Supporting Information

Controlled Synthesis of Hierarchically Crossed Metal Oxide Nanosheet Arrays for Diesel Soot Elimination

Aijing Ma,[a,b,c] Liu Gu,[b] Yingming Zhu,[d] Ming Meng,[d] Jianzhou Gui,*[a,c] Yifu Yu*[b] and Bin Zhang[b]

[a] *State Key Laboratory of Separation Membranes and Membrane Processes, School of Material Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, P. R. China*
[b] *Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, P. R. China, Email: yyu@tju.edu.cn*
[c] *School of Environmental & Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, P. R. China, Email: jzgui@hotmail.com*
[d] *School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, P. R. China*

EXPERIMENTAL SECTION

All chemicals were of analytical grade and used as received without further purification. Aqueous solutions were prepared using distilled water.

Preparation of the FeO_x substrate

In a typical procedure, one piece of iron foil (2 cm × 2 cm × 0.05 cm) was sonicated in acetone, ethanol and distilled water, sequentially. After drying under N_2 atmosphere, the as-obtained iron foil was placed in alumina boat, which was immediately heated to 500 ^oC in a muffle furnace. After calcination for 4 h, the FeO_x substrate was prepared.

Preparation of hierarchically crossed metal oxide (MO, M=Co, Ni, Mg) nanosheet array on FeO_x substrate

Firstly, the FeO_x substrate was dipped into 100 mL 0.1 M $M(NO_3)_x{\cdot}nH_2O$ (M=Co, Ni, Mg) aqueous solution. After impregnation for 1 h, the sample was taken out with a tweezer and dried at 120 ^oC for 15 min. Then, the sample was calcined at 350 ^oC for 30 min in air to finish the first loading cycle. The loading cycle was repeated for 4 times to obtain the metal oxide crossed nanosheet array on FeO_x substrate.

In addition, the sample of Co_3O_4 with 2 times of loading cycle (Table S1) was also synthesized for comparison study.

Preparation of hierarchically crossed composite metal oxide ($CoBa_xO_y$ and $CoMg_xO_y$) nanosheet array on FeO_x substrate

The preparation process of the hierarchically crossed composite metal oxide nanosheet array on FeO_x substrate was the same as the crossed Co_3O_4 nanosheet array on FeO_x substrate described above except that the cobalt nitrate precursor solution was replaced by mixed metal nitrates solution. The details of reaction conditions for the preparation of composite metal oxide crossed nanosheet array were displayed in Table S1.

Preparation of Co_3O_4 nanoparticles on Si and TiO_2 substrates

The preparation procedure was the same as that for Co_3O_4 crossed nanosheet array/FeO_x substrate except for the substrate.

Characterization: The scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope (SEM, 5 kV). Transmission electron microscopy (TEM) images were obtained with JEOL-2100F system equipped with EDAX Genesis XM2. The X-ray diffraction (XRD) patterns of the samples were recorded on Bruker D8 diffraction meter using Cu Kα (λ= 0.15418 nm) as radiation source. Raman experiments were performed on Invia Reflex spectrometer of RENISHAW Company. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG ESCALAB 220i-XL system. The C1s peak was used as the reference to calibrate the XPS spectra. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a Perkin-Elmer Diamond TG/DTA instrument.

Activity evaluation

The catalytic activities of the samples for soot combustion were evaluated by the TG/DTA technique using Printex-U soot (Degussa) as the model reactants. The mix of catalysts and soot particulates was achieved by deposition contact mode according to our previous works[1-3]. First, the soot was dispersed in ethanol under ultrasonic assistance. In the next step, the produced suspension was dropped on the surface of the monolithic catalysts and dried at 60 °C. The weight ratio of soot to catalyst is 1:20. The mixture of soot and catalyst were then heated from room temperature to 650 °C at a slope of 5 °C min^{-1} in an atmosphere of 600 ppm NO, 10 vol % O_2 and balanced N_2 with a flow rate of 50 mL min^{-1}. After the temperature-programmed oxidation experiment, a DTG curve with a complete weight loss peak was obtained. In this work, T_m, defined as the temperature at which the soot was oxidized with the maximal rate, was used to evaluate the performance of the catalysts.

Table S1 Details of the reaction conditions for the fabrication of hierarchically crossed MO nanosheet array on FeO_x substrate.

