Nano Today (2010) **5**, 15—20

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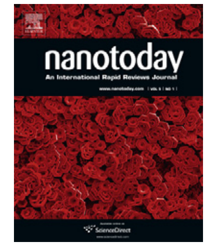

RAPID COMMUNICATION

Direct imprinting of microcircuits on graphene oxides film by femtosecond laser reduction

Yonglai Zhang [b,c], **Li Guo** [b], **Shu Wei** [c], **Yinyan He** [c], **Hong Xia** [b], **Qidai Chen** [b], **Hong-Bo Sun** [b,*], **Feng-Shou Xiao** [a,*]

[a] *Department of Chemistry, Zhejiang University, Hangzhou 310028, China*
[b] *State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China*
[c] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China*

Received 26 November 2009; received in revised form 28 December 2009; accepted 31 December 2009
Available online 19 January 2010

KEYWORDS
Graphene;
Femtosecond laser;
Reduction;
Microcircuit;
Patterning

Summary Graphene microcircuits have been successfully created on graphene oxide films *via* direct femtosecond laser reduction process according to preprogrammed patterns. Atomic force microscopy (AFM) characterization shows that surface height of the micropatterns was lower than the rest of the film due to the loss of oxygen confirmed by XPS and XRD techniques. The electric resistivity and conductivity of as-reduced graphene have strong dependences on output power of femtosecond laser. Moreover, current—voltage curves of graphene microcircuits show typical linear relationship, indicating the stable conductivities. The micro-nanoprocessing of graphene through femtosecond laser technologies might open the door for applications of graphene-based materials in electronic microdevices.

Introduction

In recent years, interests in graphene-based materials are exploding due to their unique properties [1—7]. Especially, for electrical applications, two-dimensional graphene sheets demonstrate great potential for future use in microdevices [8—10]. Generally, graphene sheets synthesized through chemical-oxidative exfoliation of graphite were of benefit to solution-processing compatibility, which imparts tractable nature to graphene for further applications [11]. However, the oxygen-containing graphene suffers from poor electric conductivities due to the presence of abundant defects, which significantly hinders its electrical applications, and therefore, post-reduction was essential [12—14]. On the other hand, the use of graphene in electronic microdevices requires refined control of various complex patterns of integrated circuits [15,16]. Novel transfer printing methods were developed for fabricating graphene patterns by employing elastomeric stamps [17,18]. Shadow mask was used for patterning solution-processed graphene oxide (GO) films through etching or reducing the

* Corresponding authors. Fax: +86 431 516 8624.
E-mail addresses: hbsun@jlu.edu.cn (H.-B. Sun), fsxiao@mail.jlu.edu.cn (F.-S. Xiao).

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doi:10.1016/j.nantod.2009.12.009

exposed part of the GO films [19,20]. In addition, patterned graphene was also prepared by a successful epitaxial growth on a pre-patterned substrate [21,22]. However, it is still difficult to fabricate complex patterns with higher resolution and smaller size on graphene films. The lack of micro-nanoprocessing technologies for fabricating graphene into complex patterns constitutes the main trammel of its applications in electronic microdevices. Therefore, it would be of interest to develop new method for patterning and reduction of solution-processed graphene oxides through a simple process.

It is worth noting that femtosecond (FS) laser has been widely used for producing micrometresized feature and three-dimensional (3D) microdevices due to its advantages of nanometre spatial resolution and 3D prototyping capability since 1994 [23,24]. Afterward, the resolution of microdevices or micropatterns has been significantly improved [25]. In this work, FS laser was used to fabricate graphene microcircuits by direct reduction and patterning of GO films. Various complex patterns were successfully created through this simple FS laser nanowriting pathway. The patterned graphene was synchronously reduced and thus represent well conductivity for electrical applications.

