

Review

A Review on the Development of Adding Graphene to Sn-Based Lead-Free Solder

Yilin Li ^{1,†}, Shuyuan Yu ^{2,†}, Liangwei Li ¹, Shijie Song ¹, Weiou Qin ¹, Da Qi ¹, Wenchao Yang ^{1,*} 
and Yongzhong Zhan ^{1,*}

- ¹ State Key Laboratory of Featured Metal Materials and Life-Cycle Safety for Composite Structures, MOE Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, School of Resources, Environment and Materials, Guangxi University, Nanning 530004, China; ly1001020@163.com (Y.L.); llw2534632267@163.com (L.L.); songshijie200010@163.com (S.S.); 18775837632@163.com (W.Q.); qdksyjs2020@163.com (D.Q.)
- ² Shenzhen Customs Industrial Products Testing Technology Center, Shenzhen 518067, China; szciqysy@126.com
- * Correspondence: wcyang@gxu.edu.cn (W.Y.); zyzmatres@163.com (Y.Z.)
- † These authors contributed equally to this work.

Abstract: In the electronics industry, graphene is applied with modified lead-free solder. This review presents advances in the preparation, strengthening mechanisms, and property characterization of graphene composite solders. Graphene composite solders are divided into two main categories: unmodified graphene and metal-particle-modified graphene. The unmodified graphene composite solders are classified according to the different solder systems. Metal-particle-modified graphene composite solders are classified according to different metal particles. However, there are still challenges with graphene composite solders. The main challenge is the poor bonding of graphene to the substrate and the nonuniform dispersion. Future directions for the development of graphene composite solders are proposed. They can provide some reference for the development of new graphene composite solders in the future.

Keywords: graphene; lead-free solder; particle reinforcement; composite solder; strengthening mechanisms; preparation method



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1. Introduction

With the rapid development of the electronics industry, solders have been further used in electronic devices. The Sn–Pb solder has been used on a large scale due to its excellent wettability and outstanding mechanical properties. Sn–Pb solder is used in the electronics industry to connect electronic components to the substrate and ensure electronic devices' proper functioning [1,2]. However, the toxicity of Pb endangers human health and the ecological environment [3]. Therefore, researchers have developed new Sn-based lead-free solders to replace traditional Sn–Pb solders [4]. Currently, developed lead-free solders are mainly Sn-based lead-free solders [5]. The main solder systems included are Sn–Cu [6], Sn–Ag [7], Sn–Zn [8], Sn–Ag–Cu [9], Sn–Bi [10], etc. The current demand in the electronics industry is for versatility and portability. Therefore, no Sn-based lead-free solder can perfectly replace the traditional Sn–Pb solder [11].

Numerous researchers have improved the performance of Sn-based lead-free solders by adding nanoparticles to the solder matrix or through alloying [12]. Various types of nanoparticles are used to modify lead-free solders, including metals particles (such as Al, Co, Ni, Mo, etc.) [13–15] and nonmetals (such as ZrO₂, carbon nanotubes, graphene, SiC) [16–19]. Graphene is a two-dimensional carbon material with outstanding electrical and thermal conductivity and a high surface area. It has been the most researched material in the last decade and is used in various fields [20]. Graphene has also been used to modify

existing Sn-based lead-free solder alloys. There are two types of graphene-enhanced lead-free solder: unmodified graphene-enhanced lead-free solder and solder that has been treated with metal particles. In the initial exploration, graphene was added to the solder matrix as a reinforcing phase [21,22]. Although the performance of the composite solder has been improved to some extent, there are still some challenges [23]. For example, graphene is prone to agglomeration and has poor bonding strength with the solder matrix. To overcome these difficulties, researchers have modified graphene before adding it to the solder matrix. The Performance comparison of major lead-free solders are shown in Table 1.

Table 1. Performance comparison of major lead-free solders.

Type	System	Eutectic Temperature (°C)	Eutectic Composition (wt.%)	Characteristics	References
Binary	Sn–In	120	Sn–51In	Good wettability Low melting point, poor plasticity, high cost	[24]
	Sn–Bi	138	Sn–57Bi	High mobility Poor processability and low ductility	[25,26]
	Sn–Pb	183	Sn–37Pb	Good overall performance Tissue is easy to coarsen, easy to creep	[27]
	Sn–Zn	198	Sn–9Zn	High intensity, resourceful Easy to oxidize, poor wettability	[28]
	Sn–Ag	221	Sn–3.5Ag	High strength, creep resistance High melting point and high cost	[29]
Ternary	Sn–Cu	227	Sn–0.7Cu	High strength, creep resistant, resourceful The melting point is too high	[6]
	Sn–Ag–Cu	217	Sn–3.5Ag–0.9Cu	High strength and creep resistance Higher cost	[9]
Adding granules	Ag, Al, Ga, Sb, carbon nanotubes, boron nitride nanotubes, graphene nanosheets (GNSs)	-	-	Improving the melting point of lead-free solders Improvement of mechanical properties of lead-free solders	[11,30,31]

Graphene has been widely used in the field of Sn-based lead-free solder. It is added to different systems of Sn-based lead-free solder to improve performance. Therefore, it is necessary to summarize the effects of graphene addition on different Sn-based solder systems. It is also discussed regarding the preparation process, research status, and future development, which is much needed. There are currently reviews on the application of graphene in Sn-based lead-free solders. It is discussed by classifying graphene in the class of nanoparticles or carbon nanomaterials. However, there is a gap in the reviews that separately present the application of graphene in different systems of Sn-based lead-free solders.

This paper aims to help provide direction for the further development of graphene composite solders. The microstructure, mechanism of improvement, and preparation technique of graphene composite solders are initially covered in this paper. Afterward, graphene is divided into unmodified and metal-particle-modified graphene for review. The effect of adding unmodified graphene on the performance of lead-free solders in different systems is discussed according to the different classifications of solder systems. According to the type of metal particles, the effect of adding different metal particles to modify graphene on the performance

of lead-free solders is discussed. Future research prospects for graphene-reinforced Sn-based composite solders are covered in the last section. This study aims to establish a theoretical foundation for creating high-performance graphene composite solders. It is envisaged that this research would help further graphene's use in solders.

2. Structure and Properties of Graphene

Graphene has numerous excellent properties. Therefore, graphene has been widely used in various fields. This section will focus on the structure of graphene and the performance characteristics of graphene.

2.1. Structure of Graphene

British scientists Geim et al. [32] discovered graphene in 2004. Graphene is a single-atom, two-dimensional crystal formed by the sp^2 hybridization linkage of carbon atoms. It is the most desirable two-dimensional material and the hardest nanomaterial ever discovered. Graphene is an isomer of carbon with a thickness of <0.35 nm. It is an advanced two-dimensional material with a hexagonal atomic structure with one carbon atom at each vertex [33]. Graphene exhibits nonpolar properties, and nonpolar dehydroformer acids with aromatic rings can provide good wettability on graphene through nonpolar interactions on the surface [34]. SEM images of graphene bonding properties and monolayer graphene are shown in Figure 1 [35]. The different forms of graphene are shown in Figure 2 [35].

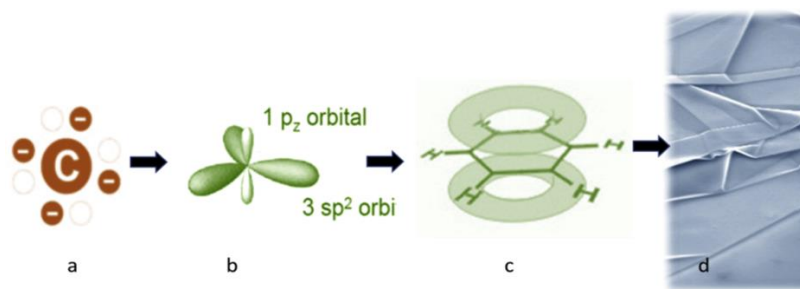


Figure 1. (a–c) Fundamental aspect of graphene bonding properties and (d) SEM image of single-layer graphene. Reprinted from Ref. [35].

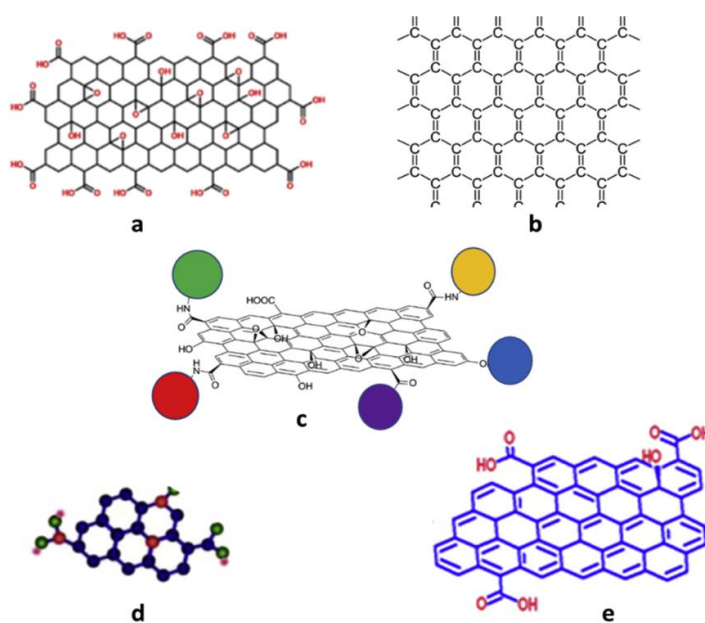


Figure 2. Different forms of graphene: (a) graphene oxide, (b) pristine graphene, (c) functionalized graphene, (d) graphene quantum dot, and (e) reduced graphene oxide. Reprinted from Ref. [35].