	$M(NO_3)_x\cdot nH_2O$ solution (0.1 M, Total Content)	Times of loading cycle	Mole ratio[a]
Co_3O_4[b]	$Co(NO_3)_2\cdot 6H_2O$	2	1:1.2 (Co:Fe)
Co_3O_4	$Co(NO_3)_2\cdot 6H_2O$	4	1:0.32 (Co:Fe)
NiO	$Ni(NO_3)_2\cdot 6H_2O$	4	1:0.41 (Ni:Fe)
MgO	$Mg(NO_3)_2\cdot 6H_2O$	4	1:0.63 (Mg:Fe)
CoBaO	$9Co(NO_3)_2\cdot 6H_2O:1Ba(NO_3)_2$	4	1:0.07:0.34(Co:Ba:Fe)
CoBaO[c]	$9.5Co(NO_3)_2\cdot 6H_2O:0.5Ba(NO_3)_2$	4	1:0.03:0.37(Co:Ba:Fe)
CoMgO	$9Co(NO_3)_2\cdot 6H_2O:1Mg(NO_3)_2\cdot 6H_2O$	4	1:0.06:0.22(Co:Mg:Fe)

[a]: The mole ratio of different elements is obtained through EDX results; [b]: The sample is prepared to investigate the formation mechanism of crossed MO nanosheets array; [c]: The sample is prepared to demonstrate the adjustability of different components in the composite metal oxide.

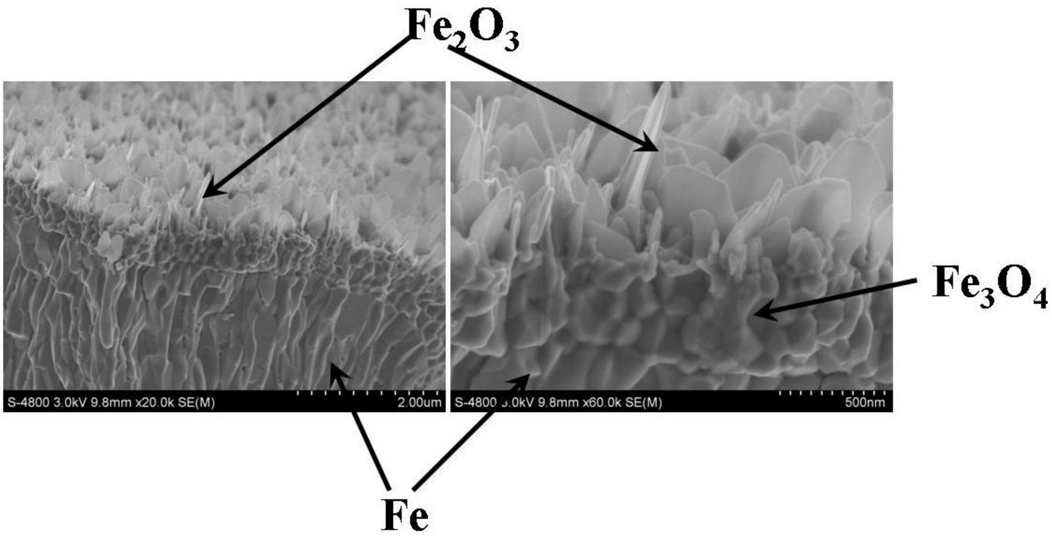

Fig. S1 The side-view SEM images of the FeO_x substrate.

