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## FEATURE ARTICLE

#### Review on latest design of graphene-based inorganic materials

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The breathtakingly fast evolution of research on graphene and its modification methods in the recent 8 years has made possible the various preparations and applications of its derivatives. These hybrid structures exhibit excellent material characteristics including high carrier mobility and radiate recombination rate as well as long-term stability since graphene sheets possess super electrical conductivity, mechanical flexibility and good optical transparency. Besides, the versatile and fascinating properties of the nanostructures grown on 10 graphene layers make it possible to fabricate high-performance electronic, optoelectronic and catalytic devices. This review presents an overview of the latest design of structure, synthetic methods and applications of graphene-based inorganic nanocomposites. The challenges and perspectives of these emerging hybrid heterostructures are also discussed.

#### 1. Introduction

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15 Since graphene, a single-layer carbon sheet with a hexagonal packed lattice structure, was discovered by Novoselov et al. in 2004,<sup>1</sup> an exponential growth of graphene research in both the scientific and engineering fields was witnessed in the past eight years. Data from Web of Science (Fig. 1) shows that the number 20 of graphene related papers soared from 33 in 2004 to 6578 in 2011. This star material of the century has shown many unique properties, such as the quantum hall effect (OHE),<sup>1</sup> ambipolar electric field effect,<sup>2</sup> large theoretical specific surface area (2630  $m^2$  g<sup>-1</sup>),<sup>3</sup> high carrier mobility at room temperature, excellent 25 thermal conductivity (3000-5000 W m<sup>-1</sup> K<sup>-1</sup>),<sup>4</sup> good optical transparency (~97.7%)<sup>5</sup> and high Young's modulus (~1TPa).<sup>6</sup> To combine these fascinating properties with excellent characters of other nanostructures has become a popular trend among

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researchers around the world to achieve applications in multiple fields. Over the past few years, various inorganic composites have been successfully decorated on graphene sheets including <sup>55</sup> metals like Ag,<sup>7-14</sup> Au,<sup>16-23</sup> Cu,<sup>24-27</sup> Ni,<sup>28,29</sup> Co,<sup>30</sup> Pd,<sup>31-33</sup> Pt,<sup>34,37</sup> Rh,<sup>38</sup> Ru,<sup>38</sup> and metal oxides like TiO<sub>2</sub>,<sup>39-48</sup> SnO<sub>2</sub>,<sup>49,50</sup> Co<sub>3</sub>O<sub>4</sub>,<sup>51-54</sup> Fe<sub>3</sub>O<sub>4</sub>, <sup>55-59, 235,236</sup> CuO, <sup>60-62</sup> Cu<sub>2</sub>O, <sup>63-65</sup> WO<sub>3</sub> <sup>66</sup> and ZnO. <sup>67-81</sup> These inorganic components show diverse morphologies such as belts, tubes, rods, wires, particles, and polyhedrons and their 60 composites with graphene have been intensively explored in applications such as batteries, supercapacitors and photocatalysis. In recent three years, A-B-graphene ternary materials like SnO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>-graphene,<sup>82</sup> MnO<sub>2</sub>-Ni-graphene<sup>83</sup> and MoS<sub>2</sub>-TiO<sub>2</sub>graphene<sup>84</sup> were designed and fabricated to bring best play of 65 their synergetic effects. Other forms of carbon like carbon nanotubes (CNT) or carbon cloth (CC) were also compounded with graphene to achieve unexpected properties. Simultaneously, versatile and reliable synthetic routes have been developed to prepare graphene's derivatives ranging from the in situ reduction 70 to the ex situ decoration under different conditions. Emerging modified routes like gas-liquid interfacial synthesis also provide interesting platforms for the fabrication of these increasingly



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Through the incorporation with various kinds of functional materials, it is desirable to harness both the useful properties of graphene and its derivatives in composites. In this review, we s first summarize the fresh ideas in recent three years on the design of structures decorated on graphene and then provide new insights of various techniques in synthesizing the nanocomposites. Finally, we demonstrate the superb advantages of graphene–inorganic nanocomposites for a wide range of 10 applications and discuss the remaining challenges and future

prospects.