2.2. Properties of Graphene

Graphene exhibits good mechanical properties, a large specific surface area, a low coefficient of thermal expansion, and a low density. It has an electron mobility of over $15,000 \text{ cm}^2/\text{V}$ and a thermal conductivity of 5300 W/mK [36]. Detecting the physical properties of graphene is generally predicted using the Tersoff–Brenner potential function. Tsai and Tu used molecular dynamics simulations to predict the mechanical properties of monolayer graphite. The study results showed that the elastic modulus of graphene was determined to be 0.912 TPa [37]. Zheng et al. [38] successfully determined the elastic modulus of 1.086 TPa for armchair graphene and 1.05 TPa for herringbone graphene by combining quantum mechanical methods.

Lee [39] and his colleagues used the nanoindentation technique of atomic force microscopy (AFM). The Young's modulus of monolayer graphene was found to be 1.02 TPa , and the tensile strength was 130 GPa . Lee et al. [40] found that the Young's modulus of bilayer graphene and trilayer graphene was 1.04 and 0.98 TPa , respectively. The tensile strengths of bilayer graphene and trilayer graphene were 126 and 101 GPa , respectively. Lin et al. [41] prepared large-sized graphene oxide flakes (average area of 272.2 mm^2) by centrifugation and obtained an optimum elastic modulus of 13.5 GPa .

Baladin et al. [42,43] measured the thermal conductivity (K) of mechanically cleaved single-layer graphene (SLG) at $4840\text{--}5300 \text{ W/(mK)}$ using confocal micro-Raman spectroscopy at room temperature. Ruoff's team [44] measured monolayer graphene supported on an amorphous silicon substrate by measuring it at room temperature, determining the K value to be 600 W/(mK) . Schwamb et al. [45] determined the K values of thermally reduced graphene oxide (GO) flakes to be $0.14\text{--}2.87 \text{ W/(mK)}$.

Graphene is the most well-known frontier and hot area in global materials because of its exceptional qualities. New lead-free solder alloys are being developed to improve the performance of conventional lead-free solder alloys and discover a new lead-free solder material that can perfectly replace the traditional Sn–Pb solder. Researchers attempt to add graphene to lead-free solder matrixes to improve lead-free solders.

3. Reinforcement Mechanism

The strengthening mechanism of graphene-enhanced lead-free solder is particle strengthening. Particle reinforcement is the addition of second-phase reinforcing particles (metal nanoparticles, metal oxide particles, GNS, carbon nanotubes, etc.) to the lead-free solder matrix [46,47]. The modification of the solder attempts to improve its mechanical properties and microstructure, thus improving its joint reliability [23]. It has also been reported that the improved performance of graphene composite solder is due to fine crystal strengthening [48].

Tsao et al. [49] successfully added TiO_2 nanoparticles to Sn–0.7Cu solder by a mechanical mixing method. The addition of TiO_2 nanoparticles was found to refine the microstructure of the solder. Mechanical properties increased with the increase in TiO_2 nanoparticle content. However, the addition of excessive TiO_2 nanoparticles caused the mechanical properties of the composite solder to start decreasing. Zhao et al. [50] investigated the relationship between the effect of adding Fe_2O_3 nanoparticles of different sizes on wettability and wetting time. The smaller the size of the nanoparticles, the better the improvement in wettability.

Zhong's team [51] found that with the increase in the content of nano- Al_2O_3 particles, the β -Sn grains kept refining, which inhibited the growth of Cu_6Sn_5 . The best tensile strength of the composites was achieved when the content of added Al_2O_3 nanoparticles was $1.5 \text{ wt.}\%$. However, as the Al_2O_3 nanoparticles continued to increase, the nanoparticles started to aggregate. This resulted in the coarsening of the matrix grains and a significant decrease in tensile strength.

Solder wettability can be improved by adding second-phase strengthening particles. It is because these particles tend to concentrate only on the surface of the solder when they are added. This results in a decrease in surface tension, an increase in fluidity, and

an increase in wettability. The wettability decreases when the second-phase reinforcing particles are not evenly distributed throughout the solder matrix. The particle size of the added second-phase reinforcement also affects the wettability of the lead-free solder.

4. Composite Solder Preparation

Regarding the preparation methods of graphene composite solder, they can be divided into two main categories. One method is to anchor graphene to a welded substrate. The other one is the method used to modify graphene with metal particles. This subsection will focus on several preparation methods that are more commonly used today.

4.1. Composite Solder Preparation Method

Currently, the primary method of preparing reinforced composite solder is to add the reinforcing-phase particles to the lead-free solder matrix. The current methods of preparing composite solder are the mechanical mixing method, in situ generation method, fusion casting method, etc. [52–55].

4.1.1. Mechanical Mixing Method

The mechanical mixing method is to distribute graphene in the matrix by mechanical stirring. This method is easy to operate and low cost, but some of the powder will be oxidized under high-speed ball milling. Nai et al. [52] successfully dispersed Ag–GNSs into a Sn–Ag–Cu solder matrix by ball milling and mechanical stirring. Finally, the composite solder was successfully produced by hot-pressure sintering. Sayyadi's [56] team successfully prepared graphene composite solder by powder metallurgy and mechanical mixing methods. The mechanical mixing method to prepare the composite solder is shown in Figure 3.

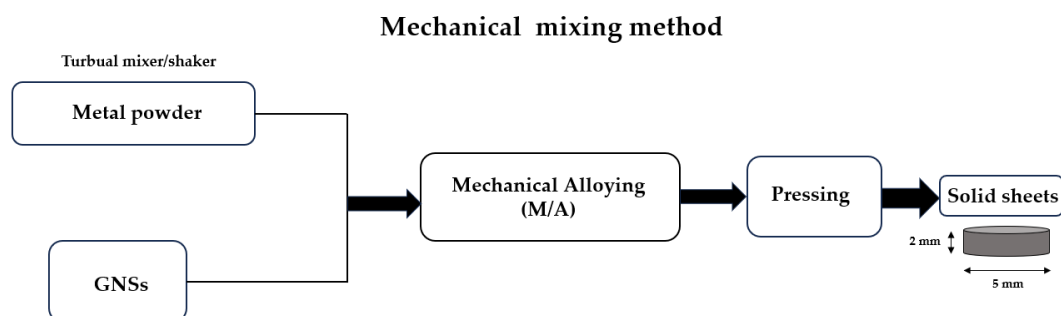


Figure 3. Mechanical mixing method process diagram.

4.1.2. In Situ Generation Method

The nano-enhanced phase in the in situ generation method is formed automatically during the manufacturing process of the solder. Two types of methods can be used at production sites. The first method is reinforcing solder materials with intermetallic compound nanoparticles by hot-rolling extrusion. Shen et al. [53] also developed an in situ synthesis method for nanocomposite solders using a rapid solidification technique. This method allows the production of composites with finely dispersed reinforcing phases to obtain better mechanical properties, avoiding interfacial defects in the preparation of conventional composites [54].

4.1.3. Casting Method

The melt casting method is a process of ball milling graphene and solder, i.e., ball milling followed by tablet pressing. The final crucible is melted to obtain the graphene composite solder. Yang et al. [55] successfully prepared Sn–20Bi–GNSs by the fusion casting method.

4.2. Metal-Particle-Modified Graphene Preparation

This subsection focuses on the preparation of four metal-particle-modified graphene methods: powder metallurgy, electrochemical deposition, chemical plating, and self-assembly. Moreover, the characteristics of these various methods are summarized at the end of this section.

4.2.1. Powder Metallurgy Method

The powder metallurgy method involves preparing metal powder using high-temperature and high-pressure methods. Firstly, the metal powder is mixed with the prepared graphene solution. Through ultrasonic shaking, graphene is uniformly dispersed in the solution, after which the composite powder is left to dry. After the mixing, the powder is placed in a vacuum hot-pressure sintering furnace to prepare the metal-particle-modified graphene composites under high temperature and pressure. Crucial to the preparation of composites is the homogeneous mixing of graphene and metal particles in the powder mixing process. Conventional powder metallurgy often uses a ball milling process for powder mixing. Mechanical collision during the mixing process will destroy the structural integrity of graphene and lead to increased defects. Because graphene itself is a two-dimensional material with a large specific surface area, it is accessible to agglomerate during the ball milling process. The schematic diagram of the powder metallurgy method is shown in Figure 4 [57].

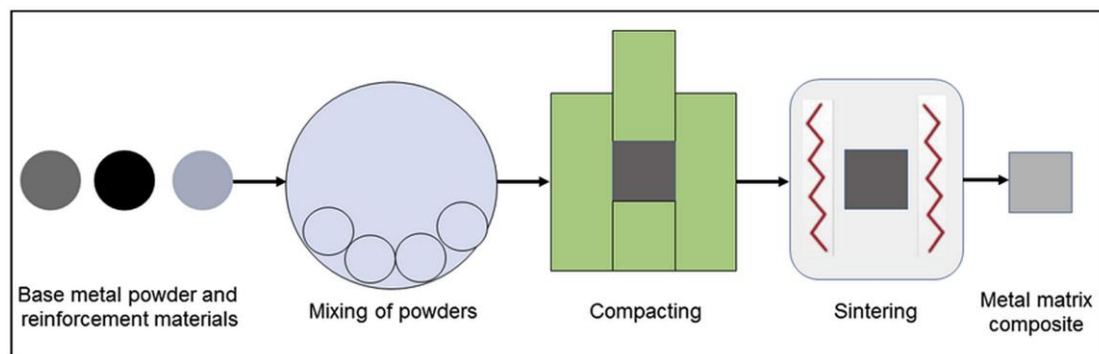


Figure 4. Schematic diagram of the powder metallurgy method. Reprinted from Ref. [57].

