Effect of particle size on the formation of the composite structure in Ni-graphene system: atomistic simulation

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Abstract. Fabrication of Ni-graphene composite with the nanoparticles of different sizes by hydrostatic pressure at 1500 K is studied by molecular dynamics simulation. The high specific surface area of crumpled graphene allow to fill its pores by metal nanoparticles and obtain composite structure at given conditions. It is observed, that temperature exceeding melting temperature of Ni nanoparticles but considerably lower than the melting temperature of graphene lead to better mixing of the structural elements. It is found, that one of the main factors in the composite fabrication is nanoparticle size. Bigger nanoparticles fully covered by graphene flakes even at high temperatures preserve its spherical shape and retard the obtaining of the composite structure. Nanoparticles of small and average size demonstrate the much better formation of the composite.

1. Introduction

Crumpled graphene, a porous structure composed of crumpled graphene flakes/sheets connected by weak van-der-Waals bonding, attained considerable attention because of its possible application for supercapacitors, electrodes, electrochemical energy storage, composites with enhanced mechanical properties [1, 2, 3, 4, 5], to name a few. Various methods to obtain crumpled graphene were developed during the last decade [6, 7]. Recently, a method of syntheses of porous crumpled graphene with hierarchical pore structure was developed which allow to control its properties and raise the utilization of pores [3].
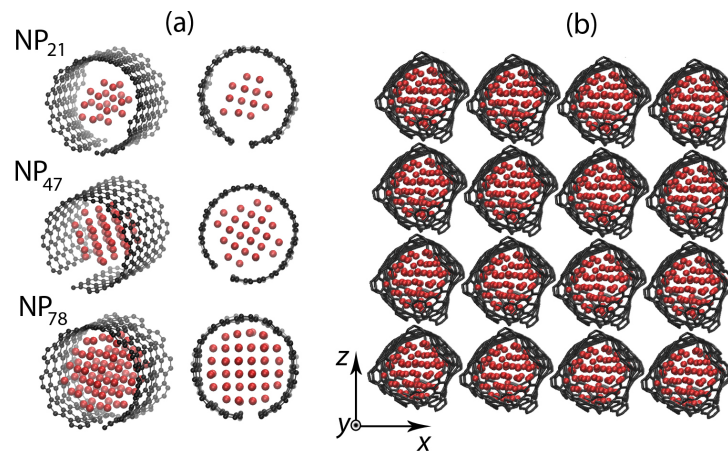
Since crumpled graphene has a high surface area-to-volume ratio, the metal inclusions can be dispersed as nanoparticles into graphene matrix to obtain a composite structure. Such combination might enhance the functional properties of components, and create a composite with much better functionality. Metal nanoparticles itself is of great interest nowadays [8, 9, 10], but recent studies have shown that the combination of graphene with metals can enhance mechanical properties of the resulting structure [11]. For example, Ni nanoparticles (NPs) have attended considerable interest because of its important role in the fabrication of the composites being used in many industrial applications. Its outstanding wettability for graphite powders opens many prospects of the combination of Ni NPs with carbon structures [12]. Thus, investigation of such combined material as crumpled graphene with the pores filled by metal nanoparticles with the goal to enhance its mechanical properties is of great interest.

In the present work, the effect of the nanoparticle size on the formation of Ni-graphene composite is investigated by molecular dynamics simulation. Three different Ni NPs composed of 21, 47 and 78 atoms are considered. Mechanical properties of the obtained composites are tested after hydrostatic tension.

2. Simulation details

Nanoparticles of three sizes are considered: 21, 47 and 78 Ni atoms (see Fig. 1a). All the NPs are wrapped by graphene flake, cut from a small carbon nanotube. Size of the NP is chosen to obtain a structure with biggest NP_{78} totally covered by GF and smallest NP_{21} allowed to move inside GF. Then, GF with nanoparticles combined to 3D structure by rotation and repeating structural element four times along x, y, and z axes (see Fig. 1b). More details of the model are presented in [4].

