3.4 μm^2, where r= 17.5 nm and L= 350 nm. Note that a ZnO thin film also grows on the porous Au catalysts, the surface area of which can be calculated from that of the Au catalysts, estimated to be equivalent to that of a half cylinder (500 nm in diameter and 1.5 μm in length) laying on an 1 μm^2 surface, given by $S=\pi rL$=1.2 μm^2. Therefore, the total effective area of ZnO NSS is 4.6 μm^2, 117% of that of the ZnO nanowire arrays.

The above analysis showed that indeed the effective surface area of ZnO NSSs is higher than that of the ZnO nanowire arrays. We also note that there are many ZnO branches hiding behind other branches, which are not counted for the total surface area calculation. Therefore, the actual increment of the surface area in ZnO NSSs should be even higher than the estimated value of 117%.

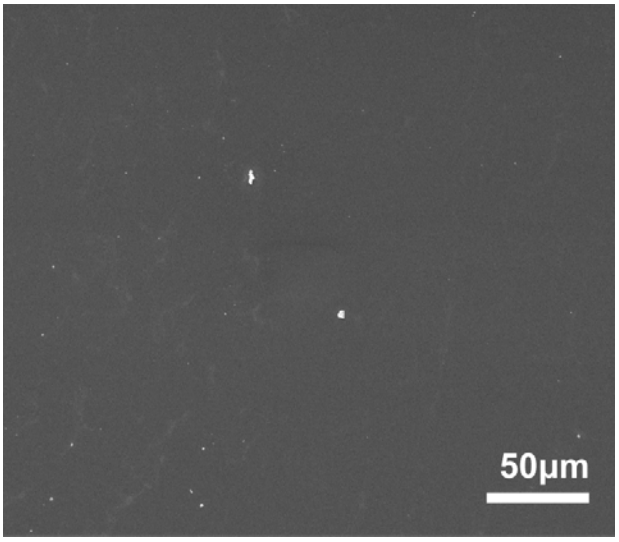

Fig. S1 SEM image of a control sample showing ZnO essentially cannot grow on bare silicon substrate.

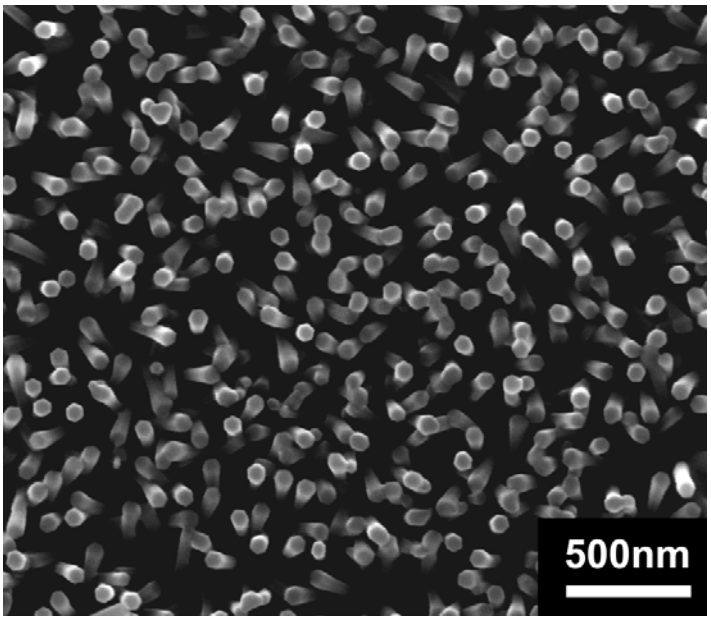

Fig. S2 SEM image of ZnO nanowire arrays synthesized on 5 nm thick Au film.

