

ACHIEVING HIGH STRENGTH AND HIGH DUCTILITY IN METAL MATRIX COMPOSITES REINFORCED WITH DISCONTINUOUS THREE-DIMENSIONAL GRAPHENE-LIKE NETWORK

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Keywords: Metal matrix composites, Graphene, Strength, Ductility

ABSTRACT

Graphene or graphene-like nanosheets have been emerging as an attractive reinforcement for composites due to their unique mechanical and electrical properties as well as their fascinating two-dimensional structure. It is a great challenge to efficiently and homogeneously disperse them within metal matrix for achieving metal matrix composites with excellent mechanical and physical performance. In this work, we have developed an innovative in-situ processing strategy for the fabrication of metal matrix composites reinforced with discontinuous 3D graphene-like network (3D GN). The processing route involves the in-situ synthesis of encapsulation structure of 3D GN tightly anchored with Cu nanoparticles (NPs) (3D GN@Cu) to ensure mixing on the molecular level between graphene-like nanosheets and metal, coating of Cu on the 3D GN@Cu (3D GN@Cu@Cu), and consolidation of the 3D GN@Cu@Cu powders. This process can produce GN/Cu composites on a large scale, in which the in-situ synthesized 3D GN not only maintains perfect 3D network structure within the composites, but also has robust interfacial bonding with metal matrix. As a consequence, the as-obtained 3D GN/Cu composites exhibit exceptional high strength and superior ductility (the uniform and total elongation to failure of the composite are even much higher than the unreinforced Cu matrix). To our best knowledge, this work is the first report validating that 3D graphene-like network can simultaneously remarkably enhance the strength and ductility of the metal matrix.

1 INTRODUCTION

Graphene, a 2D layered structure of sp² bonded carbon atoms, has attracted great attention due to its excellent mechanical, electrical and thermal properties. Of particular interest is the use of graphene or graphene-like nanosheets as reinforcements in polymer, metal, and ceramic matrix composites in order to enhance their mechanical properties, because these nanosheets possess extraordinary high elastic modulus of 1 TPa and yield strength (YS) of 130 GPa as well as large surface area ($\approx 2600 \text{ m}^2 \text{ g}^{-1}$) and a low density (2.2 g cm^{-3}).¹⁻⁴ However, most research efforts in this field have been invested in the graphene based nanofillers/polymer composites, which exhibit a remarkable increase in strength and toughness over their individual constituents,⁴⁻⁷ and much less works have been devoted to the graphene (mainly reduced graphene oxide, rGO)/metal composites.⁸⁻²⁰ A general phenomenon can be disclosed: most of them can be strengthened by the graphene, to a certain degree, but their ductility has been compromised so much, which may be ascribed to the following factors. i) the graphene nanosheets with 2D nature, large surface area and high surface energy are very prone to irreversible aggregation or re-stacking, their homogeneous distribution within the composites is thus extremely difficult to be achieved by traditional mixing methods; ii) the graphene materials utilized are usually derived from reduced graphene oxide (rGO) which has severe structural defects introduced during exfoliation and reduction processes, leading to poor

structural stability. Moreover, the high energy milling mixing widely used would further seriously damage the structure of rGO and promote interfacial reactions. In the case of high-temperature consolidating process, the stability and intrinsic strength of rGO are rather low, resulting in limited strengthening and even negative toughening effect of rGO on the metal matrix.⁸⁻²⁰

Herein, we demonstrate for the first time the fabrication of metal matrix composites reinforced with discontinuous 3D graphene-like network (3D GN), produced by an innovative processing strategy. The processing route involves the in-situ synthesis of encapsulation structure of 3D GN tightly anchored with Cu nanoparticles (NPs) (3D GN@Cu), coating of Cu on the 3D GN@Cu (3D GN@Cu@Cu), and consolidation of the 3D GN@Cu@Cu powders. This process can produce GN/Cu composites on a large scale, in which the in-situ synthesized 3D GN not only maintains perfect 3D network structure within the composites, but also has robust interfacial bonding with metal matrix. As a consequence, the as-obtained 3D GN/Cu composites exhibit exceptional high strength and superior ductility (the uniform and total elongation to failure of the composite are even much higher than the unreinforced Cu matrix). To our best knowledge, this work is the first report validating that 3D graphene-like network can simultaneously remarkably enhance the strength and ductility of the metal matrix.