Experimental

Method

Graphene oxide was prepared from purified natural graphite (Aldrich, <150 μm) by Hummers method [11]. The as-synthesized graphene oxide was dispersed into individual sheets in distilled water at a concentration of 3 mg/ml with the aid of ultrasound. Glass wafer was cleaned by ethanol with the aid of ultrasound and dried in vacuum before use. Gold electrodes were coated onto the glass wafer under vacuum through a shadow mask. Then above GO solution was spun coated at 1000 rpm on the glass wafer, dried at 95 °C and repeated for 10 times. The as-prepared GO film was used for further processing by femtosecond laser. A femtosecond laser pulse of 790 nm central wavelength, 120 fs pulse width, 80 MHz repetition rate was focused by a ×100 objective lens with a high numerical aperture (NA = 1.4) into the GO film. 600 μs exposure duration of each voxel and 100 nm scanning step length were adopted. Then the femtosecond laser directly wrote on the GO film according to preprogrammed patterns.

Characterization

The femtosecond laser was generated by Tsunami, Spectra-Physics lasers (model: 3960-X1BB s/n 2617; ccd: AMSTAR, B/W; video ccd: CAMERA). Powder X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 spectrometer. Spectra were baseline corrected using the instrument software. Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer. The 514.5 nm radiation from a 20 mW air-cooled argon-ion laser was used as the exciting source. Atomic force micrographs (AFM) were obtained using a NanoWizard II BioAFM (JPK Instrument AG, Berlin, Germany) in the tapping mode. SEM experiments were performed on a JEOL JSM-7500F scanning electron microscope (5.0 kV). Current—voltage curves of graphene microcircuits were measured from a Keithley SCS 4200 semiconductor characterization system. Optical micrographs were obtained from a Motic BA400 microscope and the charge coupled device (ccd) of the laser.

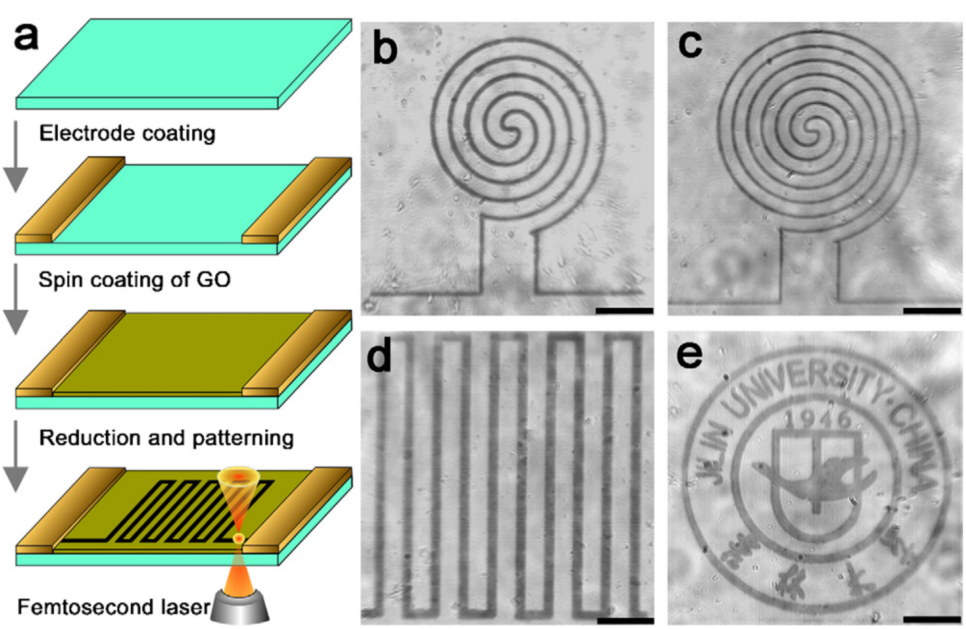

Figure 1 Preparative scheme and optical microscopy images of reduced and patterned GO films. (a) Illustration of preparative procedure of GO microcircuit; optical microscopy images of a curvilinear microcircuit (b) MC-1, (c) MC-2, comb-like microcircuit (d) MC-3, and (e) the badge of Jilin University. Scale bars, 10 μm.