25 Fig. 1 Number of papers related to graphene (2004-2011)

#### 2. New combination strategy with graphene

#### 2.1 A-B-graphene ternary materials

A vast amount of work has proved that nanoparticles could be successfully decorated on the surface of graphene especially after 30 the easy production of graphene oxide. However, only one type of substance, metal or metal oxide/sulphide is usually anchored on graphene sheets for testing in various application fields in early days. Currently there has been a new trend to compound at least two components with graphene to observe their synergetic 35 effects for better structure and results. Two types of inorganic particles or organic-inorganic combinations loading on graphene are of especial interest. For instance, Wang et al. successfully fabricated Fe<sub>3</sub>O<sub>4</sub>-Sn<sub>2</sub>O-graphene<sup>82</sup> nanocomposites with uniform dispersion and applied them in the lithium ion batteries. Their 40 results indicate that the electrochemical performance of this ternary material is better than that of Fe<sub>3</sub>O<sub>4</sub>-graphene<sup>85</sup> or Sn<sub>2</sub>Ographene<sup>86</sup> synthesized under the same conditions. The author ascribed the improved electrochemical performance to the coexistence of following two reactions:

$$3Fe + 4Li_2O \leftrightarrow Fe_3O_4 + 8Li^+ + 8e^-$$
(1)  
$$SnO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2O + Sn$$
(2)

Excessive Li<sub>2</sub>O can be formed and make the Fe nanograins recover to Fe<sub>3</sub>O<sub>4</sub> easily during the oxidation process, leading to low irreversible capacity. In addition, its initial Columbic <sup>50</sup> efficiency of the product is also higher than that of reported SnO<sub>2</sub>-graphene nanocomposites,<sup>87-90</sup> indicating that the introducing of Fe<sub>3</sub>O<sub>4</sub> component can effectively reduce the initial irreversible capacity. It is also worth mentioning that even with more components on the graphene substrate, these particles of <sup>55</sup> different kinds are mostly strongly attached on the surface of graphene and aftertreatments like sonication would not change the morphology or structure of the products.

In early years, many works on Pt-graphene materials were reported<sup>34-37</sup> since Pt was considered as a perfect catalyst and the 60 highly conductive graphene could bring better performance out of it. Recent researches revealed that for oxygen reduction reaction (ORR) in the polymer electrolyte membrane fuel cells (PEMFCs), the addition of an early transition metal to Pt can change the geometric (Pt-Pt bond distance and coordination 65 number) and electronic structures of Pt.<sup>91,92</sup> Due to these structural changes, the adsorption of -OH is mostly centered on the second metal, not on Pt, and oxygen tends to be reduced on Pt in a "four electron" process. Inspired by this phenomenon, Sun's group successfully designed and fabricated monodispersed Pt-Fe-70 graphene which exhibited significantly enhanced catalytic performance for ORR.93 The close contact between graphene and FePt facilitates p-electron polarization from graphene to FePt (via a possible coordination bonding), making the FePt surface more easily accessible for O<sub>2</sub> absorption and activation. With more 75 systems like Pt-TiO<sub>2</sub>-graphene,<sup>94</sup> Pt-lucigenin-graphene<sup>95</sup> and Ptpyrogallol-graphene<sup>96</sup> successfully synthesized, it is predictable