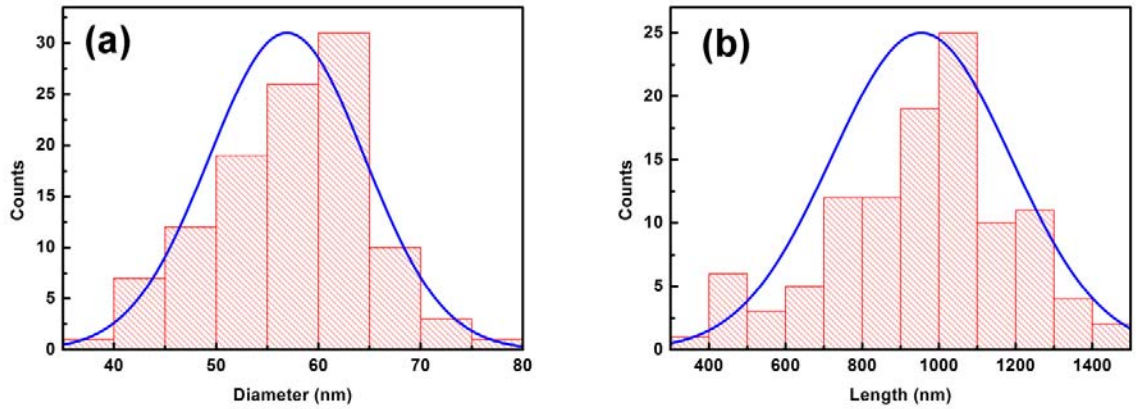

Fig. S3 Histograms of diameter (a) and length (b) of ZnO nanowires catalyzed by 300 nm diameter Au nanowires.

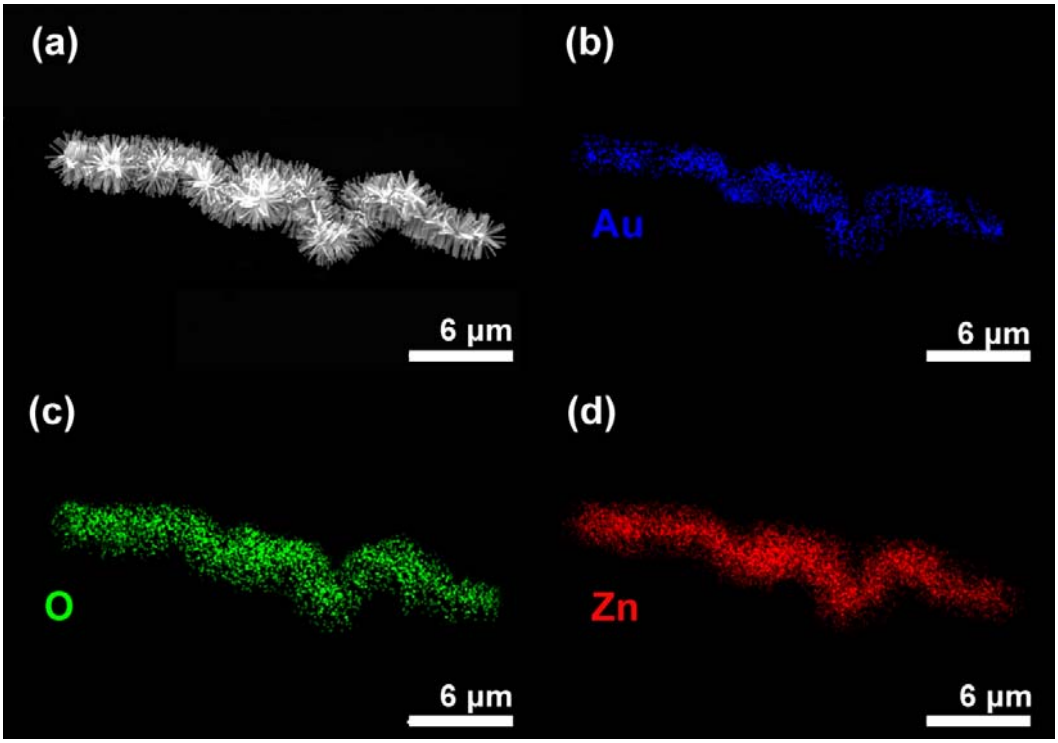

Fig. S4 EDX mapping images of a single ZnO NSS. (a) is the SEM image of ZnO NSSs. (b), (c) and (d) show gold, oxygen and zinc element distribution, respectively.