2 GENERAL SPECIFICATIONS

In essence, our novel approach for fabricating 3D GN/Cu composites consists in *in-situ* synthesis of 3D GN within metal powders to facilitate the formation of 3D GN@Cu encapsulation structure and ensure mixing on the molecular level between graphene-like nanosheets and metal, which is very different from that of conventional high energy milling or chemical route mixing of metal with rGO. As illustrated in Figure 1, this process mainly is composed of three steps. In the first step, the homogeneous solution of NaCl, Cu(NO₃)₂ and C₆H₁₂O₆ was freeze-dried to ensure the formation of assembled NaCl particles coated with ultrathin complex film of Cu(NO₃)₂-C₆H₁₂O₆ (NaCl@Cu(NO₃)₂-C₆H₁₂O₆) (Figure 1b). In the second step, the 3D assembled NaCl@Cu(NO₃)₂-C₆H₁₂O₆ particles were subjected to high-temperature heat-treatment under H₂. During this process the carbon precursor of C₆H₁₂O₆ was carbonized within the 2D-confined space between adjacent NaCl surfaces to generate GN with excellent mechanical properties and chemical stability,²⁷ while the metal precursor was decomposed and reduced to Cu NPs tightly anchored on GN, thus forming a encapsulation structure of 3D GN@Cu after removing NaCl by simple water washing (Figure 1d). Figure 2a-c show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the *in-situ* synthesized 3D GN@Cu powders. Obviously, the product exhibits a typical three-dimensional network feature, in which their walls demonstrate a clear curved profile and a very low contrast (Figure 2a-c), which are due to the ultrathin thickness (less than 3 nm) and superior mechanical flexibility of the walls composed of a few graphene-like layers (see Figure 2d).^{21, 22, 27} It can also be seen clearly that the walls of 3D GN are evenly and closely anchored with dense Cu NPs (5~50 nm) and exhibit porous network structure (average pore size of 1 μm) which replicate the interval structure of the NaCl assembly, confirming the indeed formation of quasi encapsulation structure of 3D GN@Cu (Figure 2a-c). On the basis of TGA/DTA thermal analyses, 3D graphene-like network obtained by etching the Cu NPs from the 3D GN@Cu powders has many pores in their walls, suggesting a tight bonding between GN and Cu NPs formed during the heat-treatment process under H₂, the ubiquitous encapsulation structure of 3D GN@Cu *in-situ* synthesized at high-temperature is very thermodynamically stable and would substantially increases the bonding strength between GN and metal (Cu). Furthermore, this structure can keep the coated graphene-like nanosheets isolated by the metal and thus achieve mixing on the molecular level between graphene-like nanosheets and metal. In the second step, 3D GN@Cu powders were further coated by Cu through an impregnation-reduction process in order to form a full encapsulation structure (3D GN@Cu@Cu) as well as tune the ratio of GN to Cu (Figure 1e). As can be seen in Figure 2e-f, the 3D GN@Cu is fully wrapped by Cu particles and almost no graphene-like nanosheets are exposed outside, indicating that the Cu can be conformally and tightly attached on the 3D GN@Cu. This absolute 3D GN@Cu@Cu encapsulation structure can further ensure the enclosed GN isolated by metal, impeding the graphene-like nanosheet aggregation and realizing the extraordinary even distribution of nanosheets within the composites. In the third and final step, the as-obtained 3D GN@Cu@Cu powders were consolidated by hot-pressing sintering under vacuum

(Figure 1f). In this work, bulk composites with 1.0 vol%, 2.0 vol% and 4.0 vol% GN were produced, and unreinforced Cu matrix (i. e. pure Cu) was prepared by nominally the same process for comparison.