- that the combination of Pt-X-graphene will become a new trend in the catalytic chemistry for ORR and other applications in the near future.
  <sup>80</sup> Certain material chosen to be inserted in the graphene-based nanocomposites generally plays the role of cocatalysts. For photocatalytic H<sub>2</sub> production in water splitting, TiO<sub>2</sub>-graphene
- photocatalytic H<sub>2</sub> production in water splitting, 11O<sub>2</sub>-graphene composites have always shown an enhanced catalytic efficiency compared to TiO<sub>2</sub> alone.<sup>39-48</sup> However, their activity must be further enhanced from the viewpoint of practical applications and commercial benefits. In recent years, MoS<sub>2</sub> with a layered structure has been extensively investigated as a promising electrocatalyst for H<sub>2</sub> evolution.<sup>97-101</sup> Yu *et al.* for the first time reported the synthesis of TiO<sub>2</sub> nanoparticles on a layered MoS<sub>2</sub>-<sup>90</sup> graphene hybrid for use in photocatalytic H<sub>2</sub> production and found that the activity of TiO<sub>2</sub> nanoparticles is significantly enhanced.<sup>84</sup> The H<sub>2</sub> production rate of simple combination of TiO<sub>2</sub>-MoS<sub>2</sub> and TiO<sub>2</sub>-graphene only reached 36.8 and 29.7 µmol h<sup>-1</sup>, respectively, while the ternary TiO<sub>2</sub>-MoS<sub>2</sub>-graphene hybrid



95 Fig. 2 Schematic illustration of the charge transfer in TiO<sub>2</sub>-MoS<sub>2</sub>graphene composites (Adapted from ref. 84 with permission).

achieved 165.3  $\mu$ mol h<sup>-1</sup> under the same conditions, reflecting the significance of the synergetic effect. Mechanism study (Fig. 2) shows that the photogenerated electrons in the conduction band

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#### Nanoscale

(CB) of TiO<sub>2</sub> are transferred to  $MoS_2$  nanosheets through the graphene sheets and then react with the adsorbed H<sup>+</sup> ions at the edges of  $MoS_2$  to form H<sub>2</sub>. This novel structure can bring suppression of charge recombination, improve the interfacial s charge transfer and increase the number of active adsorption sites and photocatalytic reaction centers.

In a similar design, Khalid's group synthesized TiO<sub>2</sub>-Fegraphene nanocomposites and used them in the degradation of methyl orange.<sup>102</sup> Compared to TiO<sub>2</sub>–graphene, the 10 photoluminescence emission intensity significantly decreases with the Fe doping, indicating that the recombination of photogenerated carriers is effectively suppressed. With more methyl orange molecules absorbed on the surface, enhanced degradation performance is observed for TiO2-Fe-graphene 15 sample. Therefore, it is safe to conclude that the doping of Fe in the TiO<sub>2</sub>-graphene material with an optimal concentration not only narrows the band gap of TiO2 to extend the absorption into the visible light region but also is beneficial to the separation of photogenerated electron-hole pairs.

As popular as the idea is, the three body system of PbSe-TiO<sub>2</sub>graphene nanoflakes (Fig. 3) was reported by Loh *et al.* for their unique properties in the application of infrared photodetectors.





**Fig. 3** (a) Schematic representation of multiphase assembly of the PbSe-<sup>25</sup> TiO<sub>2</sub>-graphene photodetector. (b) Large-area printed PbSe-TiO<sub>2</sub>-graphene photodetector patterns on flexible substrate (Adapted from ref. 103 with permission).

intrinsic dipole moment, and compability with solutionprocessable techniques in manufacturing.<sup>104,105</sup> The PbSe-only <sup>30</sup> film in the experiment shows a characteristic band gap in the photothermal deflection spectroscopy (PDS). Coating of graphene on it can cause the optical absorption coefficient increase by at least one order of magnitude. The adding of TiO2 then contributes to distinct band edge absorption in the UV

- <sup>35</sup> region. The whole combination promotes additional absorption in the visible–infrared regions since a tight coupling at the interface allows additional optical transition. Lacking any of the three components can lead to the damage of the performance at different levels.
- <sup>40</sup> It is noteworthy though that binding more materials on graphene does not always guarantee the best result in applications. For the Co-Ni-graphene nanocomposites obtained by a simple route, Shen and his colleagues found that only an optimal ratio of the two metals in this compound can help the reduction of 4-
- <sup>45</sup> Nitrophenol to the best.<sup>106</sup> Otherwise it may even perform worse than Ni-graphene alone. The author assumed that the difference in the catalytic activity was mainly attributed to the size and composition of the nanocomposites. The sample of Ni<sub>25</sub>Co<sub>75</sub>graphene with a smaller size was observed to possess the highest

