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Cite this: *RSC Adv.*, 2016, 6, 34422

Received 28th February 2016
 Accepted 30th March 2016

DOI: 10.1039/c6ra05238j

www.rsc.org/advances

Enhanced strength and foamability of high-density polyethylene prepared by pressure-induced flow and low-temperature crosslinking†

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We report a high-performance high-density polyethylene (HDPE) with significantly enhanced mechanical strength by means of pressure-induced flow (PIF) and low-temperature crosslinking treatment. The tensile and flexural strengths increased from 23.5 and 36.2 MPa, up to 74.8 and 78.6 MPa, respectively. This was achieved by the elongated and flattened 'brick-and-mud' like crystal structure of HDPE occurred during PIF, and an adequate crosslinking network that was formed in the amorphous region beneath the melting point. Furthermore, high strength foams of this material could also be produced under supercritical CO₂ batch foaming in solid-state.

Introduction

High-density polyethylene (HDPE), one of the most commonly used thermoplastic polymers, has relatively poor mechanical properties, *i.e.* tensile and flexural strengths. Previously, most attempts to improve its mechanical properties rely on the introduction of crosslink agents into HDPE, which can form a network between polymer chains.^{1–3} Some crosslinked HDPE (XLPE) products have been commercialized for applications such as wires, cables, pipes, heat-shrink tubes and medical packages due to their high-temperature and chemical resistance, impact resistance, environmental stress-crack resistance, superior UV resistance, low-cost, and long-term durability.^{4,5}

Owing to those advantages, XLPE has been considered as a potential substitute for high-cost engineering plastics (*e.g.*, PA, PC, PET). However, its mechanical properties are still significantly lower than that needed for structural applications such as high-pressure vessels, military containers and marine fuel tanks.

Here we show that a solid state processing method, called pressure-induced flow (PIF),⁶ may significantly improve the mechanical properties of XLPE by exerting enough pressure to the polymer below its melting temperature to elongate and flatten the crystal domains into a 'brick-and-mud' like structure. Previous studies have shown that PIF processing on many semi-crystalline polymeric materials could form oriented crystal structure with substantially improved mechanical properties.^{6–8} Recently, we found that PIF induced crystal reorientation is better than 'shish-kebabs' type crystal orientation induced in injection molding, fiber spinning or biaxially oriented isotactic polypropylene in regard to property enhancement.⁹

In this study, we demonstrate that a combination of PIF and low-temperature crosslinking of XLPE may lead to unprecedented improvement of mechanical properties of HDPE. Furthermore, the foamability of HDPE can be substantially improved, which leads to unique high-strength and lightweight HDPE products under supercritical CO₂ (scCO₂) batch foaming in solid-state.

PIF and low-temperature crosslinking

Scheme 1 illustrates the PIF and low-temperature crosslinking process. A 25 mm × 12 mm × 5 mm sample was fixed in a designed mold (Fig. 1a). By exerting enough pressure below the melting point (450 MPa at 110 °C in this case), the sample achieved sufficient flow deformation (3.5 times in this case) as shown in Fig. 1b. The operation conditions were optimized and detailed results are presented in Fig. S1.† During the PIF process, common XLPE materials are often chemically cross-linked at molten stage with temperatures higher than 150 °C.^{10,11} To preserve the elongated crystal structure after PIF, it is

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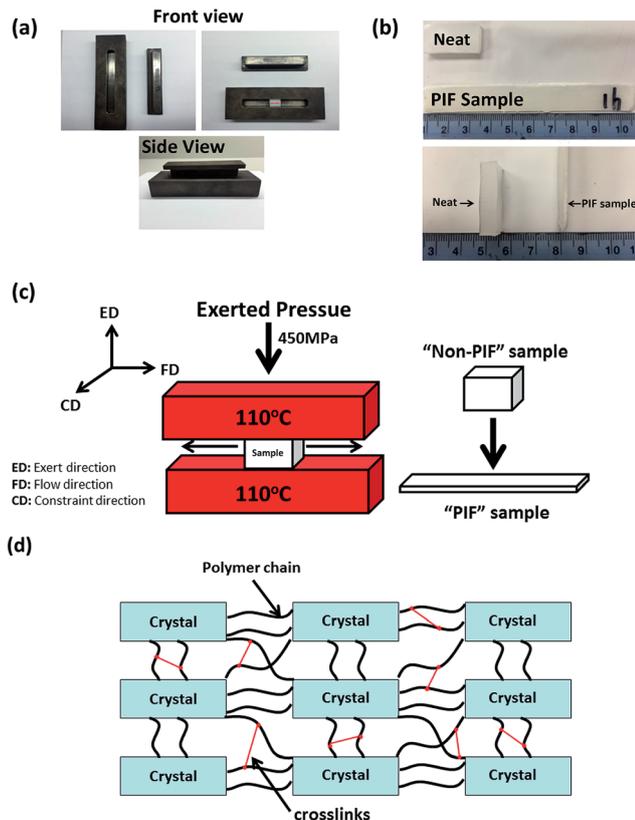
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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra05238j