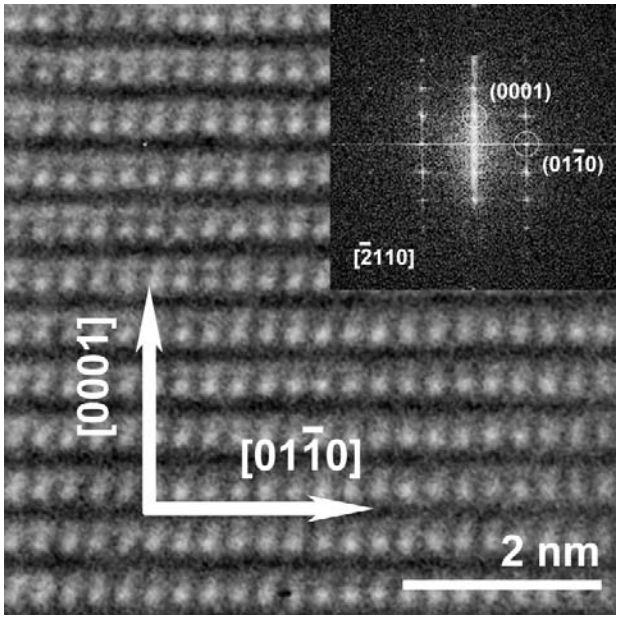

Fig. S5 HRTEM image of individual ZnO nanowire grew from Au nanowire (55 nm in diameter). Inset shows FFT image.

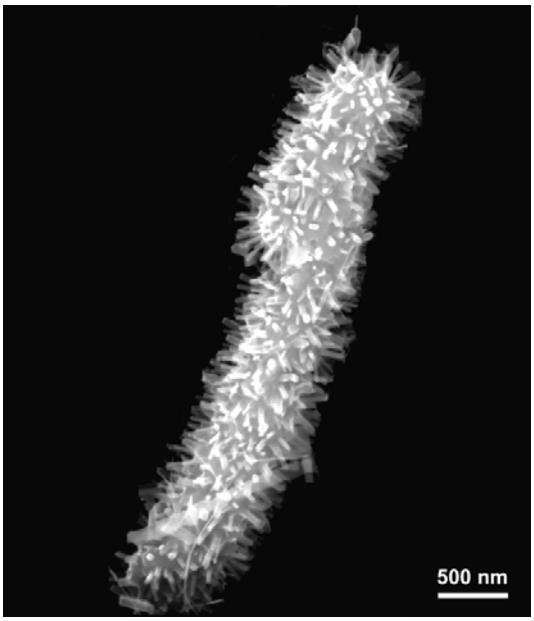

Fig. S6 SEM image of ZnO NSSs grew on a Pt nanowire.

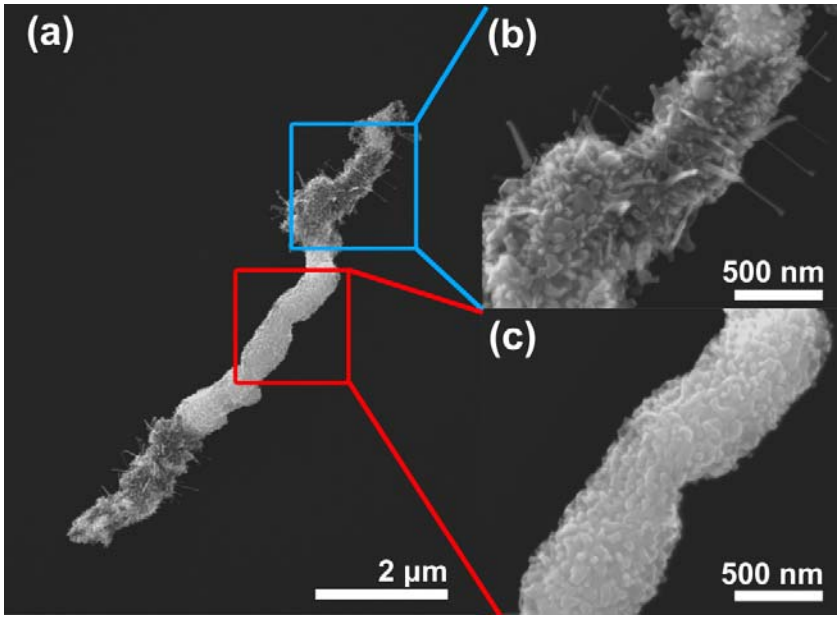

Fig. S7 The initial state of ZnO NSSs grew on the Au-Pt-Au nanowire. (a) is the overall image of ZnO NSSs. (b) and (c) are magnified images of ZnO NSSs grew on Au and Pt segment, respectively.

