Electronic supplementary information (ESI)

A plasmon-tuned 'Gold sandwich' for metal enhanced fluorescence in silica coated $NaYF_4$:Yb,Er upconversion nanoparticles

*Robeth Viktoria Manurung, Chien Ting Wu, Pradip Kumar Roy and Surojit Chattopadhyay**

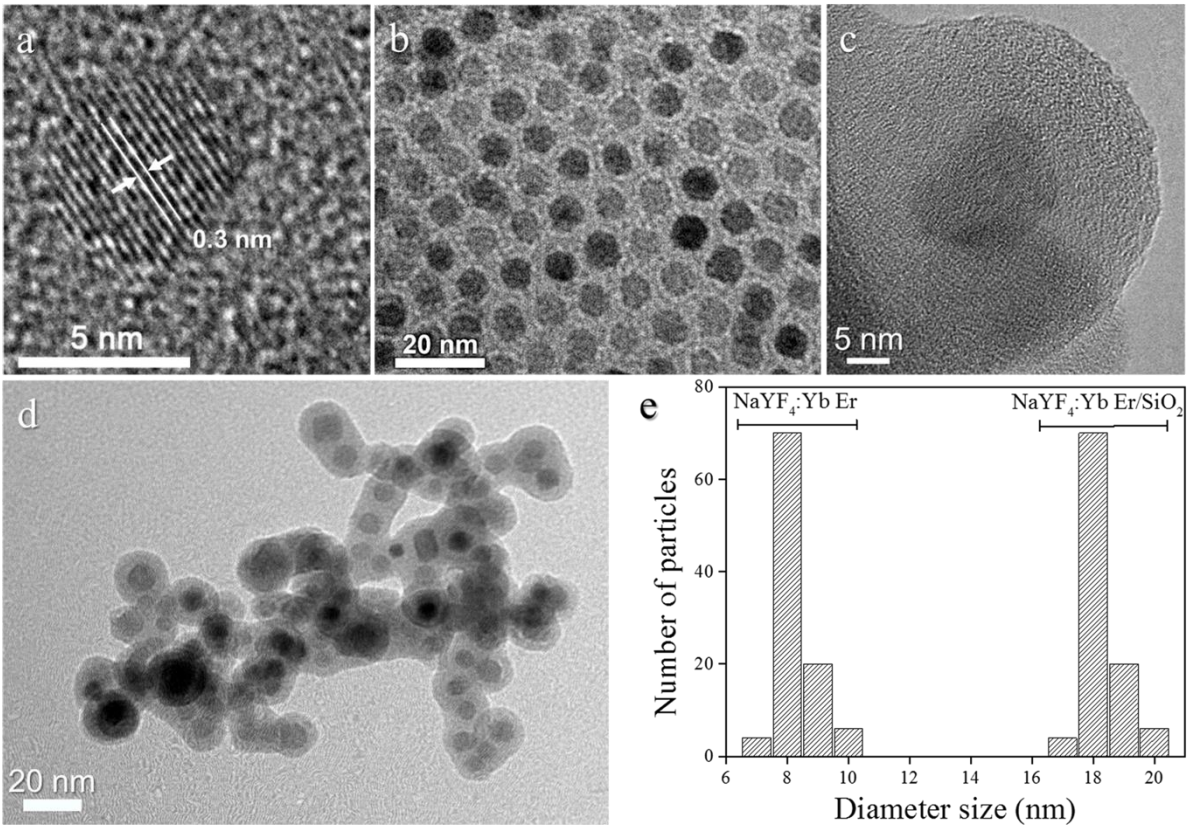

Figure S1. Characterization of the UCNPs. a) High, and b) low magnification TEM images of the core α-$NaYF_4$:Yb,Er, nanoparticles. c) High, and d) low magnification TEM images of the the α-$NaYF_4$: Yb,Er nanoparticles coated with a SiO_2 shell. e) Size distribution histogram of the core, and core-shell type nanoparticles obtained by analyzing the TEM images (n=100).