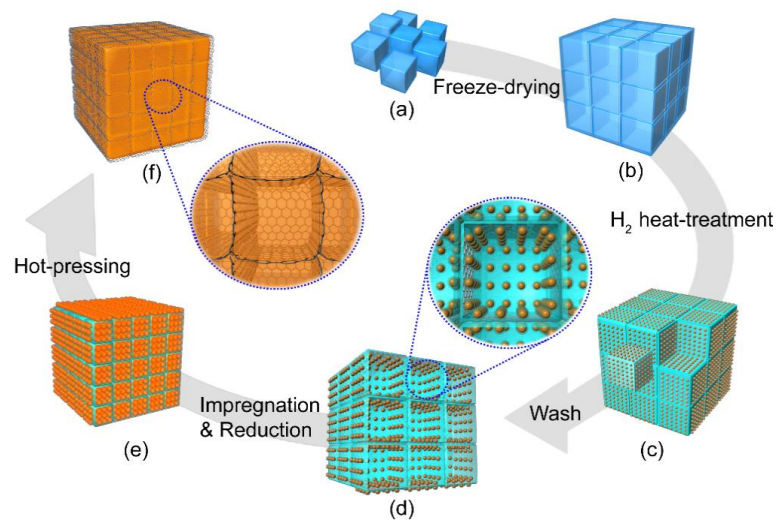


Figure 1. Schematic illustration of the overall production process for 3D GN/Cu composites. (a) $\text{Cu}(\text{NO}_3)_2\text{-C}_6\text{H}_{12}\text{O}_6$ coated NaCl, (b) $\text{Cu}(\text{NO}_3)_2\text{-C}_6\text{H}_{12}\text{O}_6$ coated assembled NaCl particles, (c) GN-Cu coated NaCl particles, (d) 3D GN@Cu powders, (e) 3D GN@Cu@Cu powders, (f) 3D GN/Cu bulk composites.

The characteristic and structural quality of the 3D GN in the composite powders and bulk materials were further evaluated by using Raman spectroscopy. As shown in Figure 2g, it can be clearly observed a G-band at $\sim 1590\text{ cm}^{-1}$, a D-band at $\sim 1330\text{ cm}^{-1}$. It is well-known that the G-band is associated with the result of a radial C-C stretching mode of sp^2 -bonded carbon, the D-band is a first-order zone boundary phonon mode associated with defects in the graphene or graphene edge.^{20, 21, 27} The intensity ratios of the D-band to the G band (corresponding to the vibrations) (I_D/I_G) of the composite powders and bulk composites are calculated as 0.83, and 0.77, respectively. The lower relative intensity of the D-band peak implies that the few-layered graphene-like materials in the composite powders and bulk composites are mainly composed of well-crystallized graphite, well consistent with the TEM observations (Figure 2d and Figure 3f).^{20, 21, 27}

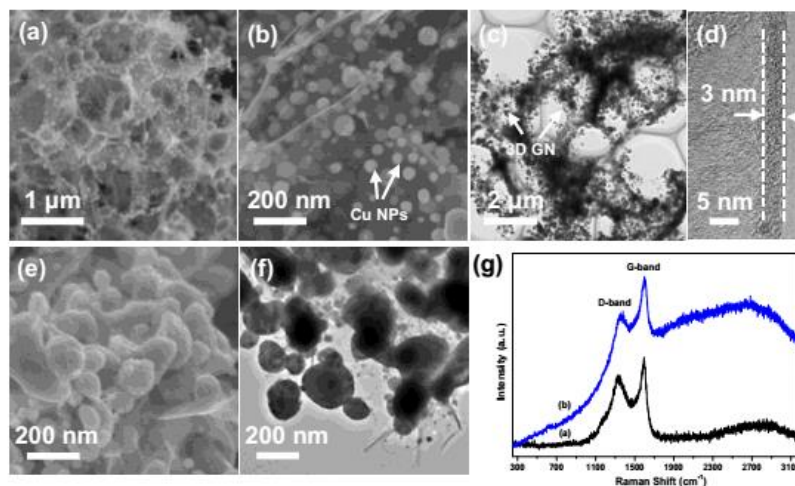


Figure 2. (a)-(b) SEM and (c)-(d) TEM images of 3D GN@Cu powders, (e) SEM and (f) TEM image of 3D GN@Cu@Cu powders with 4.0 vol% GN. (g) Raman spectra of 3D GN@Cu powders (curve a), and 3D GN/Cu bulk composites with 4.0 vol% GN (curve b).