Results and discussion

Fig. 1a shows the preparative procedures of graphene microcircuits. Firstly, gold electrodes were thermally evaporated onto a glass wafer under vacuum through a shadow mask. Then GO solution (3 mg/ml) was spun at 1000 rpm on the electrodes coated glass wafer. Subsequently, the GO film was reduced and imprinted according to preprogrammed patterns *via* direct FS laser nanowriting. As observed in Fig. 1b—d, two curvilinear microcircuits (MC-1, MC-2) and a comb-like microcircuit (MC-3) with high resolution were successfully created. The patterns could be clearly identified from optical microscopy images due to the difference in transparencies. The patterning process of MC-1 was *in situ* recorded by a CCD recorder (Supplementary Information, Video S1). It is of interest to note that complex patterns such as the badge of Jilin University could also be easily imprinted through this micro-nanoprocessing technology (Fig. 1e), indicating that any desired patterns could be directly created. SEM images of two typical patterns were shown in supplementary information (Fig. S1). The patterns of MC-2 and MC-3 could be clearly identified from the images.

In order to investigate the surface property of the reduced and patterned GO (RP-GO) films, we carefully characterized MC-2 and MC-3 microcircuits by AFM technique. AFM image shows that the thickness of as-synthesized GO film is about 55 nm (Fig. S2). After reduction and patterning by FS laser, patterns with sunken surfaces could be clearly identified from the AFM images (Fig. 2a and e). Height profile along the white line (L1, L3) shows a periodic change in surface height, indicating the smooth interface and the high resolution of the patterns. Locally magnified images give much clearer observations of three sunken channels of both MC-3 and MC-2 microcircuits (Fig. 2b and f). Height profile along the white line (L2, MC-3) shows the liner width