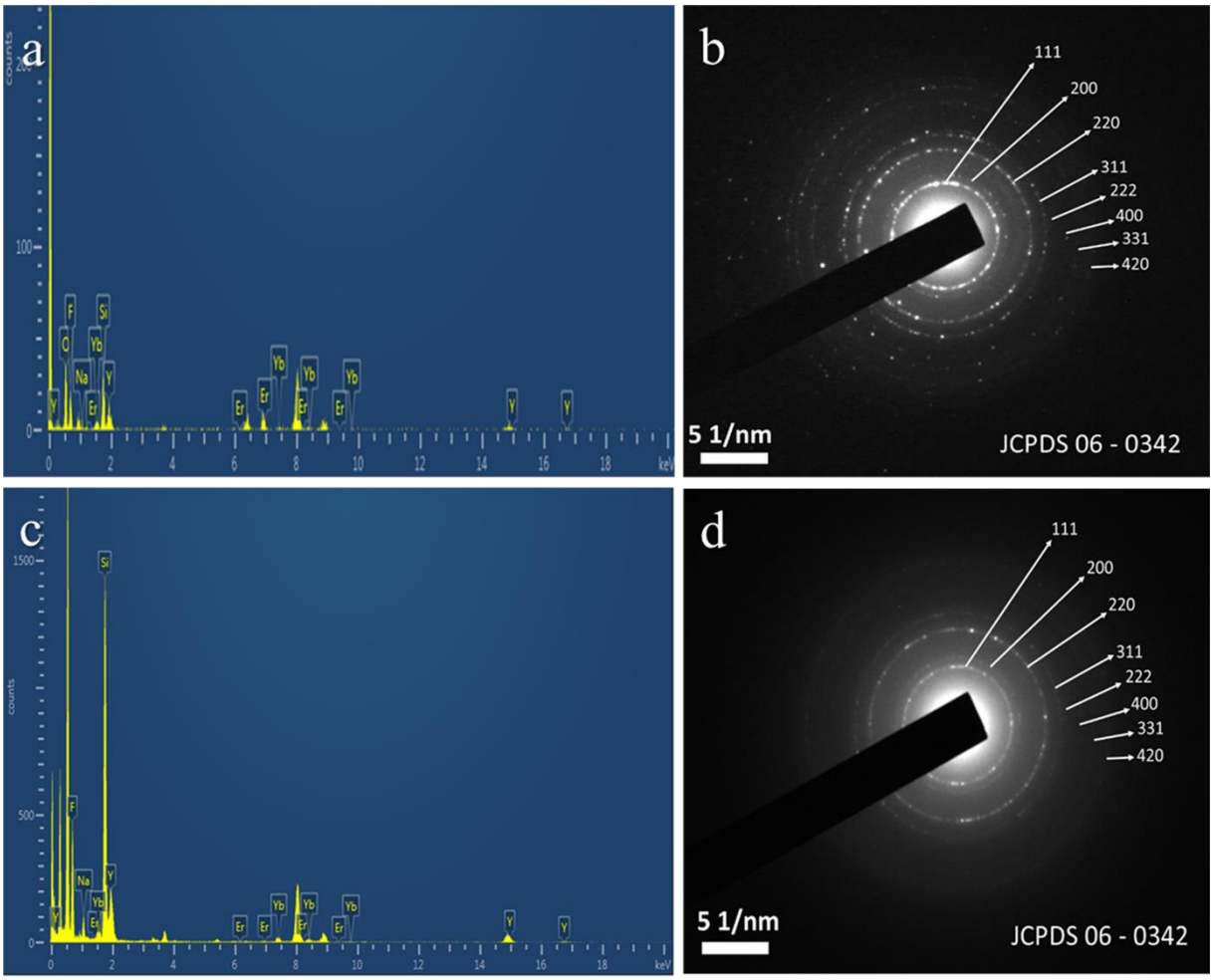

Figure S2. a) Energy dispersive X-ray spectroscopy (EDS), and b) selected area electron diffraction (SAED) data of the core, and c) EDS, and d) SAED of the core-shell type α-$NaYF_4$:Yb,Er nanoparticles. Different elemental peaks are identified by their chemical symbols in the EDS, and different diffraction rings are distinguished (by the arrows and Miller indices) according to JCPDS (06-0342).