<sup>50</sup> value of apparent rate constant  $(k_{app})$  among all samples, thus performing the best. In this case, higher percentage of Co also leads to a faster reduction since its catalytic activity is higher than that of pure Ni.<sup>107</sup> Similar result was also found by Xie's group when they try to synthesize Co-Sb-graphene for the application of <sup>55</sup> lithium ion batteries.<sup>108</sup>

When the M-graphene mode can not meet the high standards of devices like photoelectric sensors or electrochemical cells, the assistance from the third body in the material therefore becomes very necessary. The attachment of Au nanoparticles onto the 60 surface of graphene had been considered a facile way to develop biosensors with high performance in the past few years.<sup>16-23</sup> However, only a few of examples showed satisfactory properties of high sensitivity, long stability, large detection range, and good selectivity. To modify the existing system, Zhang et al. prepared 65 Au-POM-graphene hybrids without using any surface active agents. They exhibit significantly improved biosensing properties compared to Au-graphene nanocomposites,<sup>109</sup> in which POM (polyoxometalate) serves as a reducing and encapsulating molecule as well as a bridging molecule in the formation of the 70 hybrids since POMs are early transition-metal oxygen-anionic clusters and exhibit remarkably rich redox and photoelectrochemcial properties.

Different forms of carbon can be applied as the extra components as well since they possess disparate structures that 75 lead to various functions. In the application in lithium ion batteries, graphene can afford good dispersion of the nanoparticles and guarantee a high electrical conductivity of the overall electrode, which is good for the purpose of high rates. Nevertheless, the nanoparticles may still undergo successive 80 agglomeration during the Li uptake/release process, leading to capacity fading when directly exposed to the electrolyte. 50,52,58,62,87,110-116 One of the promising strategies to solve this problem is to confine the electrolyte materials within individual carbon shells and then to spread them on the surface of

- <sup>85</sup> graphene thus forming a double protection. The carbon shell can act as a buffer that minimizes volume changes and direct contact between nanoparticle and the electrolyte, facilitating the formation of a stable solid electrolyte interphase (SEI) which leads to outstanding cycling performance.
- <sup>90</sup> The Ge-C-graphene hybrid obtained by Guo's group offered proof for the effectiveness of this design.<sup>117</sup> More specifically, Ge nanoparticles first were coated by carbon resulted from oleylamine (Fig. 4) and then the carbon-coated Ge nanoparticles were dispersed on graphene sheets, in which graphene acted as an <sup>95</sup> elastic and electronically conductive substrate that guaranteed high electrical conductivity of the overall electrode. This system with double-protection structure brought super high initial charge



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Fig. 4 Schematic illustration of the synthesis route for the Ge-C-graphene nanocomposite (Adapted from ref. 117 with permission).

- <sup>10</sup> previous reports.<sup>89,120</sup> To solve this problem, they coated the SnO<sub>2</sub> nanoparticles on graphene with thin layers of amorphous carbon by a hydrothermal method using glucose as carbon source and observed superior electrochemical performance with large reversible capacity and excellent cycling performance of this <sup>15</sup> multicomponent material, better than contrast sample graphene–
- SnO<sub>2</sub> in all aspects. As an anode material for lithium batteries, LiFePO<sub>4</sub>-graphene hybrid has also been successfully prepared via various ways<sup>121-124</sup> and significantly improved rate capability and cycling stability were obtained. Zhang *et al.* assumed that due to <sup>20</sup> the two-dimension nature of graphene, the nanoparticles could not be tightly wrapped, resulting in a restricted enhancement in electrochemical activity.<sup>119</sup> By using a carbon-coating process as other researchers did, they obtained LiFePO<sub>4</sub>-C-graphene nanoflakes and studied the influence of the content of C in the <sup>25</sup> composites on their electrochemical performance. The results indicated that for electrode materials, anode or cathode, the graphene-C-X structure exhibited better electronic conductivity as well as stability and outperformed the once hot graphene-X composites in the application of lithium ion batteries.
- The art of coating carbon varies from group to group and presents the beauty of synthetic chemistry. Zhi *et al.*<sup>125</sup> obtained SnO<sub>2</sub>-carbon sheath-graphene by a hydrothermal-CVD method adopting  $C_2H_2$  as the wrapping agency (Fig. 5). The SnO<sub>2</sub>/C

C.H.