4.2.2. Electrochemical Deposition Method

Electrochemical deposition is a processing method. Positive metal ions in the electroplating solution receive electrons by introducing an external electric field. A coating is formed on the surface of the cathode substrate [58]. The advantage of the electrochemical deposition method is that the reaction rate can be controlled by adjusting parameters such as electrolyte formulation and supply voltage. Different combinations of properties are obtained by adjusting the parameters of the composite preparation. At the same time, the graphene in the solution is uniformly adsorbed with the metal particles, effectively avoiding the agglomeration phenomenon. Composites prepared by electrochemical deposition techniques can also improve the wear and corrosion resistance of the material. The electrochemical precipitation method is shown in Figure 5.

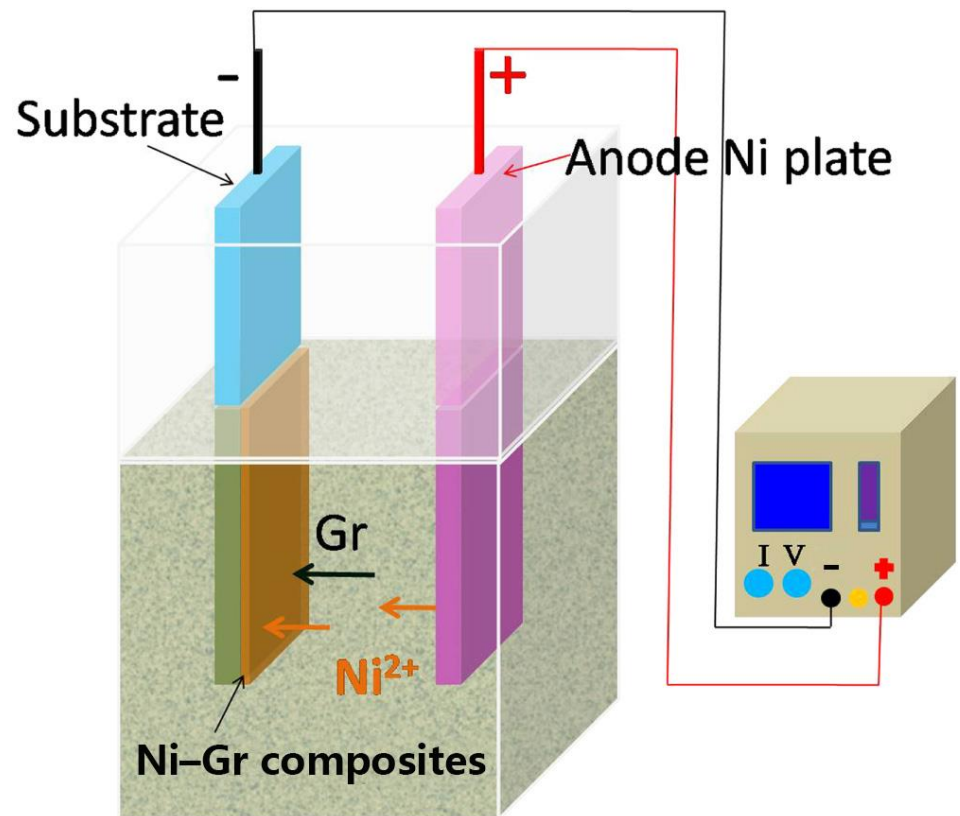


Figure 5. Schematic of the plating process: the graphene layers (Gr) and Ni^{2+} in the plating solution are co-deposited on the steel substrate to form Ni-Gr composites. Reprinted with permission from Ref. [59]. 2015, IOP Publishing Ltd.

4.2.3. Chemical Plating

The chemical plating technique refers to the absence of an electric current. With the help of a suitable reducing agent, the metal ions in the chemical plating solution are reduced to metal and deposited onto the graphene surface. Chemical plating technology is a deposition process that produces metals through controlled redox reactions under the catalytic action of metals. Due to its characteristics of low waste emissions, low environmental pollution, and low cost, in many fields, chemical plating technology has gradually replaced electroplating as an environmentally friendly surface treatment process. A schematic diagram of the electroplating method is shown in Figure 6 [60].

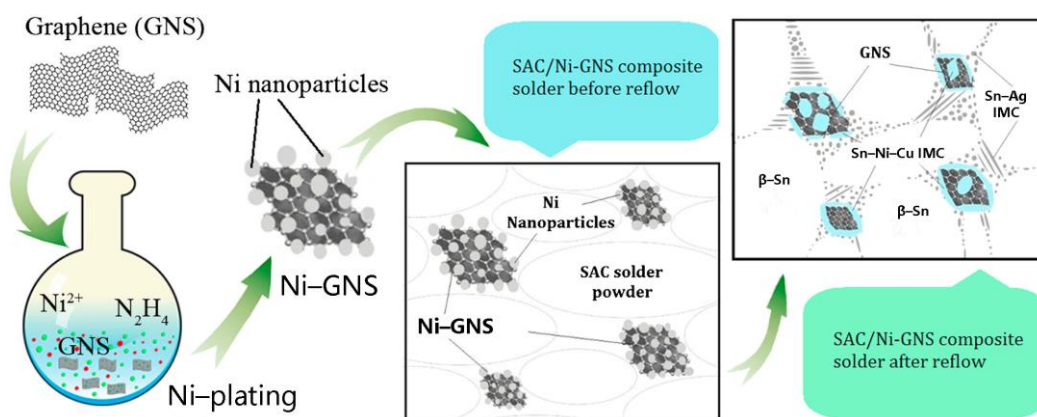


Figure 6. Schematic diagram of the chemical plating method. Reprinted with permission from Ref. [60]. 2016, Elsevier Science & Technology Journals.

4.2.4. Self-Assembly Method

By the self-assembly method, an aqueous solution of GO is mixed with metal particles. Metal particles are bound to GO through covalent or noncovalent bonds. The advantages include simple and controllable particle size, loading, and uniform distribution. Wang et al. [61] successfully anchored Ni particles to GNSs using a self-assembly method. A flow chart of the self-assembly method is shown in Figure 7.

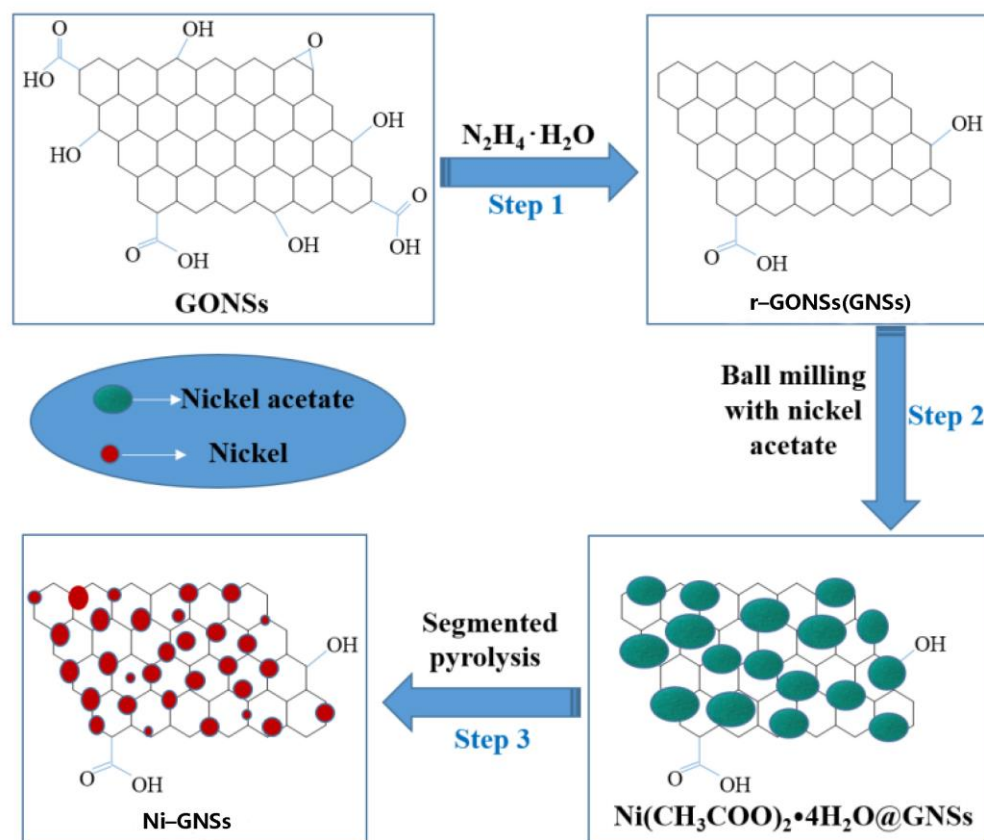


Figure 7. Self-assembly method flow diagram. Reprinted from Ref. [61].