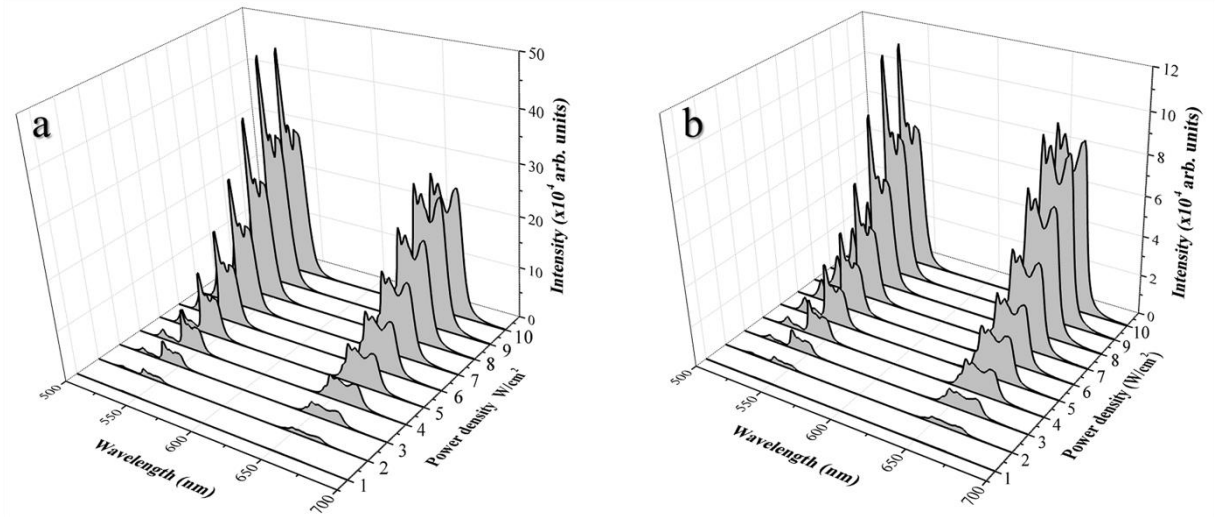

Figure S3. Up-conversion spectra emission of a) $NaYF_4$: Yb,Er in cyclohexane, and b) $NaYF_4$: Yb,Er/SiO_2 in water, under different excitation power density 1-10 Wcm^{-2} of 980 nm, respectively.