The 3D GN/Cu bulk composites, fabricated by hot-pressing sintering the 3D GN@Cu@Cu powders, were explored by confocal Raman and TEM to investigate their microstructures. As shown in Figure 3a, a clear and network-like distribution of GN which is totally different from conventional homogenous distribution of nanocarbon in MMCs can be seen in the optical image. The corresponding G-mode mapping from confocal Raman in Figure 3b demonstrates that the G-mode mapping matches well with the observed network-like structure, implying that the 3D graphene-like network structure is perfectly maintained within the composites. High-resolution TEM (HRTEM) characterization performed at the GN/Cu interface (Figure 3e-f) reveals that the GN and Cu bond very intimately, and their interfaces are free of impurities, voids, or gaps. Furthermore, an HRTEM image (Figure 3e) of a typical nanosheet displays that the nanosheet with intact structure has a few well-graphitized graphene-like layers. The graphitic sheets of the graphene-like nanosheets are very apparent, and the interlayer spacing between adjacent lattice planes is about 0.34 nm, in good agreement with the ideal graphitic interlayer space (0.34 nm). This corresponds to the Raman spectrum (see curve b in Figure 2g) conducted on the bulk composites and it further verifies the *in-situ* synthesized graphene-like nanosheets with superior structural retention in the composites.

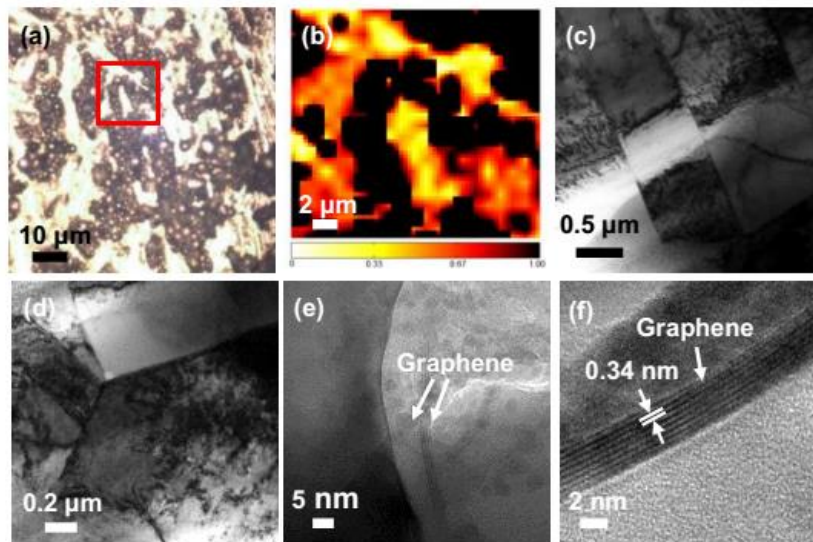


Figure 3. (a) Optical image of 3D GNs/Cu bulk after hot-pressing and (b) the corresponding G-mode mapping of the selected area of 3D GN/Cu bulk composites from confocal Raman. (c)-(d) TEM images of 3D GN/Cu bulk composites with 4.0 vol% GN, (e)-(f) HRTEM images of graphene-like nanosheets dispersed in the composites.

The tensile tests show that the 3D GN/Cu composites fabricated by in-situ strategy exhibit exceptional high strength and outstanding ductility. Figure 6a presents the engineering stress–strain curves of the composites and pure Cu, respectively. The tensile properties measured were organized and listed in Table 1. It can be seen that the composite with 2.0 vol% GN has a yield strength of 301 MPa and a ultimate tensile strength (UTS) of 318 MPa, which are 207% (from 98 to 301 MPa), and 54% (from 206 to 318 MPa) higher than that of pure Cu, respectively, while its Young's modulus (≈ 112 GPa) is about 43% larger than that of pure Cu (≈ 78 GPa). With regard to ductility, it can be disclosed that the total elongation to failure of the composites increases rapidly with the increase of GN content in the composites. With increasing the GN content from 1.0 vol% to 4.0 vol%, the elongation to failure increases evidently from 24.3% to 53.8%. The uniform and total elongation of the 4.0 vol% GN/Cu composite (43.5% and 53.8%) are all much higher than that of the pure Cu (30.6% and 38.2%). In the meanwhile, the yield strength and tensile strength of the 4.0 vol% GN/Cu