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Scheme 1 The protocol of pressure-induced flow (PIF) and cross-linking process: (a) front and side views of PIF processing mold; (b) top and side views of dimension changes of XLPE samples before and after PIF; (c) scheme of PIF-processing process; (d) schematic of PIF with crosslinking.

desirable to conduct crosslinking below the melting temperature. Here, we compounded 3 wt% 3-chloroperoxybenzoic acid (mCPBA) into HDPE before PIF and crosslinking. This allowed a mild chemical crosslinking condition at 110 °C, which is far below HDPE melting point (135 °C). By inducing oxidative species degraded from mCPBA (its half-life about 1 h at 110 °C),¹² proper crosslinking of the PE chains in amorphous domains could be achieved (Fig. 1d). The optimized time of crosslinking was set at 1 hour during the PIF process (more results and discussion are provided in ESI and Fig. S4†). Too much crosslinking tended to reduce the mechanical strength of HDPE.

We next evaluated the change of crystallization behavior using X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Fig. 1a shows the XRD curves of neat PE, PIF PE and PIF XLPE samples. All the samples were scanned along the level plane (X axis) and vertical plane (Z axis). The XRD patterns for neat PE on both scanning planes showed no significant difference, indicating that the crystal orientation is isotropic in neat PE. A distinct difference in both scanning angles was observed in the PIF PE sample (*i.e.* PE material without adding mCPBA). Although the diffraction pattern remained the same, the diffractive intensity on the level plane was significantly increased compared to that on the vertical plane. This indicates

large deformation, but no change on the crystal type of HDPE. The average crystal size can be estimated according to the Scherrer equation.¹³ Accordingly, the average crystal size on the level plane was greatly increased from 27.2 nm (neat PE) to 105.6 nm (PIF PE). A similar but less significant crystal elongation was observed on the PIF XLPE sample. The average crystal size on the level plane increased to 98.4 nm. The low-temperature crosslinking slightly hindered crystal deformation during the PIF process.

Fig. 1b shows the measured DSC curves of neat PE, PIF PE and PIF XLPE samples. Under PIF, the melting point of HDPE shifted to a higher temperature. The degree of crystallinity (X_c)¹⁴ also changed somewhat. After PIF processing, the X_c of PIF PE increased from the original 57.3% to 62.9%; while a higher X_c was reached at 67.9% by combining PIF with low-temperature crosslinking. This suggests that most crystals of the PIF PE sample remained after low-temperature crosslinking. Moreover, the presence of mCPBA additive has contributed towards heterogeneous nucleation of HDPE crystallization during mCPBA, *i.e.* X_c was increased from 57.3% to 59.4%. More DSC results are summarized in Table S1.†

Fig. 1c presents the storage modulus (E') as a function of temperature for various samples. As compared to neat PE, both XLPE (low-temperature crosslinking without PIF processing) and PIF PE samples show significantly higher moduli, which confirm that both crosslinking and PIF are beneficial for the enhancement of mechanical property. As expected, the combined PIF and crosslinking provided better property enhancement. To determine the degree of crosslinking, the gel contents were obtained *via* a p -xylene extraction at its boiling temperature.¹⁵ After the extraction and drying, the gel content was determined as shown in Fig. 1d. Neither the crystal nor the amorphous domain of neat PE and PIF PE remained after the extraction. When the low-temperature crosslinking was induced, an insoluble network was formed in amorphous domains of HDPE. Under the conditions used, we observed a 16.2 wt% residue in XLPE sample. In comparison, the PIF XLPE sample exhibited a slightly less gel content of 13.8 wt% at the same conditions. The gel contents of XLPE with various crosslinking times are given in Fig. S2.†