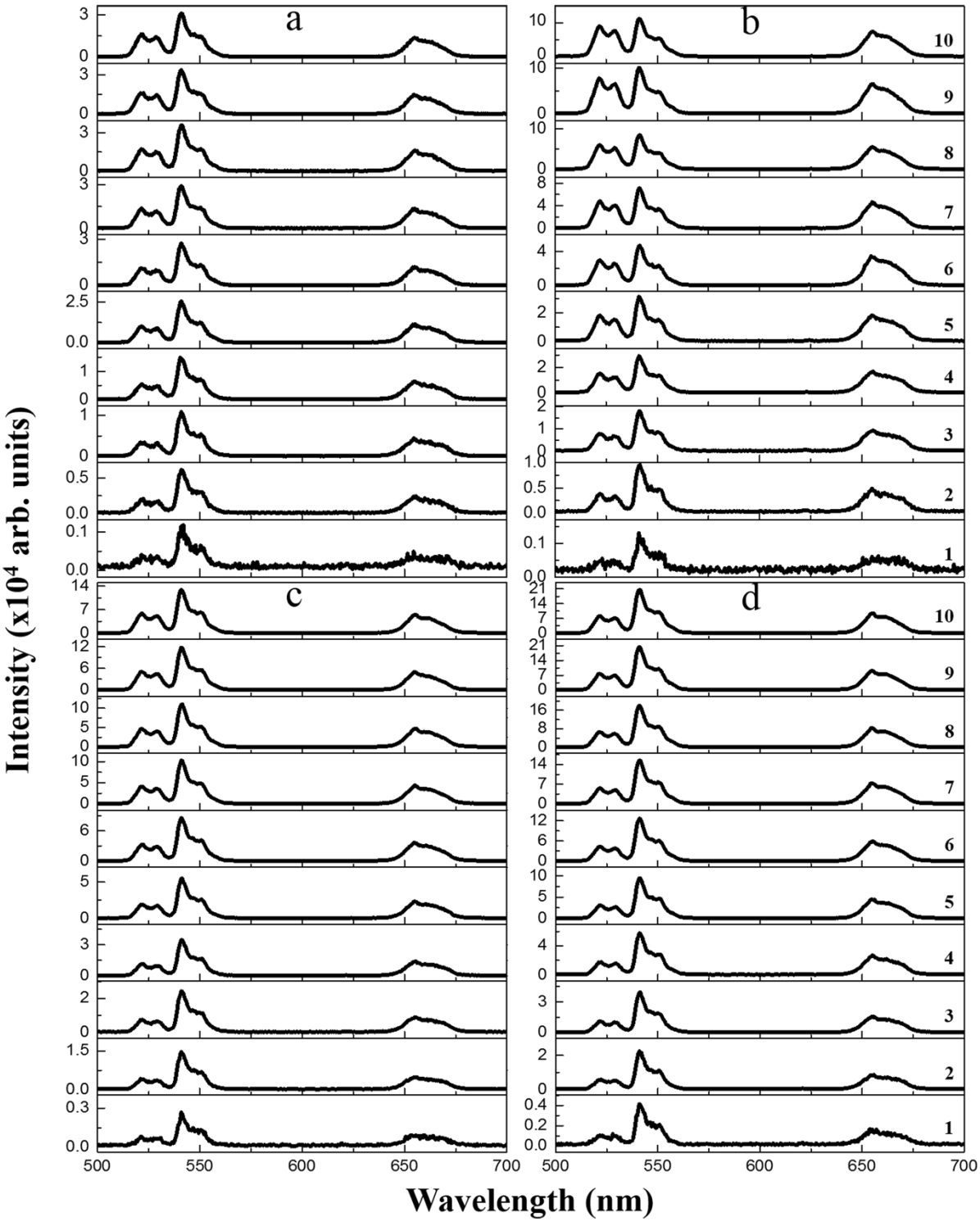

Figure S4. Up-conversion emission spectra of $NaYF_4$:Yb,Er/SiO_2 on a) Si only (0+0), b) 2 (2+0), c) 4 (4+0) and d) 8 (8+0) minutes gold coated Si substrate under 980 nm excitation with power density range 1 – 10 Wcm^{-2}. The numbers on each spectrum represent the power density in Wcm^{-2}.