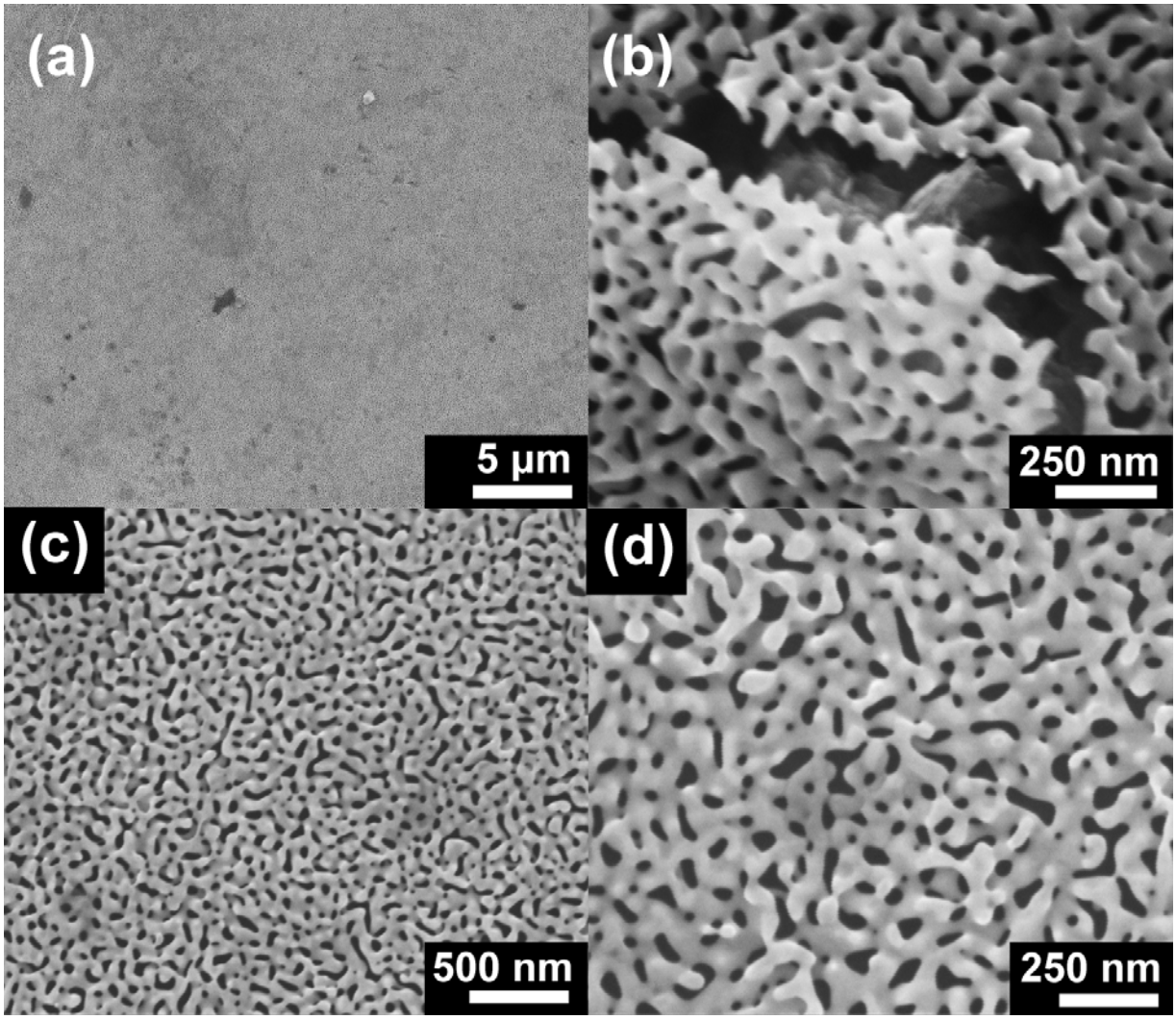

Fig. S8 (a-d) SEM images of as-growth porous Au. The diameter of each ligament is uniform and around 50 nm.