According to the composite solder preparation methods listed in this subsection, different preparation methods have advantages. The comparison of the technical characteristics of different preparation methods for composite solders is shown in Table 2. So, when choosing a compound solder preparation method, it is important to choose according to your needs, considering environmental pollution, cost, process technology, operating body, and other issues to choose the most suitable process.

Table 2. Comparison of the technical characteristics of different preparation methods for composite solders.

Preparation Method	Technical Features	References
Powder metallurgy Method	The process technology is more mature, simple to operate, and low cost, but the densification could be better, and the porosity is high.	[62]
Electrochemical deposition method	The reaction process can be controlled, effectively avoiding the problem of high-temperature grain growth in the chemical vapor deposition method, but the process is more complicated.	[63]
Chemical plating	Graphene and metal particles can form a solid interfacial bond, and the metal coating can effectively avoid graphene shedding during the wear process.	[64]
Self-assembly method	Simple and controllable particle size, loading, and highly uniform distribution.	[62]

5. Graphene-Enhanced Sn-Based Lead-Free Solder

Graphene-enhanced tin-based lead-free solders are currently concentrated in several systems, including Sn–Ag–Cu, Sn–Bi, Sn–Cu, and Sn–Ag. This subsection will be classified according to lead-free solder systems. The effects of graphene addition on different systems of lead-free solders are presented.

5.1. Sn–Ag–Cu (SAC) Composite Solder

The SAC solder system is the most commonly used lead-free alloy system in electronic soldering. SAC solder is now widely used to replace the traditional eutectic Sn–37Pb solder alloy in circuit board assembly.

In the electronics packaging process, interfacial reactions occur. Intermetallic compounds (IMCs) are produced when molten metal comes into contact with copper substrates. The formation of IMCs has a significant impact on the reliability of the solder joint. Wettability and IMC formation are both driven by interfacial energy. As a result, the reaction generates an IMC layer, and free energy is reduced, favorable to improve wettability. However, the IMC layer is brittle, resulting in the IMC layer not being too thick [9]. Otherwise, the solder joint's shear strength and reliability impact is significantly reduced. Therefore, inhibiting the growth of intermetallic compounds becomes an essential means to improve the reliability of solder joints.

Flux has an impact on the growth of IMC layers. This is because of the reduction in oxides on the solder surface and the solder paste particles. This interaction can change the diffusion process during the formation of IMC layers. Flux activation occurs during heating, reducing viscosity and spreading around the pads [65]. Karel et al. [66] compared the effects of two fluxes on IMC layers. The main discussion is the effect of the type of solder resist layer on the relationship with the IMC. Comparing Figures 8 and 9, it can be seen that the thickness of the IMC layer increases by an average of 37% on the black samples (double roughness). This shows the influence of flux type on the IMC layer. Therefore, it is necessary to consider the influence of flux when considering the growth factors of IMC layers.

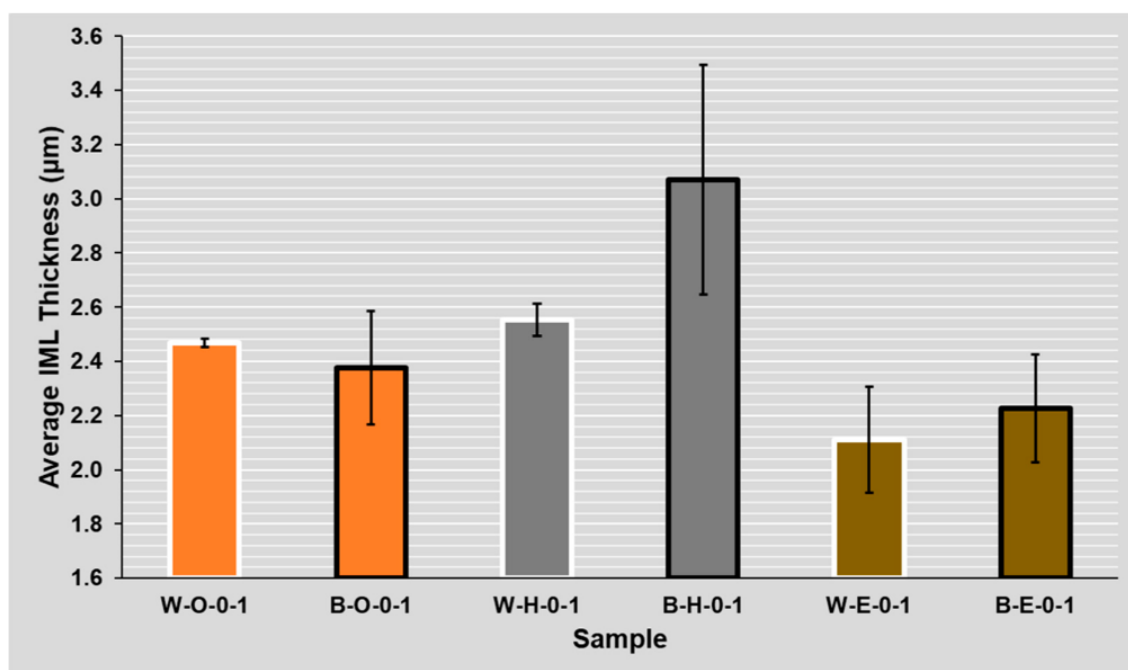


Figure 8. Solder mask influence on the average IMC thickness for samples with the ROL0 flux (Black/White)—(OSP, HASL, ENIG)—(ROL0, ROL1)—(1, 2 reflows). Reprinted from Ref. [66].

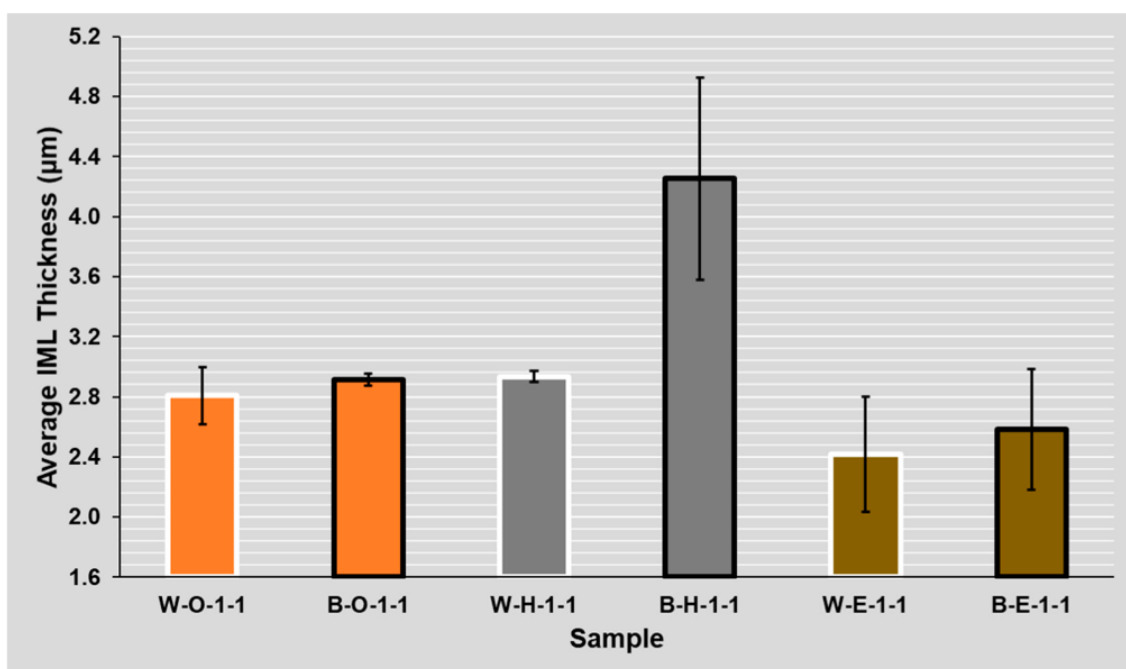


Figure 9. Solder mask influence on the average IMC thickness for samples with the ROL1 flux (Black/White)—(OSP, HASL, ENIG)—(ROL0, ROL1)—(1, 2 reflows). Reprinted from Ref. [66].

Huang and his coworkers [67] prepared SAC305–0.1GNSs samples by powder metallurgy and showed that adding graphene can effectively inhibit the growth of IMC layers. Two-dimensional graphene acts as a diffusion barrier between Cu and Sn atoms. The diffusion of Sn and Cu atoms is prevented, which inhibits IMC growth. GNSs do not create new materials when they interact with the solder substrate. Additionally, the produced composite solder junctions have a 30% higher shear strength than average.

Liu et al. [68] also showed that the addition of GNSs inhibited grain growth and obtained finer grains. During grain growth, thermodynamic resistance to IMC grain growth increases interfacial energy between the IMC grains and the substrate. On the other hand, the effective surface diffusion of IMC grains ensures their growth. Therefore, when IMC grains are in contact with the surface of GNSs, increased interfacial energy can enhance thermodynamic resistance to IMC grain growth.