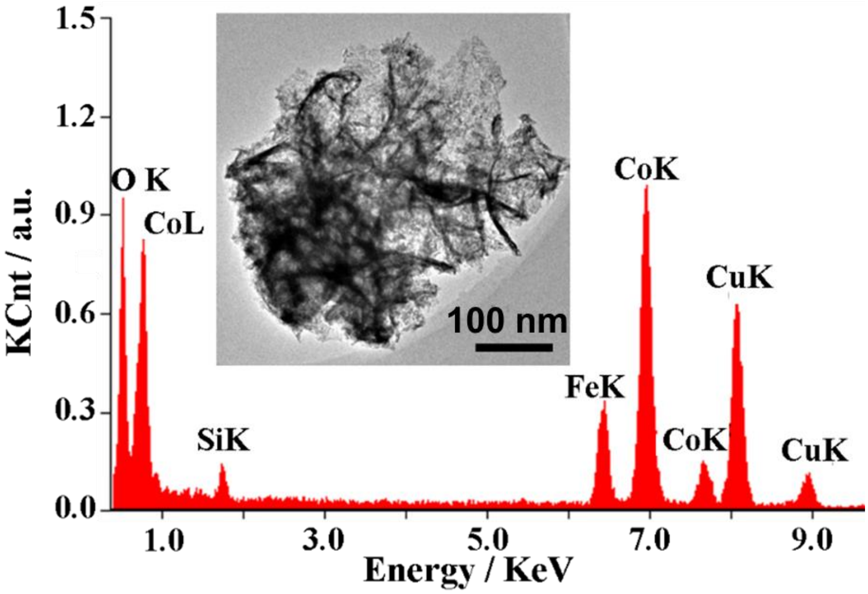

Fig. S2 TEM image and the corresponding EDX spectrum of Co_3O_4 crossed nanosheet array peeled off from FeO_x substrate by sonication.

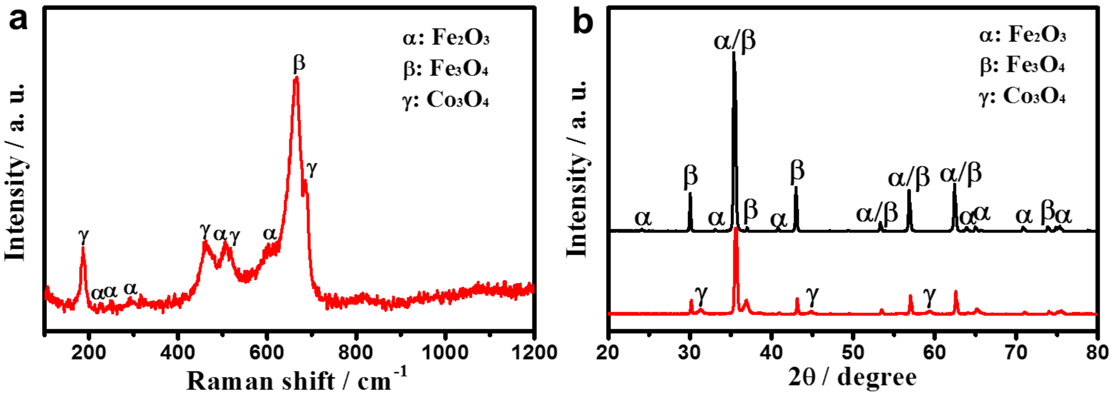

Fig. S3 (a) Raman spectrum of Co_3O_4 crossed nanosheet array/FeO_x substrate. (b) XRD patterns of the FeO_x substrates (black line) and Co_3O_4 crossed nanosheet array/FeO_x substrate (red line). As shown in Fig. S3a, the Raman peaks at 187, 462, 517, 685 cm^{-1} correspond to the F_{2g}, E_g, F_{2g} and A_{1g} modes of Co_3O_4[4]. XRD patterns in Fig. S3b (black line) proved that the FeO_x substrate was composed of Fe_2O_3 (JCPDS 33-0664) and Fe_3O_4 (JCPDS 65-3107). The Co_3O_4 (JCPDS 42-1467) was detected after thermal decomposition of cobalt nitrate on FeO_x substrate (red line in Fig. S3b), which is consistent with the Raman result.