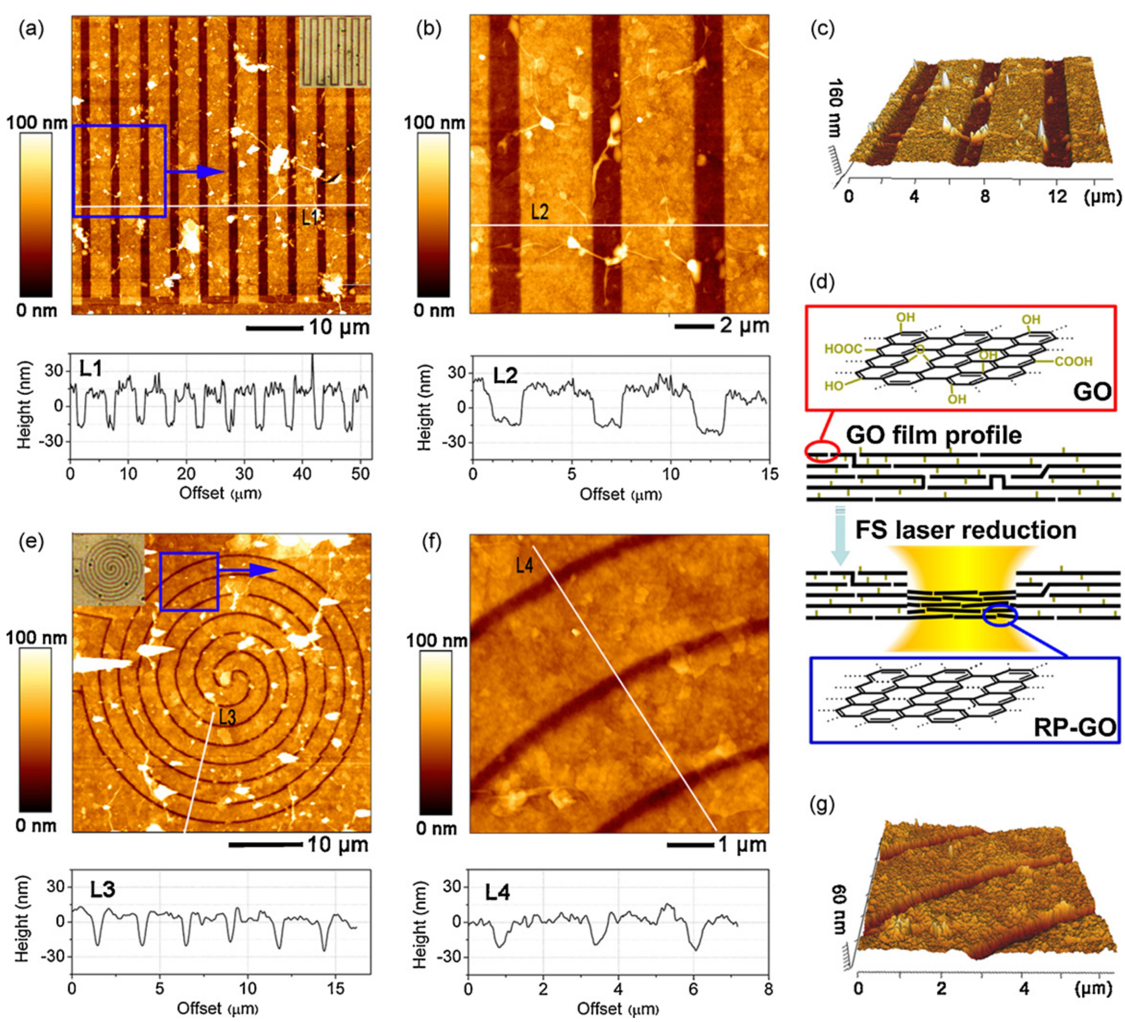

Figure 2 AFM characterizations of reduced and patterned GO films. (a) AFM image of comb-like microcircuit (MC-3) and height profile along the white line (L1), inset is the optical micrograph of the MC-3; (b) magnified image of the local pattern (blue square of a) and height profile along the white line (L2); (c) 3D image of (b); (d) illustration for the profile of GO film before and after FS laser reduction; (e) AFM image of comb-like microcircuit (MC-2) and height profile along the white line (L3), inset is the optical micrograph of the MC-2; (e) magnified image of the local pattern (blue square of d) and height profile along the white line (L4); (f) 3D image of (e).