During the soldering process, GNSs may be enriched at the solder/flux interface. The presence of GNSs reduces interfacial energy. As a result, the interfacial tension between the solder and flux is reduced, thus providing smaller contact angles and improved wetting of the solder substrate [69,70]. Adding GNSs to the solder matrix increases the material's ultimate tensile strength (UTS), and the ductility decreases by a small amount. The melting points of SAC solder and SAC–GNS composite solder were measured. When GNSs were added to the solder matrix, there was no significant change in the melting point of the solder. This is due to the alloy's melting point being a physical characteristic that is inherent to the alloy. Trace amounts of inert GNSs barely impact the melting point of nanocomposites. Additionally, the melting point of nanocrystalline alloys is slightly lower than that of bulk alloys. As a result, the melting point of SAC is not considerably impacted by the addition of GNSs.

Ibrahym's team [71] added 0.07 wt.% GNSs to the SAC solder and successfully prepared SAC305–0.07GNSs and studied the microstructure of the composite solder using the selective electrochemical etching technique; according to their report, it was shown that after electrochemical etching, GNSs in SAC305 existed in two forms: one way of existence was as fine agglomerates and the other was as large agglomerates at the solder–Cu interface on the solder's surface. The presence of large GNS agglomerates acts as a diffusion barrier and hinders the diffusion of Cu. According to the electrochemical dissolution mechanism,

the dissolution of SAC305–0.07GNSs occurs in IMCs only after the β -Sn is wholly removed, preferably using a voltage below -350 mV for electrochemical corrosion to avoid IMC dissolution. The cross-sectional microstructure of the composite solder after electrochemical corrosion is shown in Figure 10.

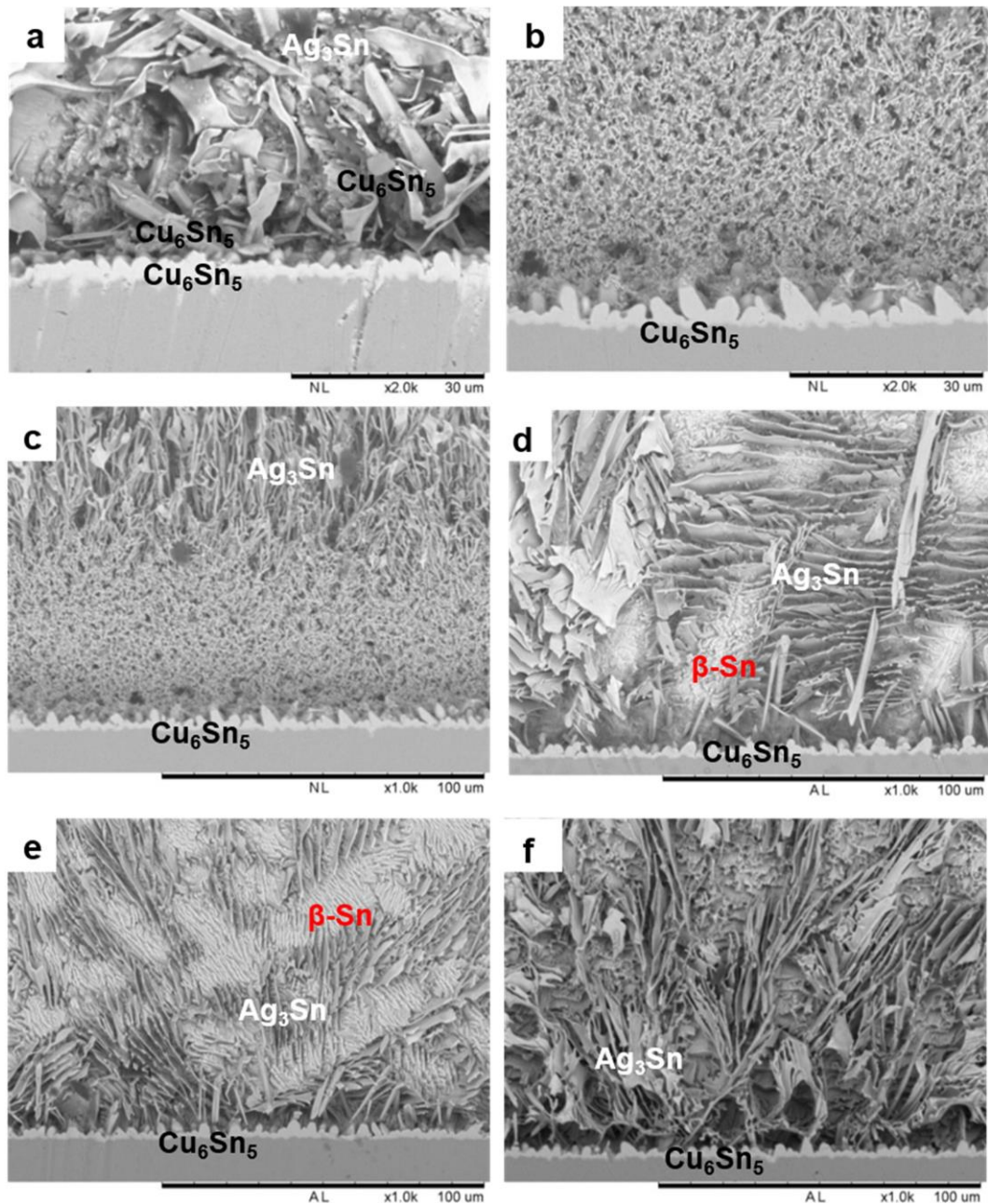


Figure 10. Cross-sectional microstructure of the (a) SAC305 solder and (b) SAC305/0.07GNSs composite solder after etching at -350 mV potential bias; cross-sectional microstructure of SAC305/0.07GNSs after etching at (c) -350 mV, (d) -440 mV, (e) -480 mV for 240 s, and (f) -480 mV for 480 s. Reprinted from Ref. [71].

5.2. Sn–Bi Composite Solder

The eutectic Sn58Bi solder alloy system has the advantage of a low melting point and high ultimate tensile strength [72,73]. Therefore, there is a lot of interest in this solder system. Many researchers are developing new Sn–Bi solder alloys in this field.

According to Yang's report [55], the thickness of the IMC layer at the interface decreased and then increased with the addition of GNSs. Figure 11 shows the thickness of the IMC layer at the Sn–20Bi–xGNS/Cu solder joint. Ma et al. [22] prepared Sn–58Bi–GNSs composite solders by the powder metallurgy method. It was found that the addition of GNSs could refine the grain size. The optimum addition amount given is 0.03 wt.%.

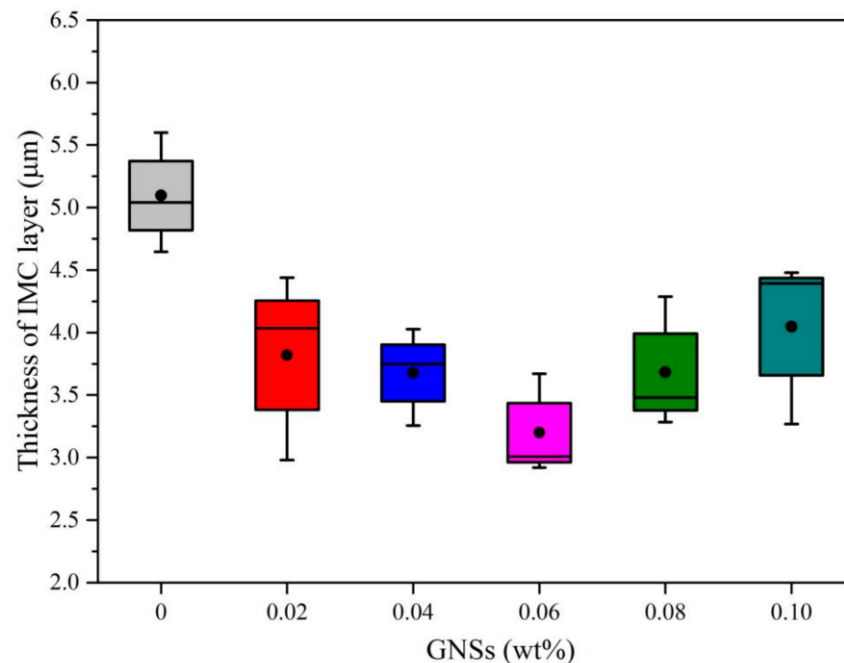


Figure 11. Thickness of the IMC layer at the Sn–20Bi–xGNS/Cu solder joint. Reprinted from Ref. [55].

In Ma's research [74], the mechanical characteristics of Sn58Bi0.7Zn–GNS solder joints were examined using the nanoindentation technique and finite element modeling. It was discovered that the improvement in the solder joints increased with the number of GNSs used. Still, after adding more than 0.1 wt.% of GNSs, the progress of the composite solder joints decreased significantly due to the mutual accumulation and slippage of GNSs. Adding GNSs improves the microstructure of the composite solder, resulting in increased tensile strength. The addition of GNSs to the Sn58Bi0.7Zn solder alloy can also serve to enhance corrosion resistance.

5.3. Sn–Cu Composite Solder

Sn–Cu lead-free solder systems are considered a viable alternative to Sn–Pb solder. This is because Sn–Cu solders offer low prices, high strength, ease of fabrication, and recycling, as well as the ability to avoid dissolution of the Cu base material in dip and wave soldering [75]. Lead-free Sn–Cu solder alloys have a very high melting point of 227 °C. However, the high temperature favors the diffusion of Sn and Cu atoms to produce IMCs [76]. The IMC layer influences solder joint reliability. Excessively thick IMC layers can cause solder joints to fracture in a brittle form. Moreover, due to the high Sn content of Sn–0.7Cu solder, whiskers are easily generated in the solder joint after soldering. As a result, it leads to less reliable solder joints.