Enhanced mechanical properties

The mechanical properties of neat PE, PIF PE and PIF XLPE samples are shown in Fig. 2a and b. The tensile strength increased substantially from 23.4 MPa for neat PE to 63.5 MPa for PIF PE. The flexural strength also increased significantly from 36.2 MPa for neat PE to 56.4 MPa for PIF PE sample. This suggests that PIF can greatly improve mechanical properties of HDPE. When proper crosslinking was introduced into the PIF process, the mechanical properties can be further enhanced. Compared to the PIF PE sample, the properly crosslinked PIF XLPE sample showed an additional 17% increase in tensile strength (74.8 MPa) and a 39% increase in flexural strength (78.6 MPa). However, over-crosslinking exhibited no benefit to the mechanical properties of PIF XLPE samples (Fig. S3†).

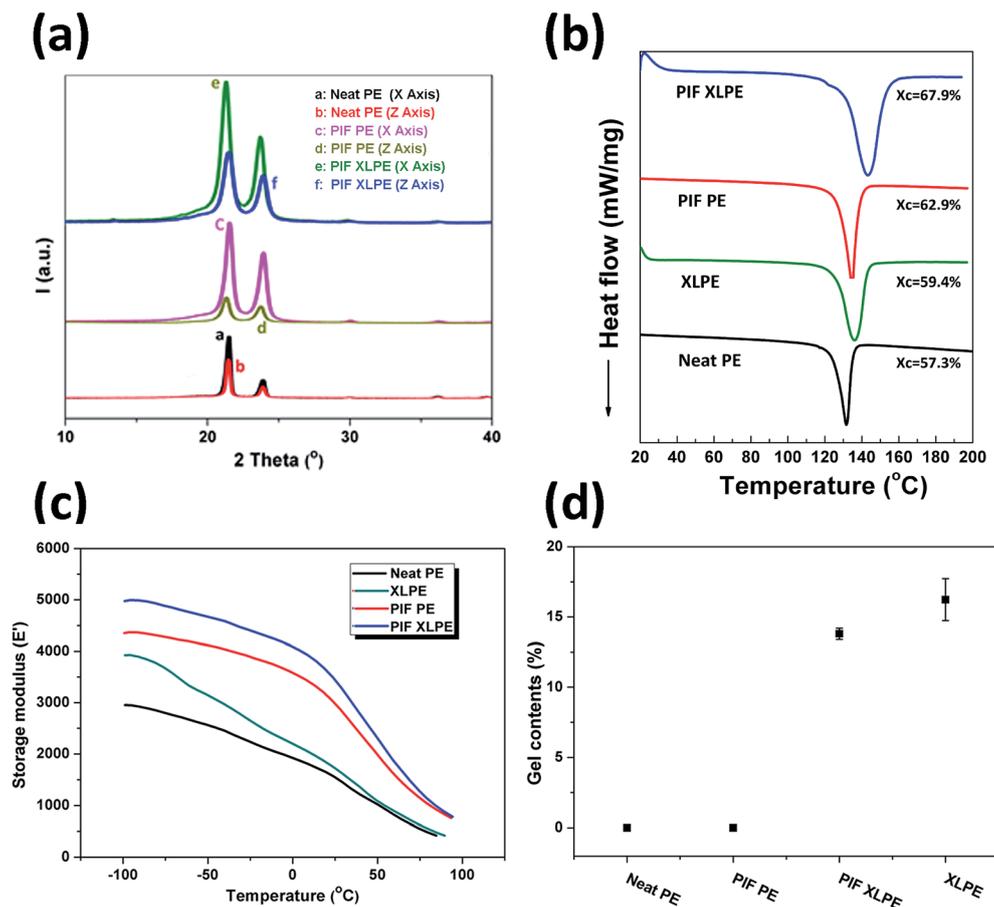


Fig. 1 Characterization of neat PE, PIF PE and PIF XLPE samples: (a) XRD patterns; (b) DSC curves; (c) storage moduli as a function of temperature; (d) the gel contents measured in boiling xylene. PIF and crosslinking conditions: 110 °C, 450 MPa and 1 h.