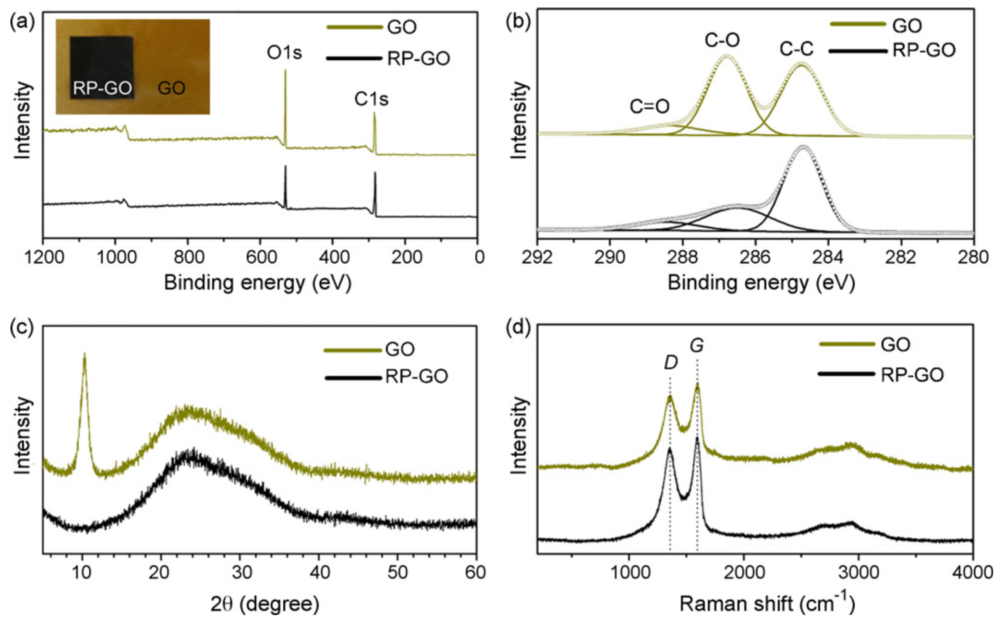

Figure 3 (a) Survey X-ray photoelectron spectra of GO and RP-GO, inset is a photograph of a RP-GO square on a GO film; (b) C1s XPS spectra of GO and RP-GO; (c) XRD patterns of GO and reduced and patterned GO (RP-GO); (d) Raman spectra of GO and RP-GO.

of about 1.5 μm and the sunken depth of about 35 nm. Magnified image of MC-2 pattern that was imprinted by single laser focal spot (Fig. 2f, L4) shows a liner width of about 500 nm and a sunken depth of about 25 nm, giving the highest resolution of the graphene patterns created by FS laser. 3D transformed AFM images of MC-3 and MC-2 patterns reveal a visual observation of the microcircuits (Fig. 2c and g). Seemingly, the laser irradiation induced surface sinking arose possibly from an effect called laser shock hardening, a process used to strengthen metals and alloys, wherein a shock wave induced by momentum transfer from photons to atoms absorbing them produces rebinding of atoms in the material. A typical criterion for the shock hardening is that a surface caves in along the light propagation direction. Here, however, FS laser beam enters and interact with the GO film from the substrate side. Therefore, the sink should be resulted from the mass loss from the GO films and as a result the rearrangement of atoms.

The nature of the mass loss is photochemical reduction. As seen in the inset of Fig. 3a, RP-GO with 2 mm square turned black from pristine deep-yellow after reduction and patterning, which is generally observed during reduction of GO. X-ray photoelectron spectroscopy (XPS) studies show both GO and RP-GO have signals of carbon and oxygen (Fig. 3a). After reduction, O1s peak intensity of RP-GO is significantly decreased compared with that of GO, demonstrating the loss of oxygen. The C1s spectra of GO and RP-GO could be deconvoluted into three peaks that corresponding to C—C, C—O and C=O, respectively. Notably, the content of carbon not bound to oxygen in GO is estimated to be about 44%, while RP-GO film shows much higher content (~61%). XRD patterns (Fig. 3c) show that GO film typically gives diffraction peak at $2\theta = 10.3^\circ$ (d-spacing of 8.6 Å), indicating the successful oxidation of raw graphite. After reduction and patterning of GO film by FS laser, the typical diffraction peak disappears, which could be related to the removal of oxygen containing groups from the GO film, in good agreement with the results of XPS. Raman spectra of GO films display two broad picks at 1354 and 1599 cm^{-1}, corresponding to *D* and *G* band, respectively (Fig. 3d). The *G* band peak is attributed to an E_{2g} mode of graphite associated with the vibration of sp^2 bonded carbon atoms. The *D* band peak is related to the vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. After reduction and patterning, *D* and *G* band peaks become sharp slightly. In addition, there is no band shift in the Raman spectrum of RP-GO film. The *D*/*G* intensity ratio of RP-GO ($I_D/I_G = 0.89$) is slightly larger than that of pristine GO ($I_D/I_G = 0.83$), which can be explained as a decrease in the size of reduced and patterned graphene domains [26].