At the same time, Sn–0.7Cu solder is more susceptible to galvanic corrosion due to the significant difference in potential between Sn and Cu [6]. Research on Sn–Cu lead-free solders has also increased domestically and internationally. However, its disadvantages must be overcome to achieve the replaceability of Sn–Cu lead-free solder, for example, high melting points, low mechanical properties, the tin-whisker-growth phenomenon, the increased possibility of conversion to gray tin, low reliability, and a series of other problems. The Sn–Cu solder system has the

advantages of high ductility, fatigue resistance, and a low price. However, the application of Sn–Cu solder in electronic packaging is limited by its high melting point and poor wettability [77–79].

Zhang’s team [80] investigated the wettability, mechanical properties, and interfacial IMC growth under solid–liquid diffusion and multiple reflow conditions. They found that adding GNSs to the Sn–Cu solder alloy improved the wettability and shear strength of the composite joint. The growth of IMCs could be inhibited by adding 0.05 wt.% of GNSs. However, the thickness of the IMC layer increased with the increase in reflow time. Under all the same conditions, the IMC layer thickness of the composite solder with GNSs added was less than that of the unmodified Sn–Cu solder. After adding GNSs, the fracture form of the composite solder changed from brittle to ductile.

Duan et al. [81] added graphene to Sn–Cu–Ti solder [82]. The results showed that if graphene were added in excess, it would reduce the fluidity of the composite solder in the molten state. During the solidification of the Cu–Sn–Ti solder alloy, the dominant phases are α -(Cu)Sn₃Ti₅ and CuSn₃Ti₅. This is because graphene adsorbed Cu–Sn–Ti during solidification, forming a predominant phase rich in C and TiC. The hardness of the Cu–Sn–Ti composite solder alloy also increased with the addition of graphene.

As research has progressed, researchers have found that alloying and particle strengthening could improve the structure and performance of conventional Sn–Cu solders [83]. On the other hand, the organization and properties of the solder can be improved by controlling the soldering process parameters [84]. In the Sn–Cu solder alloy, graphene is attached to the Cu surface as a barrier layer. It inhibits the growth of the intermetallic compound layer by hindering the diffusion of Cu atoms [85].

5.4. Sn–Ag Composite Solder

Among a range of lead-free solders, Sn–Ag solders have good wettability, mechanical properties, and resistance to thermal fatigue, making Sn–3.5Ag solders a potential alternative to Sn–Pb solders. Sn–3.5Ag has been used for 3D packaging to achieve high-quality wafer bonding [86]. The mutual solubility of Ag and Sn is very low, but the two elements can react to form the Ag₃Sn phase. Many scholarly studies have found that the Ag₃Sn phase is primarily in the matrix as needles. Sn–3.5Ag undergoes long reflow and aging, and the intact intermetallic compound solder joints can be stacked in three dimensions.

Mayappan’s group [87] added 0.07 wt.% of graphene to Sn3.5Ag and welded the composite to a Cu substrate. The formation of intermetallic compounds was observed by aging at different temperatures and times. The measured IMC layer thickness is used to calculate the growth rate (K) and activation energy value of the IMC layer. The growth rate of the IMC layer is shown in Table 3, while the activation energy is shown in Figure 12 [87]. It was found that the reaction of Sn–3.5Ag and Sn–3.5Ag–0.07GNSs with Cu substrates produced Cu₆Sn₅ IMC layers. However, Cu₃Sn was formed on the Cu substrate side at a later aging stage. This indicates an increase in the energy of diffusion and IMC formation of Sn and Cu atoms in the solder joint. They decreased the IMC growth rate after adding GNSs, which indicates an increased energy for the diffusion and IMC formation of Sn and Cu atoms in the solder joint. The values for Sn–3.5Ag/Cu and Sn–3.5Ag–0.07GNSs/Cu solder joints were calculated as 65.9 and 77.0 kJ/mol, respectively. Graphene’s high specific surface area can act as a diffusion barrier and retard the growth of IMCs. As a result, the intermetallic growth rate was reduced.

Table 3. Total intermetallic growth rate. Reprinted with permission from Ref. [87]. 2022, Elsevier Science & Technology Journals.

Aging Temperature (°C)	Intermetallic Growth Rate, K (cm ² /s)	
	Sn–3.5Ag	Sn–3.5Ag–0.07GNSs
100	0.68×10^{-14}	0.32×10^{-14}
125	4.67×10^{-14}	1.55×10^{-14}
150	37.40×10^{-14}	9.60×10^{-14}
180	42.70×10^{-14}	11.00×10^{-14}

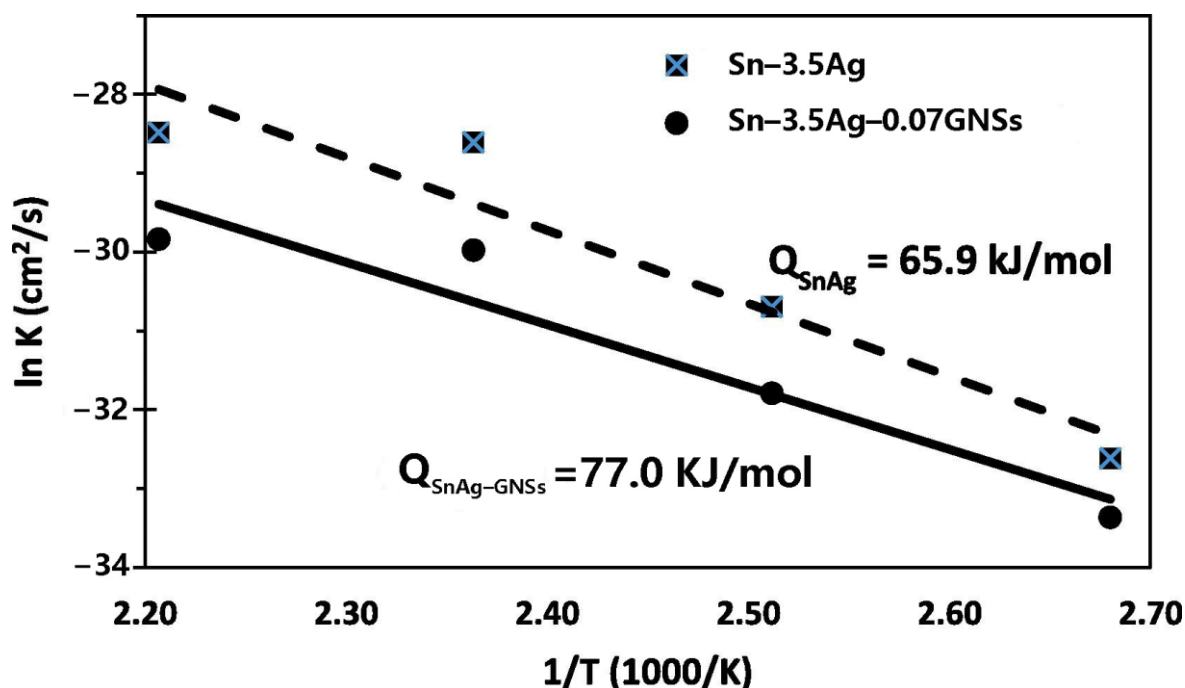


Figure 12. Arrhenius plots of the total intermetallic compound layer growth for Sn3.5Ag/Cu and Sn3.5Ag-0.07GNSs/Cu solder joints. Reprinted with permission from Ref. [87]. 2022, Elsevier Science & Technology Journals.

In conclusion, adding single graphene to lead-free solder improves the wettability, mechanical properties, shear strength, and UTS of the composite solder joints while having little to no impact on the melting point. It also refines the composite solder's microstructure and prevents the growth of IMC layers. Furthermore, too much graphene will impair the mechanical qualities of the composite solder, i.e., graphene becomes poorly dispersed, leading to its aggregation, which affects the performance of the composite solder. The poor bonding of graphene with the alloy matrix of the solder makes it easy for graphene to fall off from the solder matrix during reflow [88].

6. Metal-Particle-Modified Graphene-Enhanced Sn-Based Lead-Free Solder

To improve the retention of graphene in the solder matrix, some researchers have introduced a substance between graphene and the solder matrix. It acts as a bridge to provide a tighter bond between the graphene and the welded substrate. With further research, the researchers found graphene is modified with highly reactive metal particles and added to the solder matrix [60]. This method can enhance the performance of lead-free solder to a certain extent so that lead-free solder can be used in a broader range of places. However, for the uniform dispersion of graphene in the substrate, the current solution is through improved preparation processes and the modification of the graphene surface.

6.1. Ni-Graphene-Reinforced Sn-Based Lead-Free Solder

Ni nanoparticles are ideal for modifying graphene because Ni nanoparticles readily react with Sn-based lead-free solder alloys and can form IMC layers during the soldering process. Khodabakhshi et al. [89] plated nickel on the surface of GNSs by the chemical plating method. Then, a Ni-GNSs-SAC composite solder was prepared by the powder metallurgy method. The results showed that adding GNSs could improve the morphology of IMCs. Generated IMCs showed rounded particles and uniform dispersion. This solder's improved yield strength, tensile strength, and ductility are due to the inhibition of microstructural coarsening by ultrafine intermetallic particles and reinforcing nanosheets.