The cross-section SEM micrographs of neat PE, PIF PE and PIF XLPE samples are presented in Fig. 2c–e. The neat PE sample displays a non-orientated morphology on the fracture surface (Fig. 2c). After PIF, a highly-orientated morphology of PIF PE fracture was observed (Fig. 2d). The orientated crystals of HDPE are aligned in parallel to the flow direction and are in perpendicular to the exerted pressure direction. Similar morphology was observed in other PIF works.^{6–8,16–18} With low-temperature crosslinking, the oriented morphology (Fig. 2e) maintains and becomes more obvious. This highly oriented “brick-and-mud” structure is essential for fabricating the high-performance HDPE.

Supercritical CO₂ (scCO₂) foaming process

Fig. 3 shows the cross-section views of neat PE, PIF PE and PIF XLPE foams by scCO₂ batch foaming process. The foaming temperature was controlled at 120 °C to prevent the melting of HDPE crystals. It is difficult to achieve well-foamed HDPE in either molten or solid state because of its low melt strength and high degree of crystallinity. Compared with neat PE before and after foaming (Fig. 3a and b), it can be seen that neat PE was

hardly foamed at the given conditions. Sample density only changed slightly and there were a few large bubbles. Crosslinking of XLPE was not able to improve foaming much (Fig. 3c). Apparently, CO₂ gas diffused rapidly and released very quickly from HDPE matrix, resulting in poor foam-ability.¹⁹ The introduction of PIF was able to improve the foam-ability of HDPE as shown in Fig. 3d. Many large bubbles were formed close to the skin layer, which may be attributed to the formation of the “brick and mud” structure that slowed down the CO₂ gas diffusion. We recently observed a similar phenomenon on solid-state foaming of polypropylene (PP).¹⁷ Interestingly, a dual-mode foam structure with a combination of few large bubbles (>100 μm) and many smaller (<20 μm) and denser bubbles was observed when the PIF process was combined with the crosslinking effect (Fig. 3e). It seems that the crosslinking induced changes of viscoelastic properties of HDPE amorphous domains,^{20,21} together with the diffusion barrier resulting from elongated HDPE crystal domains by PIF, this allowed the formation of microcellular bubbles in the sample in the current scCO₂ foaming process. Since the crosslinking extent was low, it is not surprising that the large bubbles co-existed in the foamed sample. The density of as-mentioned foamed samples decreased from 0.935 g cm⁻³ for neat PE to 0.763 g cm⁻³ for PIF XLPE (Fig. 3f). Fig. S4† shows the average cell size and cell