To investigate the conductivity of RP-GO reduced by FS laser of different output powers, a series of RP-GO micro-belts were patterned. Fig. S3 shows the optical microscopy images of these RP-GO micro-belts between electrodes. The length and width of these micro-belts could be measured from these micrographs. The areas of the section were estimated by AFM data shown in Fig. S4. After measuring the resistances by a multimetre, the resistivities and conductivities of these RP-GO micro-belts could be calculated according to the method shown in Scheme S1. Fig. 4a shows the dependence of resistivity and conductivity of these RP-GO micro-belts on different output powers of FS laser. Generally, the higher the laser power, the higher the conductivity, and the lower the resistivity. In this work, RP-GO micro-belt reduced by FS laser with an output power of 3.0 mW gives the highest conductivity of 2.56×10^4 S/m and the lowest resistivity of 3.91×10^{-5} Ωm. A further increase of the output power will partly ablate the thin GO film. The detail parameter of resistivities and conductivities is summarized in Table S1. Fig. 4b shows the current voltage curves of MC-1 and MC-3 microcircuits. Both show approximate linear dependence between voltage and current, indicating the

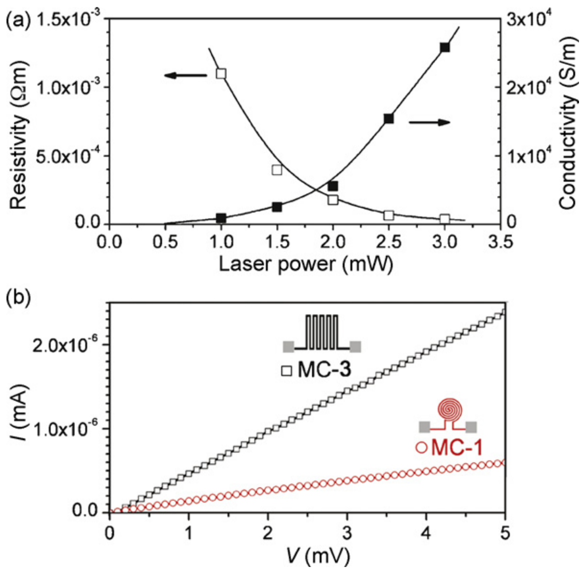

Figure 4 (a) Dependence of resistivity and conductivity of RP-GO micro-belts on laser power; (b) current—voltage curves of MC-1 and MC-3 microcircuits.

stable conductivity of the RP-GO microcircuits. In addition, the resistances of MC-1 and MC-3 evaluated from the curves were 7.8 and 2.1 MΩ, respectively.

Conclusions

In conclusion, we have successfully developed a novel method to fabricate any desired micrometre sized graphene circuits on GO films using FS laser nanowriting. Patterned graphene microcircuits were directly reduced by FS laser, and thus show significant improvement in conductivities. In addition, the resistivities of these graphene microcircuits can be easily adjusted in a certain range by altering the output power of FS laser. The outstanding electrical, optical, chemical and physical properties have already enabled graphene to possess promising applications, and this micro-nanoprocessing method would make graphene even more attractive when used as microdevices in a wide range of scientific fields.

Acknowledgements

We gratefully thank Prof. Wenke Zhang and Dr. Ningning Liu (State Key Laboratory for Supramolecular Structure and Materials, Jilin University, China) for the help of AFM characterizations. We also gratefully thank Dr. Yunfei Xie and Dr. Weidong Ruan (State Key Laboratory for Supramolecular Structure and Materials, Jilin University, China) for help of Raman spectra. This work was supported by the National Natural Science Foundation of China (60978048, 60525412, 20973079, 20773049) and State Basic Research Project of China (2009CB623507).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.nantod.2009.12.009.