Wang's team [90] also added Ni-GNSs to SAC solder, and the results showed that adding Ni-GNSs improved the ductility and UTS of the solder. Ductility and UTS are shown in Figure 13. The ductility and UTS increased and then decreased with the addition of Ni-GNSs, and the thickness of the IMC layer decreased and then increased. Solder properties were most improved when the added Ni-GNS content was 0.03–0.05 wt.%. The composite solder obtained the best wettability, thinner IMC layer thickness, and best strength and toughness.

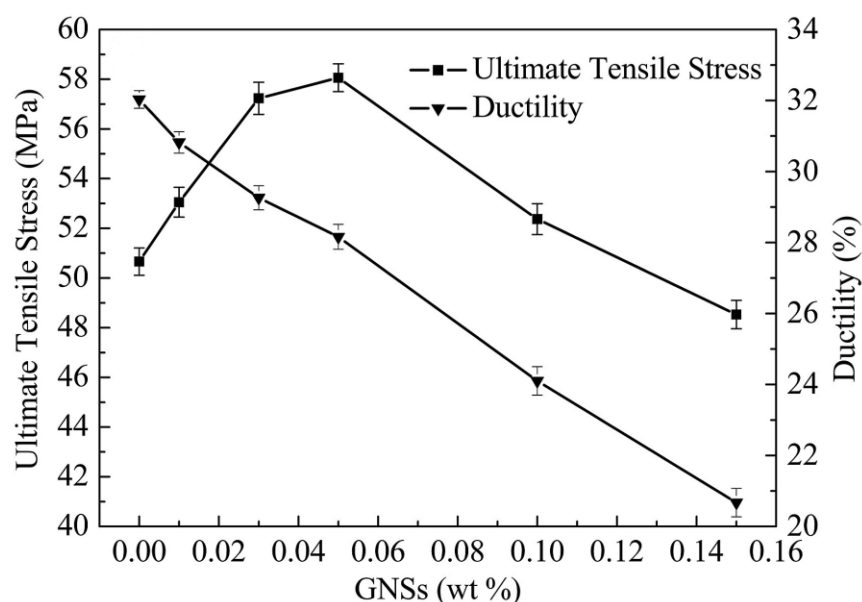


Figure 13. Ductility and UTS. Reprinted with permission from Ref. [90]. 2019, Elsevier Science & Technology Journals.

Chen et al. [60] modified graphene by Ni plating on the graphene surface via the chemical plating method. The addition of Ni-GNSs to the SAC solder resulted in a reduced wettability and increased hardness and shear strength. This is due to the uniform dispersion of $(\text{Ni}, \text{Cu})_6\text{Sn}_5$ in the solder matrix. The composite solder electric resistivity is shown in Figure 14. Still, there was no significant change in resistivity. This phenomenon can be explained based on the influence of the resistivity of the reinforcement and the amount of Ni-GNSs added. On the one hand, the resistivity of both Ni ($\sim 6.84 \mu\Omega\cdot\text{cm}$) and GNSs ($\sim 10 \mu\Omega\cdot\text{cm}$) is much smaller than that of the SAC solder ($12.9 \mu\Omega\cdot\text{cm}$). Therefore, adding Ni-GNSs helps reduce the resistivity of the composite solder. However, the amount of added reinforcing-phase Ni-GNSs is so tiny that it hardly affects the resistivity of the added solder system significantly.

Zhang's team [91] added Ni-modified graphene oxide (RGo) to SAC305 composite solder, resulting in the significant refinement of $\beta\text{-Sn}$, Cu_6Sn_5 , and Ag_3Sn grains. Still, the melting point of the SAC305 composite solder alloy did not change much after the addition of Ni-RGo. When the accumulation of Ni-RGo is 0.03 wt.%, the fracture form of the SAC305 composite solder alloy becomes a microporous aggregation type of ductile fracture. However, with Ni-RGo additions are more significant than or less than 0.03 wt.%, the fracture form is a mixture of ductile and brittle fracture properties. The reliability of the soldered joints was improved.

Sayyadi et al. [56] prepared Ni-GNS-reinforced SAC composite solder alloys by mechanical alloying. They investigated the effect of the aging phenomenon on the tensile–shear properties of solder joints. The yield and ultimate tensile strength of soldered joints increased with increasing Ni-GNS content while maintaining high elongation.

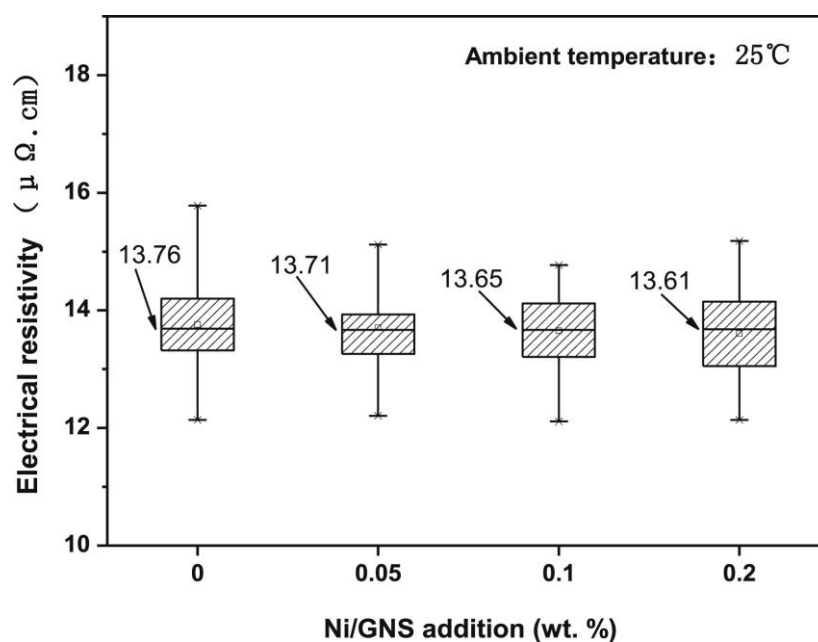


Figure 14. Composite solder electric resistivity. Reprinted with permission from Ref. [60]. 2016, Elsevier Science & Technology Journals.

The dispersion of graphene can be improved by modifying graphene with Ni particles. We found that in numerous reports. The best improvement for SAC solder was achieved by adding Ni–GNSs at 0.03 wt.%. Although the amount added is minimal, there is very little change in the inherent properties of the solder, such as melting point and electrical conductivity. However, it can inhibit the growth of IMC layers and improve the reliability of solder joints.

6.2. Ag-Nanoparticle-Modified Graphene-Enhanced Lead-Free Solder

There is a significant density difference between solder alloy and graphene, and graphene dispersion is poor. So, some researchers wished to modify graphene with silver nanoparticles. New lead-free solders with uniformly dispersed enhanced particles were obtained.

To overcome these drawbacks of graphene, Jing et al. [92] prepared Ag–GNS-modified SAC solder alloys by mechanical mixing. The Ag–GNSs/SAC solder alloy exhibited finer particle size, better wettability, and higher tensile strength than a single graphene-modified SAC solder alloy, interfacial microstructure of the Ag–GNS-modified SAC solder alloy by observation. After soldering, the IMC layer had a scallop shape at the interface. With increasing aging time, the morphology of the IMC layer changes from scalloped to nonscalloped. The addition of Ag–GNSs effectively inhibited the growth of IMCs. When the content of Ag–GNSs increases from 0.03 to 0.1 wt.%, the thickness of the IMC layer decreases. However, when the content reaches 0.2 wt.%, the thickness of the IMC layer starts to grow. During aging, the thickness of the IMC layer decreases with the increase in Ag–GNS content. The thinnest IMC layer appears when the added graphene content is 0.2 wt.%.

Xu et al. [49] added different wt.% of Ag–GNSs to SAC lead-free solder alloy by ball milling and mechanical stirring. They found that the number of particles in IMCs decreased with increased Ag nanoparticle content. At the same time, the interfacial structure became homogeneous, while the melting point did not change significantly. The wettability was improved compared with that of pure SAC solder. They also performed thermomechanical measurements on Ag–GNS-modified SAC composite solders. The thermal stability of Ag–GNS-modified SAC composite solders was improved, the maximum UTS increased, and the ductility decreased. At lower levels of Ag–GNSs, the tensile strength of the composite

solder increased. However, when the critical content of Ag–GNSs was reached, the tensile strength decreased.

6.3. Cu-Nanoparticle-Modified Graphene-Enhanced Lead-Free Solder

The bond strength between Cu and GNSs is lower than that of Ni–GNSs. However, the lattice defects of GNSs produced by high-energy grinding allow Cu nanoparticles to form strong bonds with defective GNSs. Compared with Ni and Ag, Cu has abundant resources, a low price, stronger local solid surface plasmon resonance, good electrochemical properties, and good catalytic properties [53]. Therefore, some researchers are experimenting with Cu-modified graphene. This alleviates the disadvantages of the aggregation tendency of graphene and reduces the price of producing composite solder.

The powder metallurgy technique is used to create lead-free solder with Cu–GNS reinforcement. Zhang [93] and his colleagues produced Cu nanoparticles with an average size of 13 nm. The contact angle and diffusion area of the composite solder are shown in Figure 15. With the increase in Cu–GNS addition, the spreading area of the Sn_{2.5}Ag_{0.7}Cu_{0.1}RE/Cu–GNS (SACR/Cu–GNS) composite solder first increased and then decreased, and the wetting angle first decreased and then increased. Adding an appropriate amount of Cu–GNSs improved the wettability of the composite solder. When Cu–GNSs were added at an amount of 0.05 wt.%, the SACR/0.05 Cu–GNS composite solder had a maximum spreading area of 50.5 mm², more than the base solder's spreading area. The solder alloy's spreading area rose by a factor of 55, and the wetting angle had a minimum value of 32°.