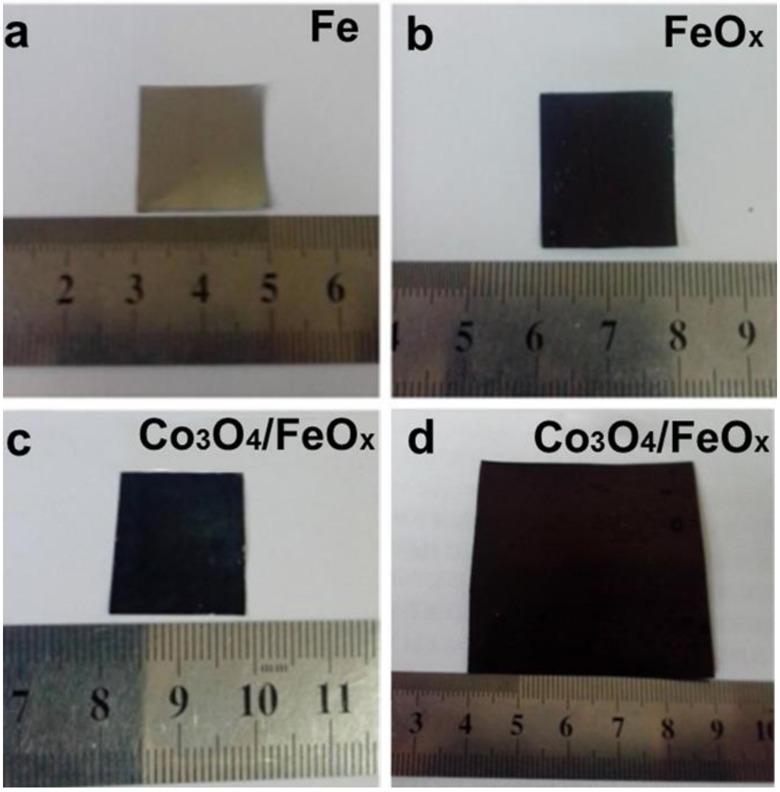

Fig. S4 The digital photographs of the same piece of (a) Fe foil, (b) FeO_x substrate and (c) Co_3O_4 crossed nanosheet array/FeO_x substrate with the size of 2 cm × 2 cm. The digital photograph of (d) Co_3O_4 crossed nanosheet array/FeO_x substrate with the size of 5 cm × 5 cm.

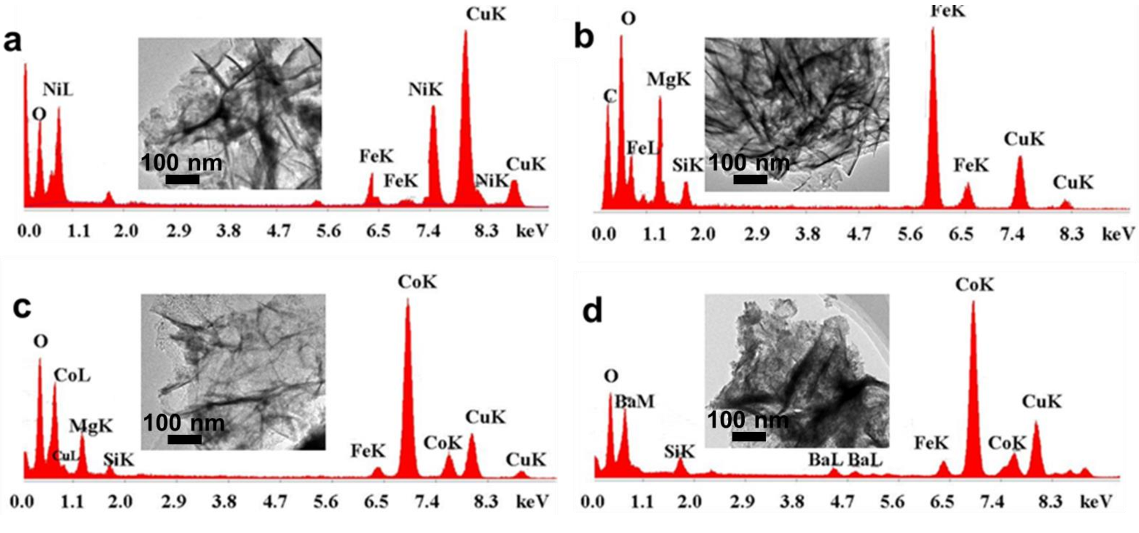

Fig. S5 TEM images and the corresponding EDX spectra of (a) NiO, (b) MgO, (c) $CoMg_xO_y$ and $CoBa_xO_y$ crossed nanosheet array peeled off from FeO_x substrate.