composite are 126% (from 98 to 221 MPa), and 39% (from 206 to 287 MPa) higher than that of pure Cu, respectively. These results definitely verify that the 3D GN is a highly effective reinforcement for enhancing both the strength and ductility of the Cu matrix. To the best of our knowledge, this work is the first report revealing that 3D discontinuous graphene-like network structure can simultaneously remarkably enhance the strength and ductility of the metal matrix. The simultaneous high strength and extraordinary ductility set the present composites apart from all the previously reported Cu matrix composites reinforced by other reinforcements, such as rGO and GN,^{14-20, 28, 29} carbon nanotube,^{30, 31} TiB₂,³² Y₂O₃,³³ and Ti₃SiC₂,³⁴ which have either low strength or low ductility (or both low) (as shown in Figure 6b). The toughness modulus, which is the energy needed to completely fracture the material, could be measured by calculating the area under the stress-strain curve.^{35,36} The toughness modulus for 4.0 vol. % reached ~126 MJ m⁻³, which is 1.7 times that of pure Cu under the same processing progress, showing a good balance between strength and ductility. It should be noted that some Cu matrix composites with high yield strength were prepared by using spark plasma sintering technique, which fabricates samples with only small sizes and thus is unsuitable for industrial mass production.^{14-16, 18, 20}

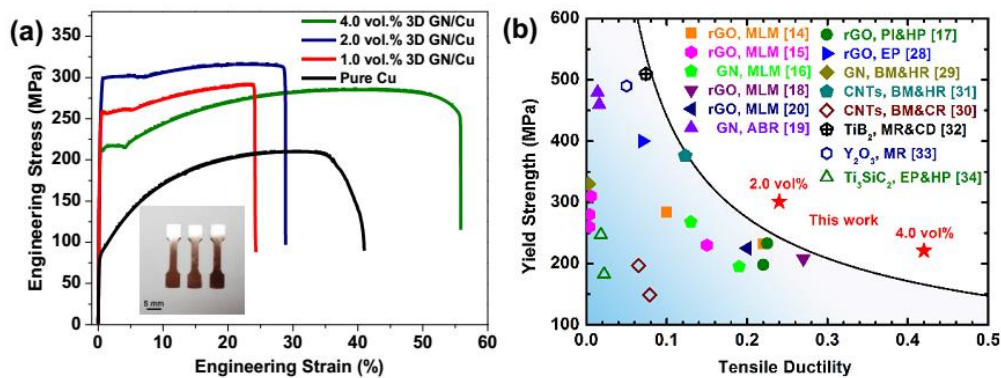


Figure 4. a) Engineering stress-strain curves for 3D GN/Cu composites and pure Cu. b) Yield strength versus total tensile elongation of Cu matrix composites in comparison with available literature data.

Toughness, defined as a material's resistance to fracture, is often related and measured as the released energy needed to cause fracture.⁴¹ In this study, the measured modulus of toughness is a compromise which combines both strength and ductility. The outstanding toughness modulus measured for 4.0 vol. % 3D GN/Cu could be explained from both the intrinsic and extrinsic aspects. Basically, intrinsic toughening is associated with the deformation of matrix grain to resist crack initiation. The 3D graphene-like networks synthesised in this work have a totally different microstructure from the commonly used graphene derivatives such as in other reported work.⁸⁻²⁰ The construction of 3D stereoscopic structure based on two dimensional building blocks of graphene walls makes an enlarged interaction zone between the reinforcement and the matrix; furthermore, an "interlocking" effect could be realized. That is, the 3D GNs are encapsulated by the Cu matrix while grain growth of the Cu matrix grains around are restricted by 3D GNs. Experimentally, we observed the discontinuous 3D GN in the bulk composites by etching the polished surface. When loaded, the matrix grains in the interaction zones deformed differently from the outside matrix grains.³⁶ Specifically, the coarse grains outside form an enlarged plastic zone resist the crack initiating in the rigid interaction zone; Extrinsic toughening, involving such processes as crack bridging which is the prime extrinsic toughening mechanisms,⁴¹ mainly focuses on the resistance of crack propagation. We consider that the superior tensile ductility in this work is chiefly expected from the 3D graphene-like network structure and the strong interfacial strength between 3D GN and metal matrix. In order to verify this, *in-situ* tensile test in TEM were performed on the composites and pure Cu, with the results shown in Figure 9, and Video S1-S3. According to the comparison between them, graphene-like nanosheet bridging and rupture are very prevalent in the composites during the *in-situ* tensile testing process. As can be clearly observed

in Video S1-S2, the crack propagations were highly blocked by the graphene-like nanosheet bridging (see Figure 9a-d and), which can effectively restrain the final fracture of the samples and thus remarkably enhance the ductility of the composites. After further loading, the graphene-like nanosheets were broken, leaving a serrated fracture surface behind, as shown in Figure 9c. In contrast, without the obstruction of 3D GN, it was shown that as soon as a crack was initiated in the pure Cu, it propagated very rapidly with little resistance, resulting in a relatively flat fracture surface behind, as shown in Figure 9f. This result certainly reveals the very strong interfacial bonding between 3D GN and metal matrix, which can effectively hinder the crack propagation and final fracture of the composite, and thus