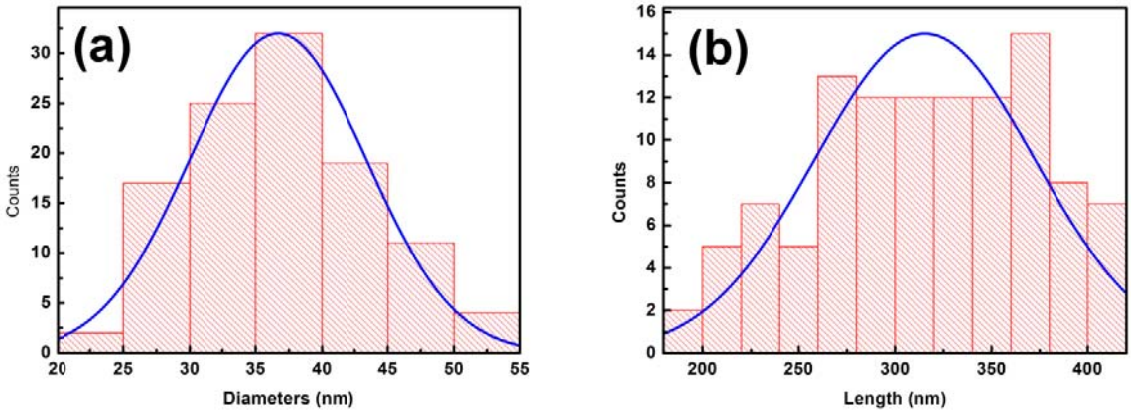

Fig. S9 Histograms of diameter (a) and length (b) for ZnO nanowires grown on porous Au film.

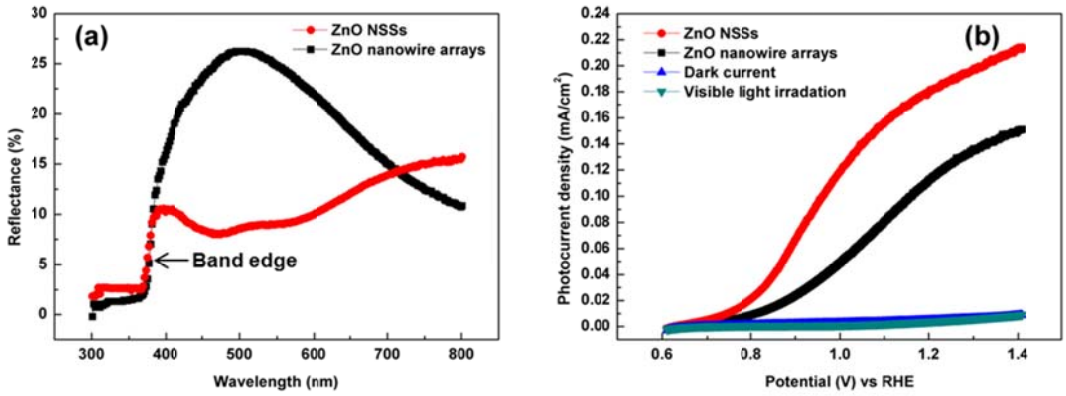

Fig. S10 (a) UV-vis reflectance spectra for ZnO nanowire arrays and ZnO NSSs. (B) LSVs recorded under visible light irradiation.

Diffuse reflectance UV−vis spectra were measured with a Cary 500 spectrophotometer attached to an integrating sphere (Labsphere DRA-CA-5500). Linear sweep voltammagrams in visible light region were recorded by adding a 420 nm long pass filter under AM 1.5 G illumination. In this setup, only visible light irradiates the samples. Fig S10b shows that under visible light illumination, the photocurrent is two orders of magnitude smaller than the photocurrent generated by the AM 1.5 G simulated light. Therefore only light absorbed by ZnO contributes to photocurrent.