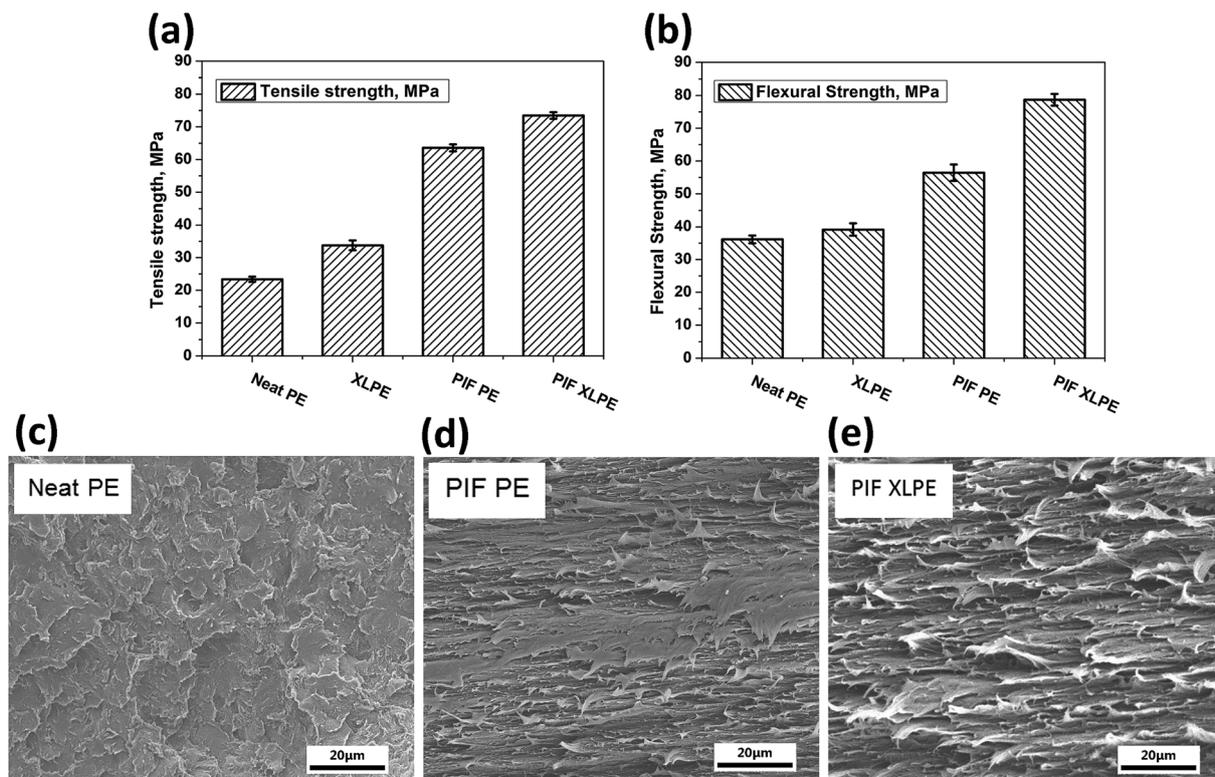


Fig. 2 Mechanical properties of neat PE, XLPE, PIF PE, and PIF XLPE samples: (a) tensile strengths; (b) flexural strengths; and (c–e) the cross-section SEM micrographs. PIF and crosslinking conditions: 110 °C, 450 MPa, and 1 h.

density statistical results of the foams. The cell size obviously decreased and cell density increased, which due to many smaller bubbles generated in PIF XLPE foam.

To evaluate the mechanical property of foam samples, compressive stress–strain behaviors were measured and presented in Fig. 4a. The normalized compressive stresses of neat

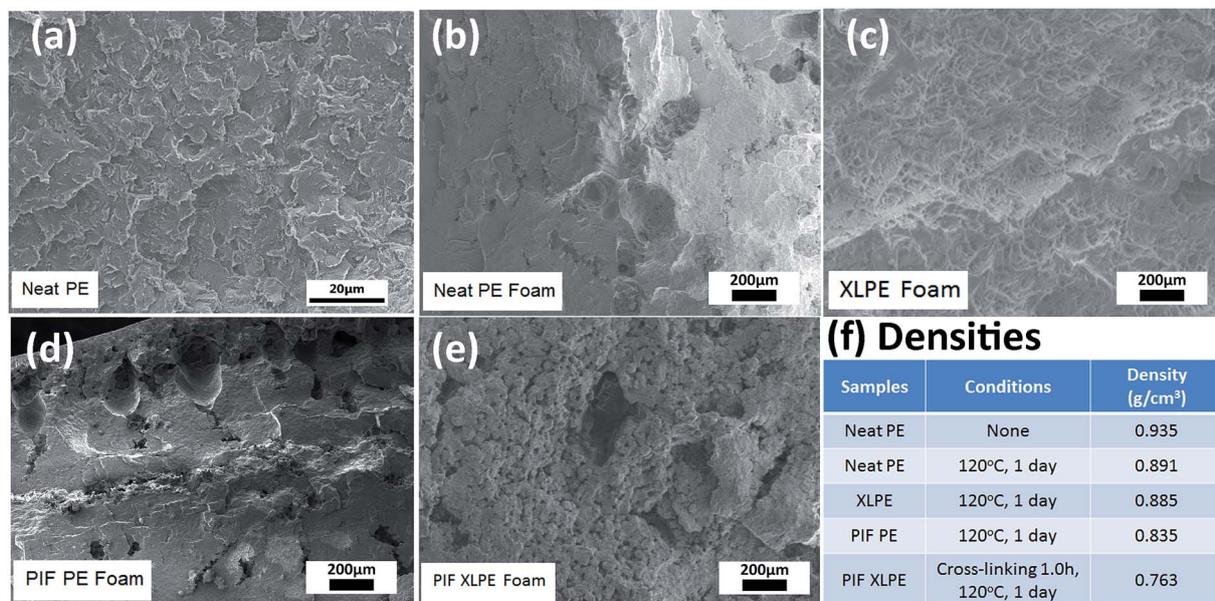


Fig. 3 SEM micrographs and densities of various PE samples using scCO₂ batch foaming: neat PE (a) before and (b) after foaming; (c) XLPE after foaming; (d) PIF PE after foaming; (e) PIF XLPE after foaming; (f) densities of all samples. All the samples were saturated at 120 °C, 20 MPa scCO₂ for 1 day.

