Supporting Materials:

EDX characterizations To demonstrate the hollow structure of ZnO HNSs fabricated in our work, EDX measurements on several comparable samples have been done as shown in Figure S1. It can be found that the concentration of C element was as high as 49% for the assembled PS nanospheres sample (a) and maintains at the rather high concentration of 20% after depositing the ZnO film in sample (b). The concentration of C element reduced significantly to 7% after the annealing process under 500 °C in N_2 ambient for 30 minutes (sample (c)). Additionally, the concentrations of C and O in sample (c) have the same level with those in sample (d), which contains only ZnO film on silicon substrate without PS nanospheres. This indicates that the PS nanospheres had been efficiently evaporated away during the annealing process.

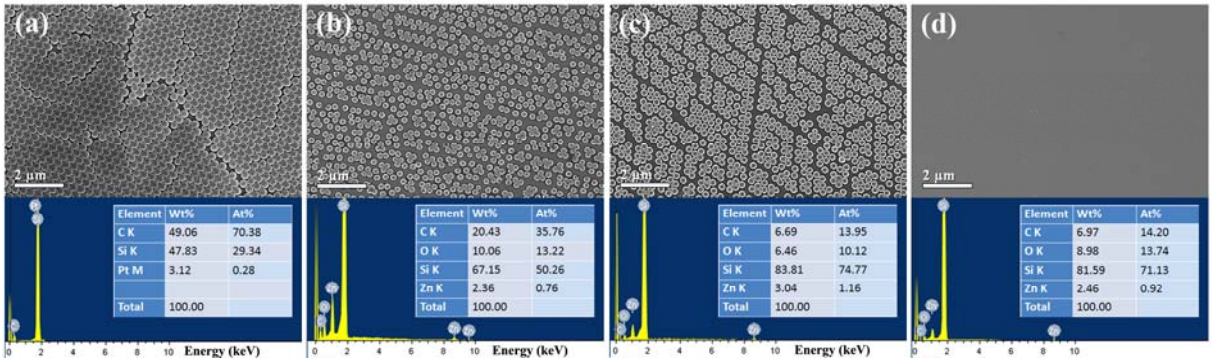

Figure S1. Large area EDS characterizations of different samples: (a) Assembled PS nanospheres on silicon substrate. (b) PS nanosphers coated with ZnO film (20 nm) on silicon substrate (PS-ZnO core/shell structure). (c) As-prepared ZnO HNS structure by annealing PS-ZnO core/shell structure. (d) ZnO film on silicon substrate.

SEM characterization To further prove the realization of ZnO-HNS structure, the SEM characterization on the inverted ZnO-HNS array piece, which was intentionally striped from the Si substrate, has been carried out (shown in Figure S2),.

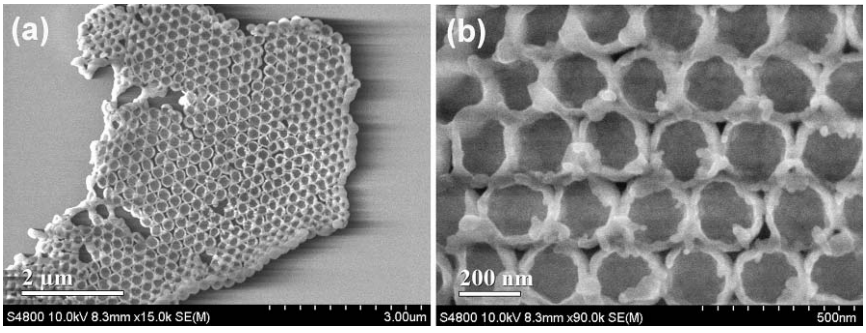

Figure S2. Inverted ZnO HNS structures (a) and (b) in different magnifications.