Supplementary information

Nanospheres@Nanorods Hybrid Arrays Generated by One-Pot Process on Substrates Used for Low-Reflecting Surface

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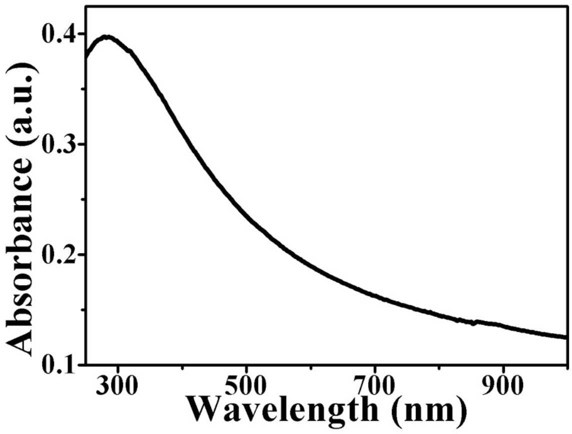

Figure S1. UV-Vis absorption spectrum of nanospheres separated from nanospheres@nanorods hybrid arrays. Nanospheres were obtained by several times of mild centrifugation of precipitates from the solution in deionized water, and before centrifugation the suspension was ultrasonically treated. Then the suspension was centrifugated under high rotation speed to precipitate nanospheres. Finally, the nanospheres were dispersed on quartz substrate for absorption test. The absorption peak of the spheres is located at wavelength of 280 nm, which is much smaller than that of ZnO, indicating the incorporation of Er into ZnO. The absorption well below 300 nm is also important for the application in Si solar cells as the main absorption wavelength of Si is 300-1100 nm.

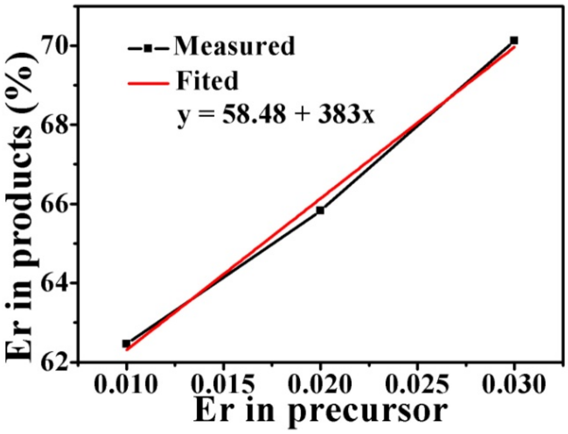

Figure S2. Plot between the content of Er atom (Er/(Er+Zn)) in the nanospheres and the concentration of Er (Er/(Er+Zn)) in the precursor. The results are obtained by EDX of TEM; each data was measured for three times of different particles. We noted that erbium oxide maybe the main content, here.

Table S1. Effect of molar ratio of $Zn(NO_3)_2$ to $Er(NO_3)_3$ on nanospheres in nanospheres@nanorods hybrid arrays.

Zn:Er	$Zn(NO_3)_2$	$Er(NO_3)_3$	Particle shape/average size
99:1	19.8 mM, 99%	0.2 mM, 1%	Spheres, ~85 nm
98:2	19.6 mM, 98%	0.4 mM, 2%	Spheres, ~65 nm
97:3	19.4 mM, 97%	0.6 mM, 3%	Spheres, ~55 nm
95:5	19 mM, 95%	1 mM, 5%	Irregular Spheres, ~ 25 nm
90:10	18 mM, 90%	2 mM, 10%	Irregular Spheres, ~15 nm
75:25	15 mM, 75%	5 mM, 25%	Little irregular Spheres