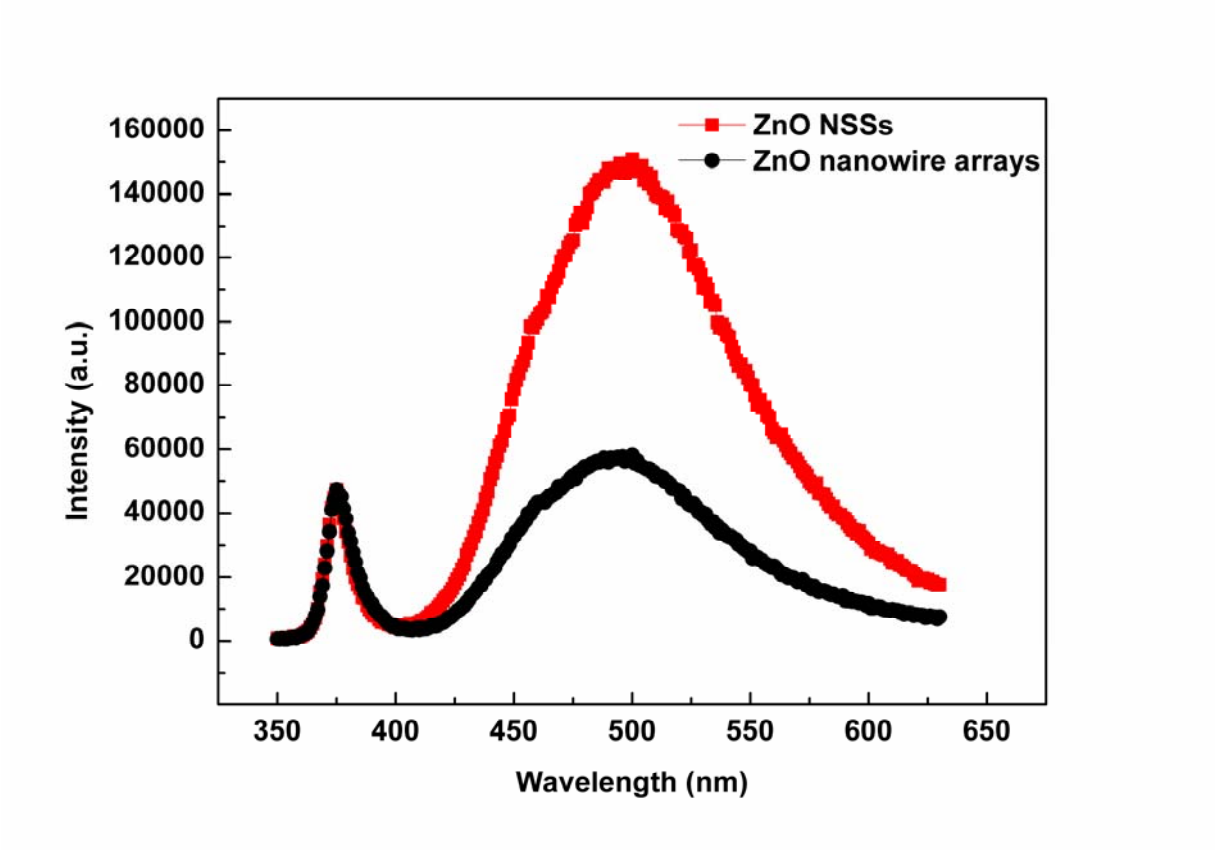

Fig. S11 Photoluminescence (PL) spectra for ZnO NSSs and ZnO nanowire arrays.

As shown in PL spectra, the band edge for both samples is the same at 375 nm which is consistent with the band edge measured by reflectance spectra.

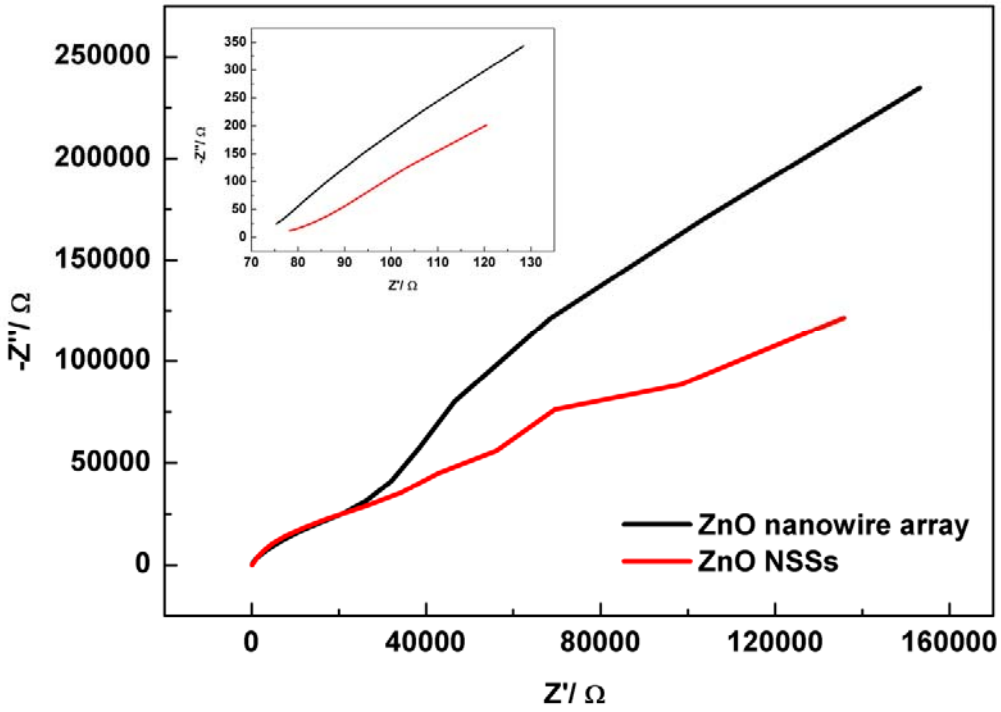

Fig. S12 Electrochemical impedance spectroscopy (EIS) of ZnO nanowire array and ZnO NSSs electrodes.