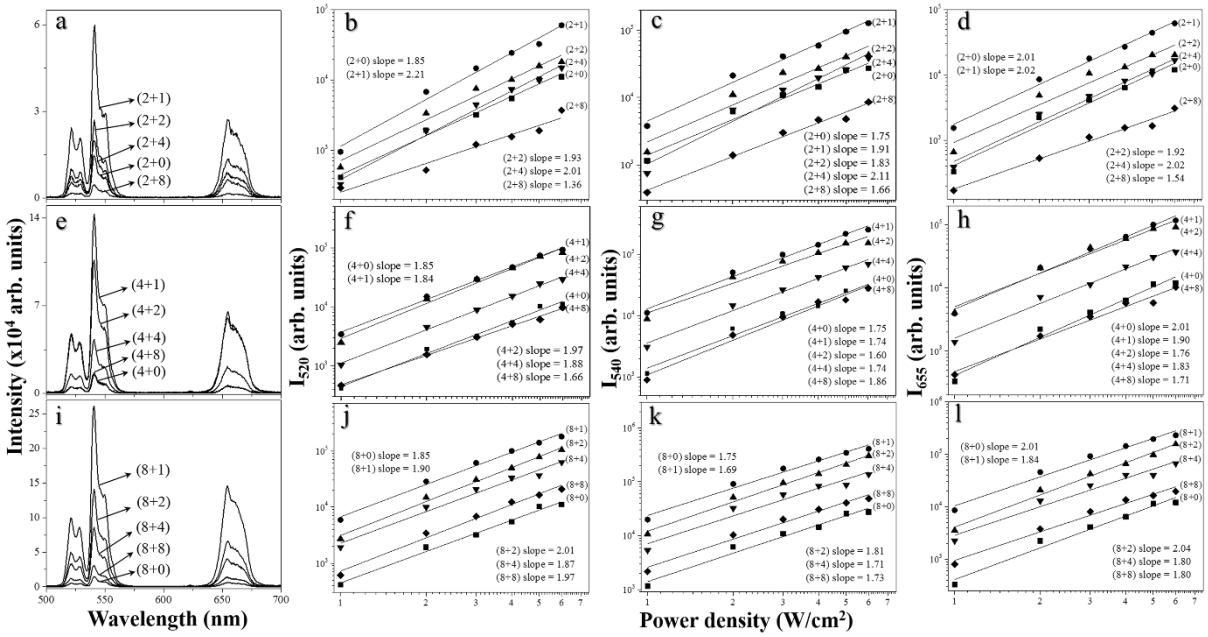

Figure S5. Up-conversion luminescence spectra, and power dependence of the 520, 540 and 655 nm signature peaks of $NaYF_4$:Yb,Er/SiO_2 on (a-d) 2+0, 2+1, 2+2, 2+4, 2+8; (e-h) 4+0, 4+1, 4+2, 4+4, 4+8, and (i-l) 8+0, 8+1, 8+2, 8+4, 8+8 minutes sandwich (bottom and top) gold coating, respectively. Laser power density of 4 Wcm^{-2} was used in (a, e and i). The legends in each plot are written in the (B+T) format which represents sputtering time (in minutes) of the bottom and top gold coating, respectively. The slopes, indicating the number of photons involved in the upconversion process, are mentioned against each plot fitted linearly.

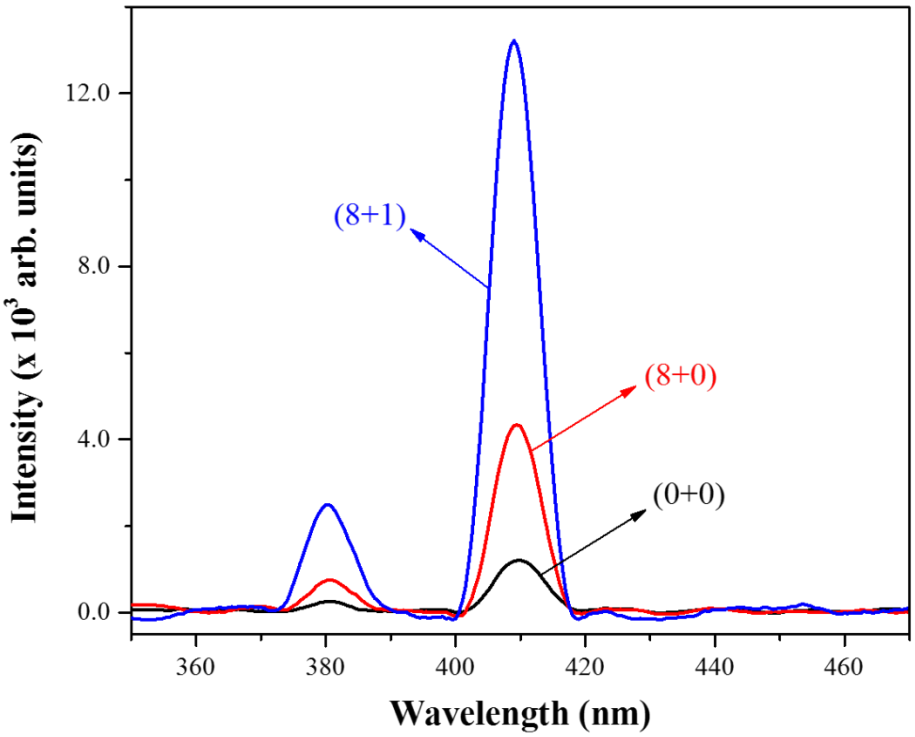

Figure S6. Up-conversion luminescence spectra of the $NaYF_4$:Yb,Er/SiO_2 UCNPs dispersed on Si only (0+0), on Si with 8 min Au coating (8+0), and Si with 8 min bottom and 1 min top Au coating (8+1) configuration, under 2 Wcm^{-2} power excitation. The figure shows enhancement of the blue emissions at 383, and 410 nm when using the gold sandwich where multiphoton (n>3) absorption processes were observed.