CVD

2

+SnCl

Hydrolysis

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GO RGO-SnO<sub>2</sub> RGO-Sn@C nanocables 40 b) С 1600 RGO-Sn (Charge) RGO-Sn (Discharge) RGO-Sn@C nanocabl RGO-Sn@C nanocabl 1400 mAh g' 1200 1000 Capacity ( 800 600 45 400 200 30 Cycle Number

Fig. 5 a) Schematic of procedures for the synthesis of SnO<sub>2</sub>-C-graphene.
50 b) Cycling performances of SnO<sub>2</sub>-C-graphene nanocables and Sn-graphene electrodes at a rate of 50 mA/g. c) SEM image of the product (Adapted from ref. 125 with permission).

nanocables with an average diameter of ca.100 nm protruded from graphene substrate in high density. Interestingly, the carbon ss sheaths were found not fully filled, which might be caused by the volume shrinkage by SnO<sub>2</sub> during the cooling process. This vacancy structure then became more attractive when used in lithium ion batteries since it was expected to be beneficial for accommodating the huge volume change during the lithium <sup>60</sup> insertion/extraction process. This assumption was then confirmed by the electrochemical evaluations of the material. More amazing about this work is that these nanocables with a uniform diameter and high aspect ratio are also capable of being easily tailored into other interesting one-dimensional nanomaterials like carbon <sup>65</sup> nanotubes with one open end or SnO<sub>2</sub> nanotubes, providing novel perspectives for nanomaterial synthesis.

More complicated designs have been adopted in the biology field for immune sensors to achieve sensitive, accurate and facile detection. For example, Yu's group developed an electrochemical munoassay using Au-CNT-graphene composite modified electrode (Fig. 6). The CNT and graphene provided effective antibody immobilization matrix and made the immobilized immunocomponents possess high stability and bioactivity.<sup>126</sup> In this device, CNT-graphene coupling produces a synergic effect



75 Fig. 6 Fabrication processes of Au/TH/MCM-41 nanomaterials and measurement protocol of the electrochemical immunosensor (Adapted from ref. 126 with permission).

on the electroanalytical performance of the resulting electrode material. The Au nanoparticles decorated on the surface of the <sup>80</sup> coupling not only improve the electron transfer rate, but also increase the surface area to capture a large amount of primary antibodies. In the field of biology, an issue about the usage of graphene is its water solubility, which usually limits its further application in biosensing and other areas. Graphene sheets are hydrophobic and tend to form agglomerates in water.<sup>127</sup> The A-B-graphene structure can effectively solve this problem and has been employed by some research groups for the fabrication of a series of chitosan-graphene-magnetic nanoparticles hybrids for various applications.<sup>128</sup>

<sup>90</sup> The simple structure of graphene-X is gradually fading and novel designs of multicomponent-graphene materials currently are leading the application-driven synthetic chemistry. Nevertheless, despite their advantages brought by synergetic effects, some problems like loose connection between <sup>95</sup> components and poor stability still exist in some cases. For example, Fe nanoparticles easily fall out after repeatedly washing for the Pt-Fe-graphene composites and POMs in the Au-POMgraphene hybrid tend to decompose during application. These drawbacks might not evidently affect the properties of the <sup>100</sup> materials as the authors discussed, yet it is still urgently important to find solutions for the accurate control of each part of these A-B-graphene ternary or even quaternary materials in the future for improved performances.

#### 2.2 Graphene-based three-dimensional (3D) materials

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Graphene-based materials are normally considered as 3D structure since the carbon sheets are usually wrinkled and decorated with nanoparticles to form a net-work structure. However, these structures are not rigid enough and often collapse 5 and distort severely after usage since graphene sheets are too thin and soft to maintain the whole system as it originally is.