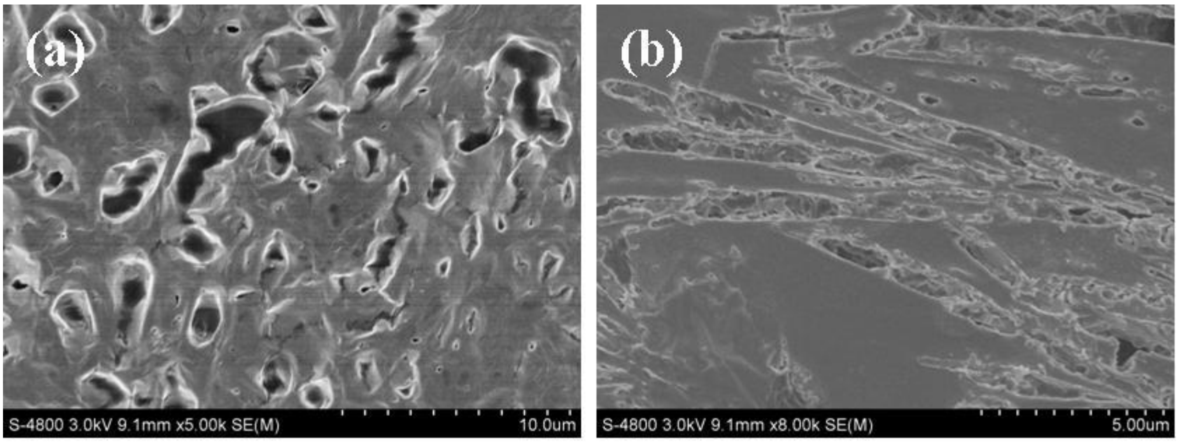

Fig. S6 SEM images of cobalt nitrate on (a) Si and (b) TiO_2 substrates.

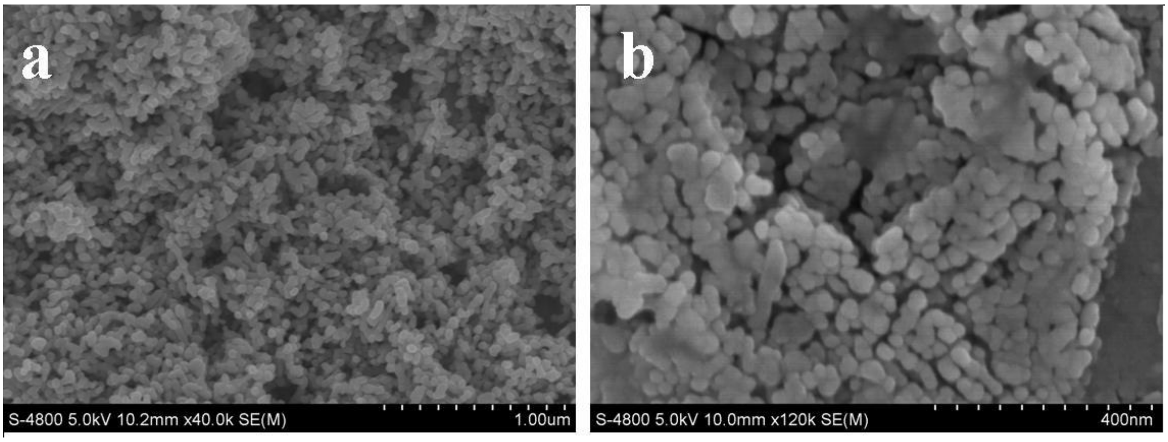

Fig. S7 SEM images of Co_3O_4 on (a) Si and (b) TiO_2 substrates.

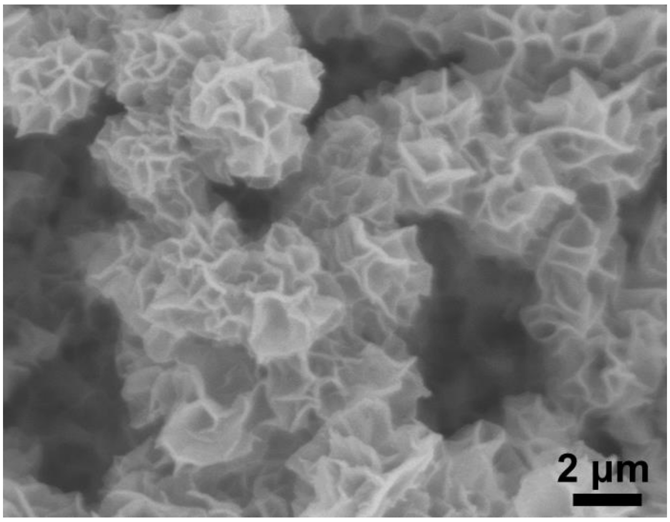

Fig. S8 SEM image of Co_3O_4 crossed nanosheet array/FeO_x substrate after catalysis evaluation for soot elimination.