Table 1. Er doped UCNPs emission enhancement at 540 nm emission only,

Geometry	Size of UCNP nanostructure (nm)	Plasmonic structure	Plasmonic material	Enhancement factor	Reference
Core NP	65	Pillars	Au	2.2	1
Core NP	30	Wire	Ag	2.3	2
Core NP	30	Sphere	Au	4.8	3
Core NP	30	Island	Au	5.1	4
Core NP	40	Rods & spacer	Au	22.6	5
Core NP	300	Platelets	Ag	22	6
Core NP	32	Grating	Ag	25	7
Core-shell NP	45	Particles	Ag	14.4	8
Core-shell NP	40	Particles	Au	9.59	9
Core-shell NP	50	Spheres	Ag	4	10
Core-shell NP	30	Shell	Au	2.5	11
Core-shell NP	90	Shell	Au	21	12
Core-shell NP	50	Shell & rod	Au	6.5	13
Thin film	~75 × 400	Island	Ag	3.3	14
Thin film	5 – 15	Island	Ag	10.1	15

Refferences

[1] H. P. Paudel, L. Zhong, K. Bayat, M. F. Baroughi, S. Smith, C. Lin, C. Jiang, M. T. Berry, P. S. May, *J. Phys. Chem. C*., 2011, **115**, 19028.

[2] W. Feng, L. D. Sun, C. H. Yan, *Chem. Comm.*, 2009, **29**, 4393.

[3] S. Schietinger, T. Aichele, H. Q. Wang, T. Nann, O. Benson, *Nano Lett.*, 2010, **10**, 134.

[4] H. Zhang, D. Xu, Y. Huang, X. F. Duan, *Chem. Comm.*, 2011, **47**, 979.

[5] A. L. Feng, M. Li You, L. Tian, S. Singamaneni, M. Liu, Z. Duan, T. J. Lu, F. Xu, M. Lin, *Sci. Rep*., 2015, **5**, 7779.

[6] Y. L.Wang, N. Mohammadi Estakhri, A. Johnson, H. Y. Li, L. X. Xu, Z. Zhang, A. Alù, Q. Q. Wang, C. K. Shih, *Sci. Rep.*, 2015, **5**, 10196.

[7] D. Lu, S. K. Cho, S. Ahn, L. Brun, C. J. Summers, W. Park, *ACS Nano*, 2014, **8**, 7780.

[8] P. Yuan, Y. H. Lee, M. K. Gnanasammandhan, Z. Guan, Y. Zhang, Q. Xu, *Nanoscale*, 2012, **4**, 5132.

[9] W. Ge, X. R. Zhang, M. Liu, Z. W. Lei, R. J. Knize, Y. Lu, *Theranostics*, 2013, **3**, 282.

[10] F. Zhang, G. B. Braun, Y. Shi, Y. Zhang, X. Sun, N. O. Reich, D. Zhao, G. Stucky, *J Am. Chem. Soc*., 2010, **132**, 2850.

[11] A. Priyam, N. M. Idris, Y. Zhang, *J. Mater. Chem.*, 2011, **22**, 960.

[12] P. Kannan, F. A. Rahim, X. Teng, R. Chen, H. Sun, L. Huang, D. H. Kim, *RSC Adv.*, 2013, **3**, 7718.

[13] C. Zhang, J. Lee, *J. Phys. Chem. C*, 2013, **117**, 15253.

[14] J. Shen, Z. Q. Li, Y. R. Chen, X. H. Chen, Y. W. Chen, Z. Sun, S. M. Huang, *Appl. Surf. Sci.*, 2013, **270**, 712.

[15] Y. Wu, X. Shen, S. Dai, Y. Xu, F. Chen, C. Lin, T. Xu, Q. Nie, *J. Phys. Chem. C*, 2011, **115**, 25040.