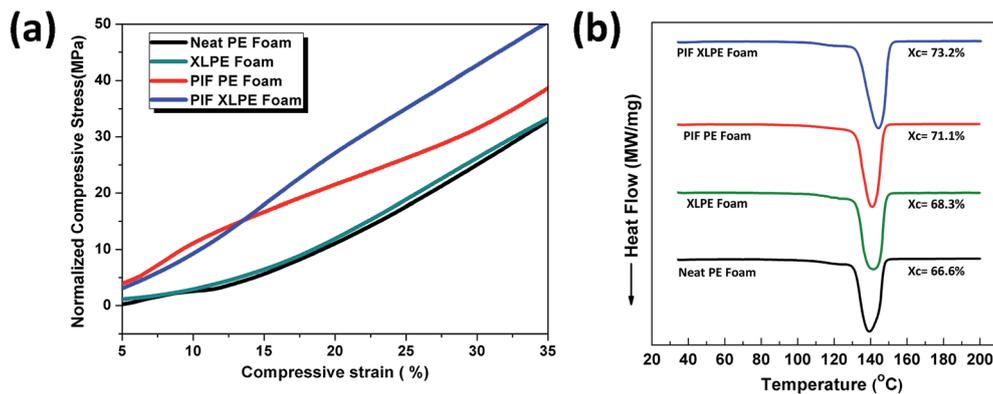


Fig. 4 Compressive properties and crystallization of various PE foamed samples using scCO₂ batch foaming: (a) normalized compressive behavior; (b) DSC curves.

PE and XLPE foam samples almost show the same curves which means only crosslinking has a little effect on the compressive strength of HDPE foam, and the strength of PIF foamed samples are significantly higher than those of non-PIF foamed samples. It is noted that the compressive stress could be further improved by combining PIF with crosslinking. The original compressive stress-strain results are shown in Fig. S5.† Comparing Fig. 4b with Fig. 1b, the crystallinity of the foamed samples increased slightly because scCO₂ is known to enhance crystallization in PE.^{22,23} It is interesting to note that the HDPE sample with the highest crystallinity could reach the lowest foam density when PIF and crosslinking were combined in processing. This also explains why the foamed PIF XLPE sample has even higher compressive strength than the solid XLPE sample.

Conclusions

In conclusion, a high-strength HDPE was successfully fabricated by combining PIF processing with low-temperature crosslinking. Compared to the neat PE, the tensile and flexural strength of PIF XLPE were substantially increased by 220% and 117%, respectively. The oriented crystals, larger crystal size, and cross-linked amorphous domains of HDPE played key roles in the enhancement of mechanical properties. In the case of scCO₂ batch foaming in solid state, such unique structure can also increase the polymer matrix viscoelasticity and gas diffusion barrier, and consequently improve the foam-ability of HDPE. The resultant HDPE density was decreased ~15%. These results have, for the first time, demonstrated an efficient route to prepare high-strength HDPE materials with lighter weight, which is promising for many industrial applications.

Acknowledgements

The authors are grateful to Drs Shih-Yaw Lai and Wen-bin Liang of National Institute of Clean-And-Low-Carbon Energy (Beijing, China) for kindly providing the raw high-density polyethylene materials, and also would like to acknowledge the financial support of Ohio Third Frontier Program, National

Nature Science Foundation of China (No. 51573063), the Zhejiang Nature Science Foundation (No. LY15E030005), the Guangdong Nature Science Foundation (No. S2013020013855, No. 9151064101000066), and National Basic Research Development Program 973 (No. 2012CB025902) in China. Tai-rong Kuang and Da-jiong Fu would like to acknowledge the Chinese Scholarship Council for their financial support and the Nanoscale Science and Engineering Center for the facilities to enable the author to study at the Ohio State University.

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