It shows that the ZnO NSSs (76 Ω) have a comparable cell resistance to ZnO nanowire arrays (72 Ω), based on the intercepts with the Z' axis in the high frequency range (shown in inset of Fig. S12).

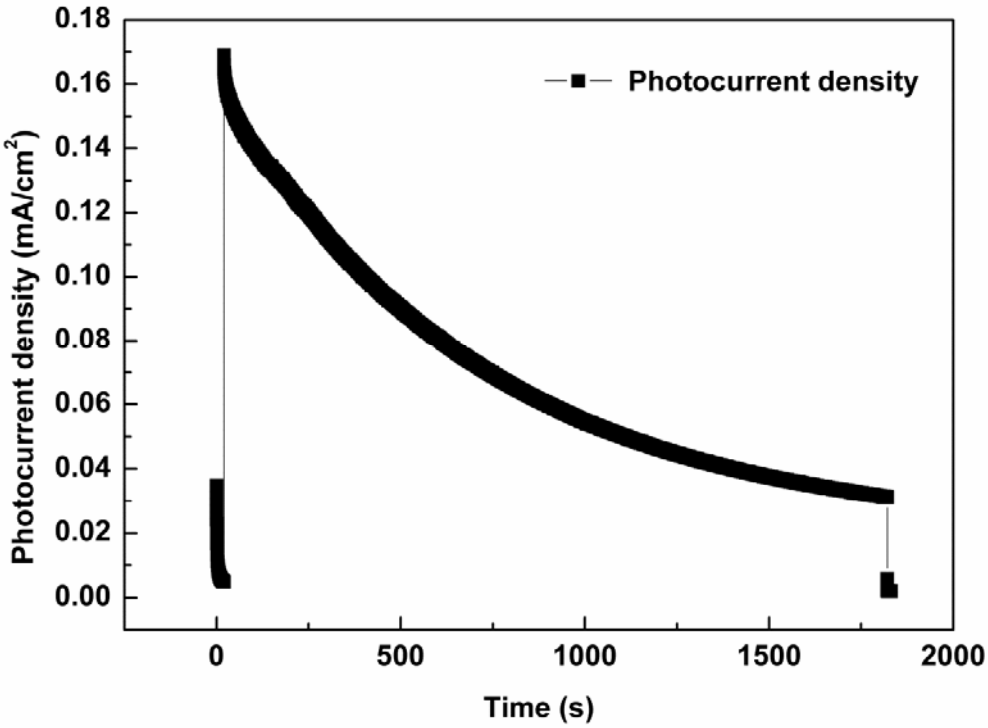

Fig. S13 Stability test of ZnO NSSs for 30 min under 100 mW/cm^2 AM1.5 G at 1.21V vs. RHE.

Stability testing was carried out by using 0.1 M Na_2SO_4 in 0.1 M potassium phosphate buffer as the electrolyte solution (pH 7) in a typical three-electrode cell setup, wherein ZnO NSSs (catalyst: porous Au) served as the working electrode; Pt wire as the counter electrode, and Ag/AgCl/Sat. KCl as the reference electrode. Films were sealed against an O-ring during testing. The exposed film area to illumination and electrolyte was 0.212 cm^2. The applied potential during the test was 1.21V (RHE). First, the photocurrent was recorded in the dark for 20 s, and then the sample was irradiated by an AM 1.5G simulated light (100 mW/cm^2) for 30 min. At last, the light was blocked and the sample kept in dark for a final 10 s.

As shown in the curve, after only 30 min, the current density decreases by 81%. This result is consistent with other studies[2] .

References

1. Y. Ding, Y. J. Kim and J. Erlebacher, *Adv Mater*, 2004, **16**, 1897-1900.
2. K. Sun, Y. Jing, C. Li, X. Zhang, R. Aguinaldo, A. Kargar, K. Madsen, K. Banu, Y. Zhou, Y. Bando, Z. Liu and D. Wang, *Nanoscale*, 2012, **4**, 1515-1521.