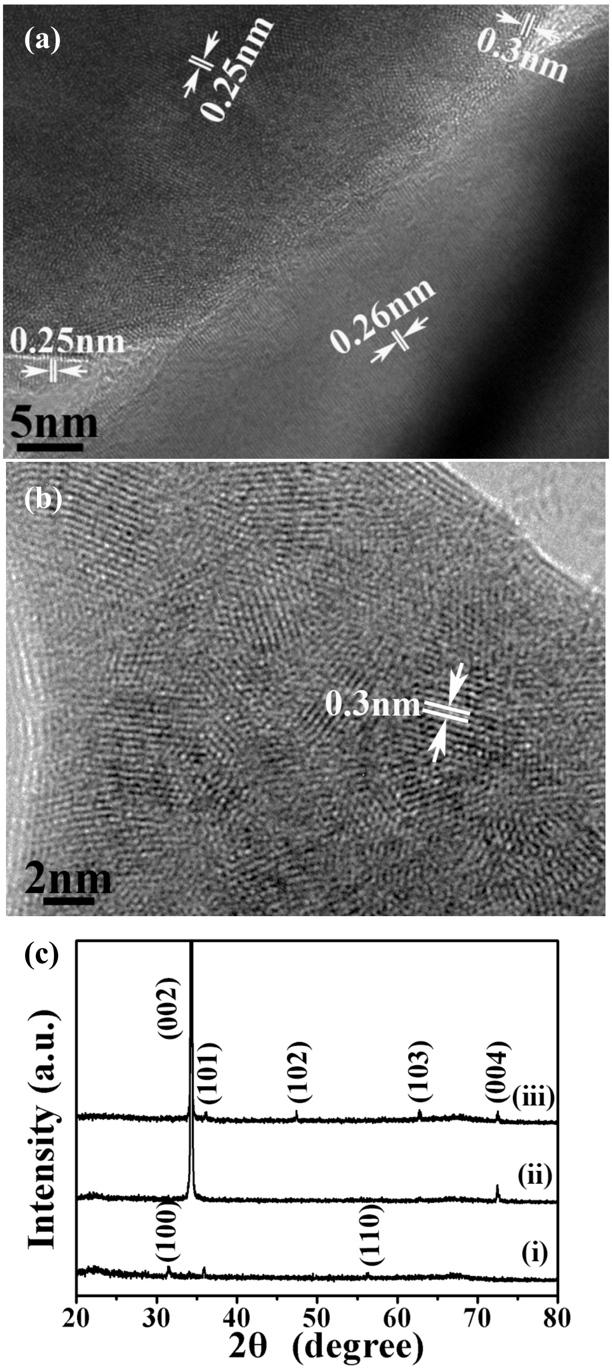

Figure S3. HRTEM images of a)Ns@NrHys and b) nanospheres, and c) XRD patterns of the as synthesized samples on silicon substrate, i) nanospheres obtained using the method as mentioned in Figure S1, ii) ZnO nanorods grown without the addition of erbium precursor, and iii) Ns@NrHys. The structure of nanospheres can also be indexed to wurtzite zinc oxide.

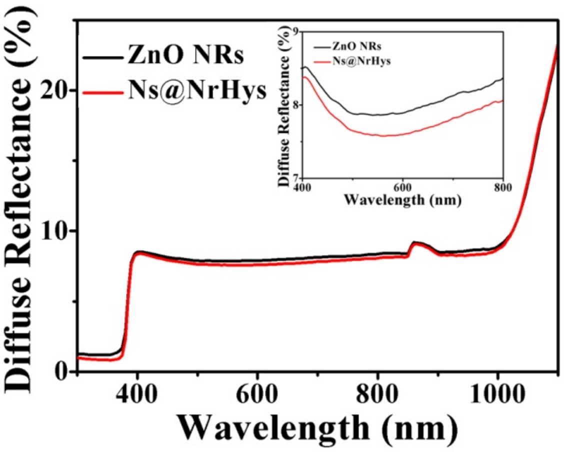

Figure S4. The reflectance of ZnO NRs (black line) and Ns@NrHys (red line) on silicon wafers in the case of similar morphologies. We have grown a number of samples, and have selected two samples with similar length and diameter of nanorods while the density of nanorods maybe a little different. Because the the existence of Er will affects the growth of ZnO nanorods, it is almost impossible to grow two samples that have the same morphology of ZnO nanorods where one contains spheres while the other has only nanorods. We can see that the reflectance of the Ns@NrHys structures was obviously lower than that of pure ZnO NRs. Nanospheres were reported to be useful for increaseing absorption of Si nanowires by scattering.[1] More light would be limited within the wires by the insertion of nanospheres as the spheres will scatter light that might pass between the nanowires, and the reflection of the samples would possibly decrease.[1] Hence, nanospheres will help to limit lights within the hybrid structures, as the spheres and ZnO NRs do not absorb visible light, lights will possibly go into and then be absorbed. Thus, the reflection of Ns@NrHys structures was lower than that of pure nanorods. However, the proportion and size of spheres and other factors might be responsible for the antireflection properties.

References

1. M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, *Nature Mater.*, 2010, **9**, 239-244.