Figure 1. (a) An example of nanoparticles of different sizes inside graphene flake in two projections. (b) Example of the simulation cell with Ni NP_{78} before hydrostatic compression. Ni atoms are shown by red and carbon atoms - by black color.
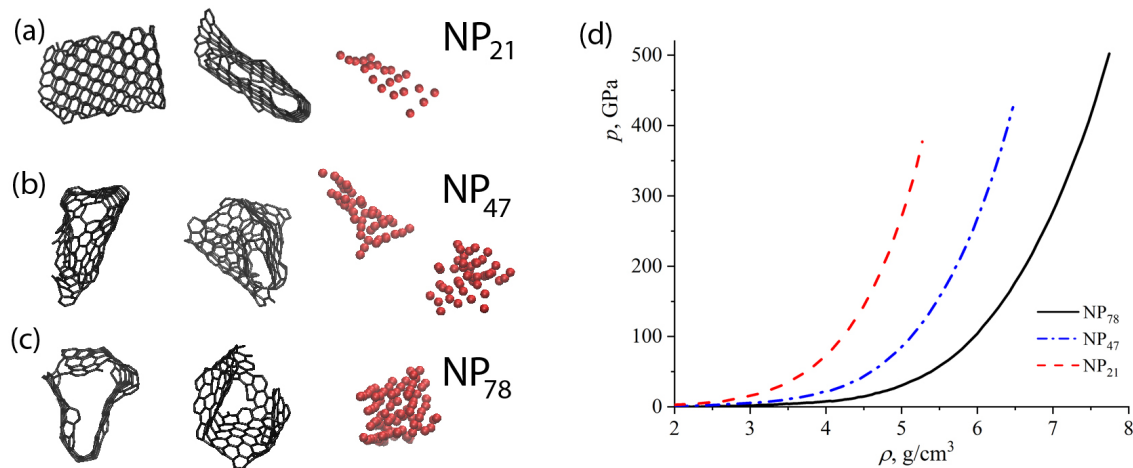
The composite structure is fabricated by the application of hydrostatic compression (HC) to the initial simulation cell. Hydrostatic compression can be conducted at zero or room temperature, but to facilitate the formation of new bonds, HC is conducted at 1500 K. At this temperature, Ni NPs will be melted [4], while graphene is far from melting temperature [13], but new covalent bonds will appear due to the thermal fluctuations. To study the mechanical response of the final composite structure, hydrostatic tension is applied.

Simulations are performed using the large-scale atomic/molecular massively parallel simulator package. The adaptive intermolecular reactive empirical bond order potential (AIREBO) [14] is used to describe the interatomic interactions between carbon atoms, which include both covalent in the basal plane of graphene and van-der-Waals interactions between GFs. Previously, AIREBO potential was repeatedly used for simulation of crumpled graphene [15, 16, 17, 18, 19, 20, 21, 22, 4]. To describe interatomic interaction Ni-Ni and Ni-C, Morse interatomic potential is used with parameters D_e=0.4205 eV, R_e=2.78 Å and β=1.4199 1/Å for Ni-Ni [23]; and D_e=0.433 eV, R_e=2.316 Å and β=3.244 1/Å for Ni-C obtained by *ab-initio* simulations [24, 25].

3. Results and discussion

In Fig. 2a-c examples of structural elements after HC at 1500 K is presented. Flakes and nanoparticles are shown separately for clarity. As can be seen, all NPs are melted during

compression. Corresponding stress-density curves are presented in Fig. 2d. NP_{21} easily melt and spread over graphene plane. Immediate folding of GF took place with the formation of rigid structure: such structural state of graphene is stable, the formation of covalent bonds on the edges of GF is observed. Typical snapshots of GFs and NP is shown in Fig. 2a. These planar graphene flakes filled with Ni atoms can be easily rotated and packed more closely to each other in the 3D structure. Final density after compression to $\varepsilon=0.3$ is the lowest and equal to about 5 g/cm^3 at lowest required stresses.
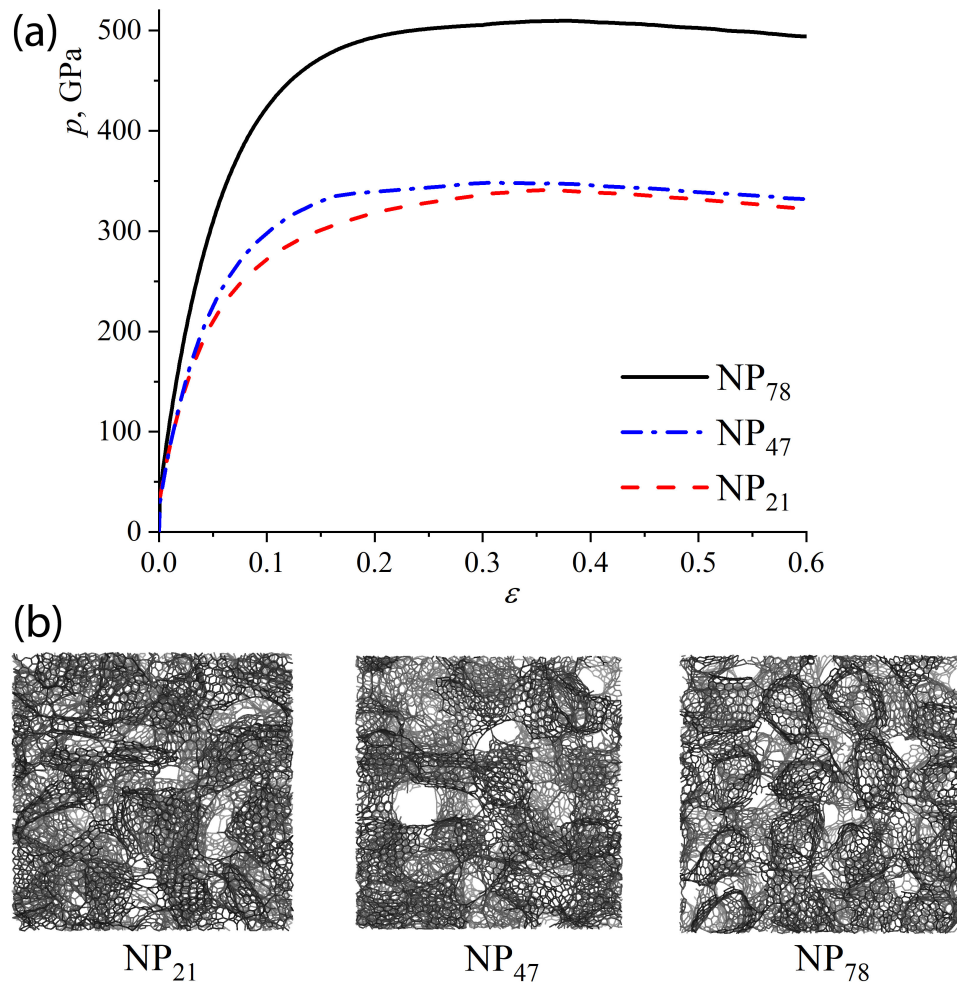