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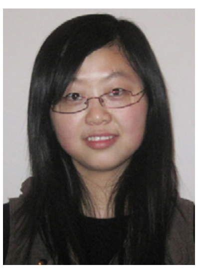
Dr. Yonglai Zhang was born in Liaoning, China in 1981. He received his B.S. in Chemistry (2004) and Ph.D. in Inorganic Chemistry (2009) from Jilin University. Since 2004, he started a continuous academic project involving master and doctor study under the guidance of Prof. F.-S. Xiao in the State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University. In 2008, he had worked in Fritz-Haber-Institut of the Max-Planck-Gesellschaft for three months on the TEM characterization. After received his Ph.D, he joined in Prof. H.-B. Sun's group in the State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University. His current research is focused on the fabrication of nanostructures for polymer and graphene-based materials.

Li Guo was born in Liaoning, China in 1985. She received her B.S. in Electronics (2008) from Jilin University. Since 2008, she is a graduate student in Jilin University under the guidance of Prof. H.-B. Sun in the State Key Laboratory of Integrated Optoelectronics, Jilin University. Her research is focused on the micro-nanofabrication of graphene-based materials and semiconductors by femtosecond laser.

Shu Wei was born in Jilin, China in 1983. She received her B.S. in Chemistry (2006) from Jilin University. Since 2007, she started a continuous academic project involving master and doctor study under the guidance of Prof. F.-S. Xiao in the State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University. Her research is focused on the synthesis and characterization of mesoporous polymers and applications of graphene-based materials.



Yinyan He was born in Hunan, China. Since 2006, she became an undergraduate in Jilin University, majoring in chemistry of materials. In 2006, she joined in Prof. F.-S. Xiao's group in the State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University. Her research is focused on nanostructured carbon materials.

Associate Prof. Hong Xia was born in Shuangcheng, China in 1980. She received her B.S. and Ph.D. degree in Chemistry from Jilin University in 2001 and 2006. She joined the faculty at Jilin University in 2006, where she is now an associate professor of photo-electronics. Her research is focused on micro-nanofabrication by laser based on functional resins and polymers.

Associate Prof. QiDai Chen was born in 1976 in Shandong, China. He received his B.S. in Physics (1998) from University of Science and Technology of China. In 2004, he received his Ph.D. from Institute of Physics, Chinese Academy of Sciences. After postdoctoral work at the Osaka City University at Japan, he joined the faculty at Jilin University in 2006. His main research is focused on laser micro-nanofabrication and ultrafast spectroscopy.

Prof. Hong-Bo Sun received the B.S. and the Ph.D. degrees in electronics from Jilin University in 1992 and 1996, respectively. He worked as a postdoctoral researcher in University of Tokushima, Japan, from 1996 to 2000, and then as an assistant professor in the Department of Applied Physics, Osaka University. He became a project leader under PRESTO (Precursory Research for Embryonic Science and Technology, Japan) program in 2001, and won Outstanding Young Scientist Award issued by the minister of MEXT (Ministry of Education, Culture, ports, Science & Technology, Japan) in 2006. Since 2006, he has been working a full professor (Changjiang Scholar) at Jilin University, China. His team was supported by PCSIRT (Program for Changjiang Scholars and Innovative Research Team at University, China). Prof. Sun's research has been focused on laser micro-nanofabrication in the past 10 years, particularly in exploring novel laser technologies including direct writing and holographic lithography, as well as their applications on microoptics, micromachines, microfluids, and microsensors.

Prof. Feng-Shou Xiao received his B.S. and M.S. degrees in the Department of Chemistry, Jilin University, China. From there he moved to the Catalysis Research Center, Hokkaido University, Japan, where he was involved in collaborative research between China and Japan. He was a Ph.D. student there for two years, and was awarded his Ph.D. degree at Jilin University in 1990. After postdoctoral work at the University of California at Davis, USA, he joined the faculty at Jilin University in 1994. For his research in nanoporous materials, Prof. Xiao has been recognized with the National Outstanding Award of Young Scientists in National Science Foundation of China in 1998 and Thomson Scientific Research Fronts Award in 2008. Currently he is the secretary of Asia-Pacific Association of Catalysis Societies. Since December 2009, he is a full and distinguished professor of Chemistry in Zhejiang University.