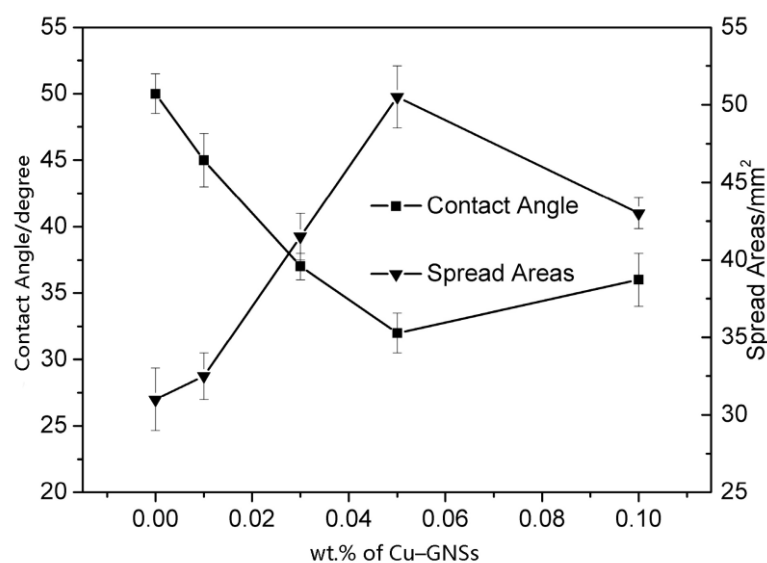


Figure 15. Contact angle and diffusion area of the composite solder. Reprinted from Ref. [93].

They also proposed that GNSs tend to drift with the solder and even float to the solder/fluid interface to improve the wetting angle because Cu–GNSs and molten solder have different densities [94]. Due to the decreased surface tension, the interfacial Cu–GNSs lead to an imbalance at the solid–liquid interface [95]. Additionally, the accumulation of Cu–GNSs in the solder/molten solder interface is made possible by the effective link between the two materials due to the modification of the Cu nanoparticles [89]. The mechanical properties and tensile fracture diagrams of the composite solder are shown in Figure 16 [93]. When the introduction of Cu–GNSs was 0.03 wt.%, the best mechanical properties were obtained. The tensile strength was 59 MPa and 29% elongation, which was nearly 19% higher than the tensile strength of 62 MPa of the substrate. Therefore, in a SACR/Cu–GNS composite solder with 0.03–0.05 wt.%, the Cu–GNS addition has the best wettability and mechanical property combination. Additionally, grain refining and load transfer are responsible for the rise in tensile strength.

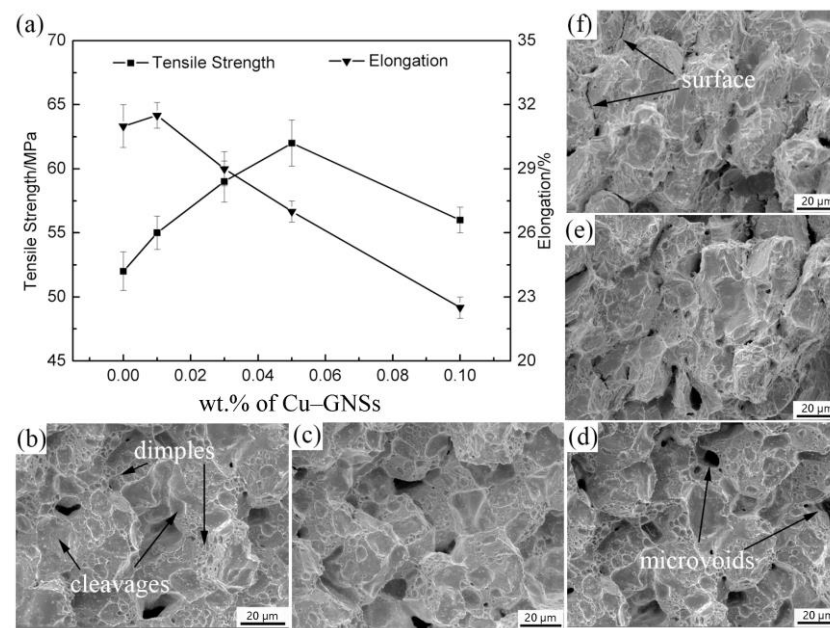


Figure 16. (a) Mechanical properties of Sn2.5Ag0.7Cu0.1RE/Cu-GNS composite solders; tensile fracture graphs corresponding to (b) 0 wt.%; (c) 0.01 wt.%; (d) 0.03 wt.%; (e) 0.05 wt.%; (f) 0.10 wt.% of Cu-GNS additions. Reprinted from Ref. [93].

Gui et al. [96] prepared Cu-modified GNSs (Cu-GNSs) using a chemical modification method (the preparation process is shown in Figure 17) [96], where Cu-GNSs were added to the solder flux to form a composite solder. As the Cu-GNS content in the solder increased, the spreading area of the SAC solder on the substrate first decreased and then increased; the wettability angle decreased most significantly, reaching 14.43%. Cu-GNS addition could improve the wetting of the solder; the best wetting enhancement was attained at an addition amount of 0.1 wt.%. Additionally, including Cu-GNSs can significantly lower the thickness of the IMC layer by preventing the formation of the IMC layer at the SAC305/Cu interface. After adding Cu-GNSs, the shear strength of the composite joints was sharply enhanced, and the shear strengths of the joints treated with different fluxes were 57.68, 58.92, and 63.07 MPa, respectively. Moreover, the fracture type switched from tough–brittle to ductile.

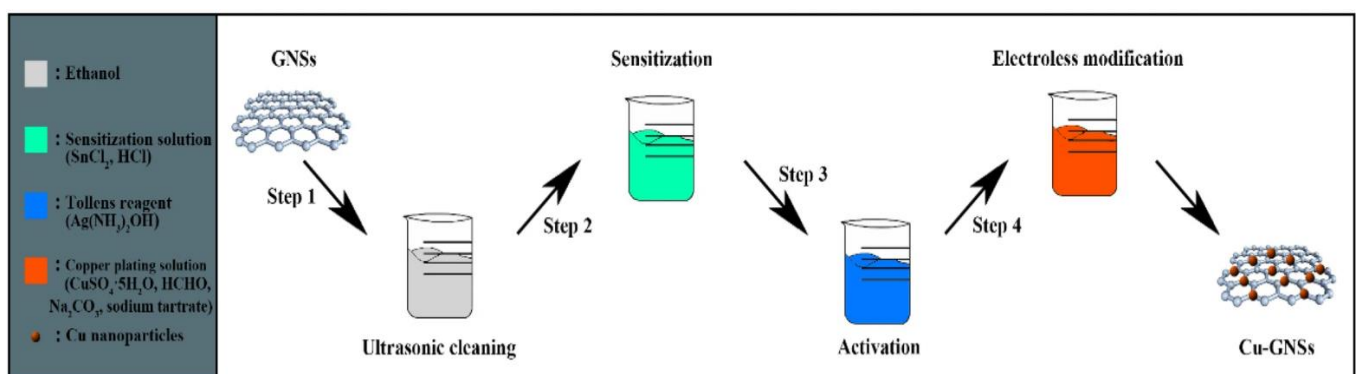


Figure 17. Cu-modified GNS preparation process. Reprinted with permission from Ref. [96]. 2022, Springer New York LLC.

In conclusion, mechanical mixing and chemical plating are the primary preparation techniques for lead-free solder modified with graphene and metal particles. The addition of metal particles and modified graphene gives the composite solder better performance. It can refine IMC grains and inhibit IMC growth. It can also improve UTS, thermal stability,

wettability, reliability, and yield strength. Furthermore, the addition of metal-particle-modified graphene has little effect on the resistivity of the composite solder. The effect of adding graphene on lead-free solder is shown in Table 4. Therefore, graphene should be modified with metal particles that have similar properties to precious metals and are inexpensive. This will facilitate the large-scale industrial production of the newly developed graphene composite solders.

Table 4. Effects of adding graphene.

Graphene Types	System	Effects
GNSs	SAC	Inhibits IMC growth, refines grain size, improves wettability, and enhances mechanical properties
	Sn–Bi	Inhibits IMC growth and refines grains
	Sn–Cu	Inhibits IMC growth and improves solder joint reliability
	Sn–Ag	Inhibits IMC growth
Metal particles modified with graphene	-	Inhibits IMC growth, improves mechanical properties, improves bonding problems, improves solder joint reliability, and improves dispersion

7. Conclusions

This paper systematically reviews the research results, strengthening mechanisms, and preparation methods of graphene composite solders. The following conclusions were drawn:

1. The main current challenges of graphene composite solders include the problem of binding graphene to the solder matrix and the problem of uniform dispersion;
2. The current main approaches to addressing the challenges of graphene composite solders are improved preparation methods and metal particle modification of graphene;
3. Future work will focus on the development of graphene composite solders with high dispersion, strong adhesion, structural integrity, and low cost.

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Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

Conflicts of Interest: The authors declare no conflict of interest.

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