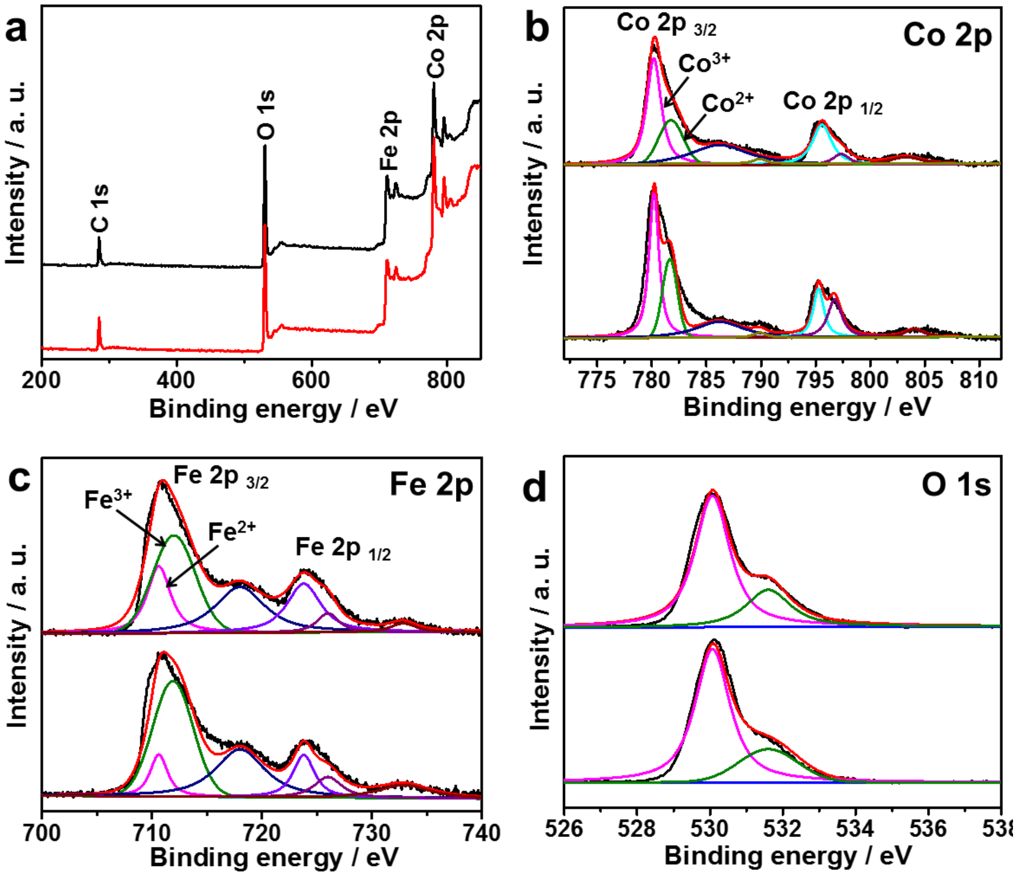

Fig. S9 XPS spectra of Co_3O_4 crossed nanosheet array/FeO_x substrate before (upper) and after (lower) catalysis evaluation for soot elimination: (a) survey scan XPS spectra, (b) Co 2p deconvolution spectra, (c) Fe 2p deconvolution spectra, (d) O 1s deconvolution spectra.

References

1. Y. F. Yu, M. Meng and F. F. Dai, *Nanoscale*, 2013, **5**, 904.
2. Y. F. Yu, J. L. Ren, D. S. Liu and M. Meng, *ACS Catal.*, 2014, **4**, 934.
3. J. L. Ren, Y. F. Yu, F. F. Dai, M. Meng, J. Zhang, L. Zheng and T. D. Hu, *Nanoscale*, 2013, **5**, 12144.
4. V. G. Hadjiev, M. N. Iliev and I. V. Vergilov, *J. Phys. C: Solid State Phys.*, 1988, **21**, L199.