Figure 2. (a-c) Examples of graphene flakes and nanoparticles during hydrostatic compression at 1500 K. (d) Stress–density curves after hydrostatic compression at 1500 K.

In case with NP_{47}, several types of structural configurations are found: planar and spherical-like. Typical snapshots of flakes and NP is presented in Fig. 2b. This structure can be compressed to 6.45 g/cm^3 and can be considered as the intermediate case between NP_{21} and NP_{78}. From one hand, some flakes considerably crumpled which made the formation of the composite easier, from the other hand, some NPs preserve its shape due to the corresponding crumpling of GF.

The highest density is achieved for structure with NP_{78} due to the high density of metal particles. The dominant shape of NP is preserved: at the very beginning of compression process, before melting of NPs, GFs cover nanoparticle inside and form spherical structural element. When melting starts, the shape of NP has slightly changed forced by edges of graphene flake. Finally, composite with NP_{78} composed of rigid, almost spherical structural elements.

In Fig. 3 stress-strain curves at hydrostatic tension is presented. It should be noted, that hydrostatic tension is conducted at 0 K. As it can be seen, curves for the structures with NP_{21} and NP_{34} close to each other. Maximum stress value is 300 GPa, while for NP_{78} maximal stress is almost two times bigger. From the snapshots, can be seen that for NP_{78} nanoparticles covered by GF and during tension can be easily separated from each other like rigid spheres. Large pores appear over the whole structure uniformly.

For composite with NP_{21}, Ni atoms freely spread inside the pores and not retard the interaction between separate graphene flakes which results in the formation of the composite structure. The intermediate case of NP_{47} shows the same mechanical behavior (same stresses) but much more pores can be observed at tension $\varepsilon=0.6$. Thus, for obtaining a good composite better to chose small nanoparticles which will be better spread in the structure. However, the search for the equilibrium size of nanoparticles between 21 and 47 Ni atoms can show when better mechanical properties can be achieved.

Figure 3. (a) Stress–strain curves after hydrostatic tension. (b) Snapshots of the structure at tension $\varepsilon=0.6$. Only carbon atoms are shown.

4. Conclusions

In summary, the fabrication of the composite on the basis of crumpled graphene and Ni nanoparticles and its final mechanical response is investigated by molecular dynamics. The composite structure was obtained by hydrostatic compression at high temperatures of 1500 K which allow to melt the nanoparticles and facilitate the bond breaking and formation in graphene between neighboring flakes. The main factor under consideration is the size of nanoparticles inside pores of crumpled graphene. For a structure with big nanoparticles (NP_{78}), GF fully cover the metal nanoparticle which results in much more difficulties in the formation of chemical bonds between neighboring flakes than for structure with smallest NP_{21}. Small nanoparticles spread over the crumpled graphene flakes and in its pores which lead to the better mixing of the structural elements.

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6. References

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