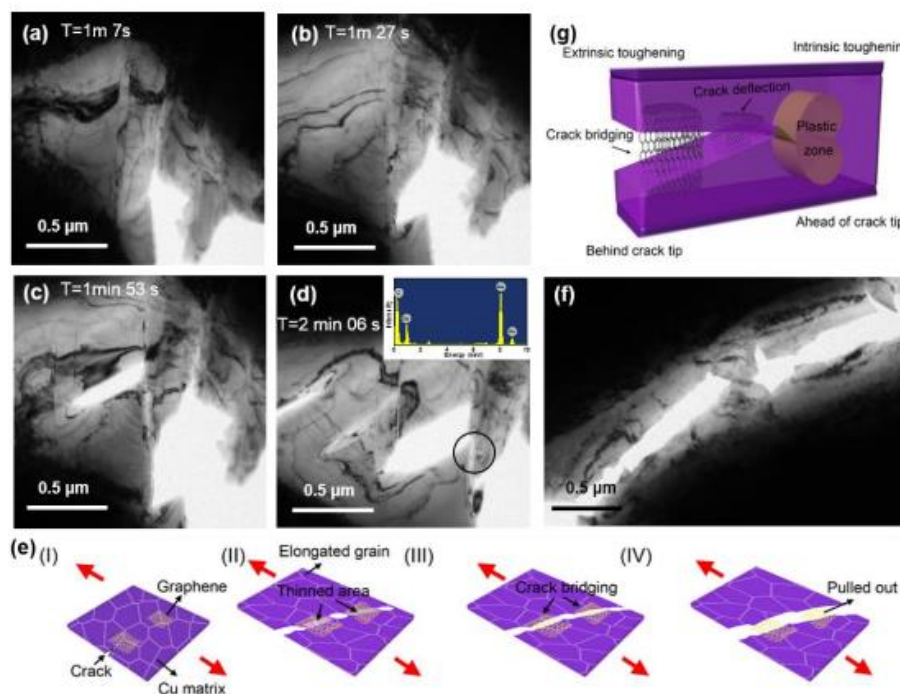


Figure 5. (a-d) Screenshots of *in-situ* TEM tensile test of 3D GN/Cu bulk composites with 4.0 vol% GN (Video S1), showing the hindrance on crack propagation and final fracture of the Cu matrix by the GN dispersed in the Cu grain. Inset of (d) EDS spectrum of the area indicated with black circle. (e) Schematic illustration of the observed crack bridging effect of GN. (f) A typical TEM image of pure Cu after *in-situ* TEM tensile test. (g) Schematic illustration of the toughening mechanism of GN in Cu matrix.

3 CONCLUSION

In summary, we have successfully manufactured metal matrix composites reinforced with 3D discontinuous graphene-like network, via an *in-situ* synthesis strategy, which enables the robust interfacial bonding between graphene-like nanosheets and metal as well as ensures the excellent structural retention of 3D graphene-like network structure throughout the composites. As a result, the fabricated 3D GN/Cu composites demonstrate both high strength and ductility. The yield strength and the elongation to failure of the 4.0 vol% 3D GN/Cu composite are 221 MPa and 53.8%, respectively, which are ~126% and ~41% higher than that of unreinforced Cu matrix. Furthermore, this unique strategy may be extended to other reducible metals (such as Co and Ni) for fabricating 3D GN-strengthened metal matrix composites to elevate strength and ductility.

4 ACKNOWLEDGEMENT

We thank Prof. Ju Li for meaningful suggestions. The authors also gratefully acknowledge the financial support by the National Natural Science Foundation of China (No. 51422104, No. 51472177,

No. 51531004) and Foundation for the Author of National Excellent Doctoral Dissertation of China (No. 201145), and Program for New Century Excellent Talents in University (NCET-12-0408).

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