- Consequently, aggregation and stacking between individual graphene sheets driven by the strong  $\pi$ - $\pi$  interaction greatly compromise the intrinsic high specific surface area of graphene. <sup>10</sup> Furthermore, the high conductivity of graphene is also largely
- compromised due to intersheet contact resistance. In view of the above problems, more ordered and stiff 3D structured materials are considered to be combined with graphene like nanofoams or arrays instead of nanoparticles, belts or wires in recent years. For
- 15 instance, in the application of lithium ion batteries, nano-sized LiFePO<sub>4</sub> (LFP) usually exhibits higher rate of lithium ion diffusion and better electrical conductivity compared to bulk materials. Nevertheless this strategy adversely affects the tap density and volumetric energy density, hampering its use in 20 industrial-scale technologies. Therefore, the development of unique geometrical structures such as 3D porous architectures is promising since such networks could provide high tap density and a porous structure that facilitates the fast and efficient transfer for mass and charge. With more percolation from the 25 electrolyte into active materials by the interconnected open pores of the structure, more efficient use of the batteries can be then realized.<sup>129-131</sup> In their design of 3D LiFePO<sub>4</sub>-graphene material, Sun et al.<sup>132</sup> took advantage of the CO and CO<sub>2</sub> formed in the annealing process to obtain porous structure from the xerogel

30 precursor (Fig. 7). In comparison with bare LFP, the 3D



Fig. 7 SEM images of 3D LiFePO<sub>4</sub>-graphene (Adapted from ref. 132 with permission).

LiFePO<sub>4</sub>-graphene material showed enhanced Li ion insertion/extraction kinetics. The authors assume that the 35 embedded graphene possesses a higher degree of graphitization than amorphous carbon, which increases the speed of electron migration. The graphene acts as a bridge to increase electrochemically accessible surface area, thus significantly reducing the inert zones and leading to high specific capacity.

- For the same idea of inserting graphene into a 3D structure, Xu's group employed the electrophoretic deposition (EPD) method to lay graphene sheets on nickel nanofoams (NF) and electrochemically decorated MnO<sub>2</sub> on the surface of it to obtain a multicomponent porous material for lithium ion batteries.83
- 45 Needle-like MnO<sub>2</sub> nanostructures were uniformly grew on the surface of graphene, which then was closely coated on the 3D cross-linked grid structure of NF. Compared to normal MnO<sub>2</sub>graphene materials, the macroscopic pores of NF and open pore structure of graphene effectively shortened the length of ion
- 50 diffusion and significantly enhanced the electrochemical

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Graphene foam obtained by chemical vapor deposition (CVD) 55 method<sup>133-135</sup> is also a promising material that can alleviate the aforementioned problems that plague the performance of graphene composites. They are seamlessly continuous and highly conductive that is free of defects and intersheet junctions. Their porous structure is ideal to serve as the scaffold for the 60 fabrication of monolithic composite electrodes. Dong et al. chose graphene foam as template and synthesized 3D Co<sub>3</sub>O<sub>4</sub>-graphene nanowire composites (Fig. 8), which can serve as a free-standing monolithic electrode and exhibit excellent performance in supercapacitor application and in enzyme-free electrochemical 65 detection of glucose.<sup>136</sup> The specific capacitance

performance of the active material. Close interfacial contact

the electric conductivity of the electrode.



Fig. 8 SEM images of (a) 3D graphene nanofoams (b) Co<sub>3</sub>O<sub>4</sub>-graphene nanowire composite (Adapted from ref. 136 with permission).

was several times larger than that of the previously reported <sup>70</sup> Co<sub>3</sub>O<sub>4</sub>-graphene composite electrodes<sup>53,137</sup> and much more larger than those of other reported graphene-based composite electrode like MnO<sub>2</sub>-graphene,<sup>138</sup> NiO-graphene<sup>139</sup> and PANI-graphene.<sup>140</sup> For glucose detection, when the graphene foam skeleton was taken out, the electrochemical capacity of Co<sub>3</sub>O<sub>4</sub> nanowires 75 synthesized under the same conditions was much smaller and their response to glucose was also much less sensitive and slower, suggesting the importance of 3D graphene support.

Assembling ordered nanotubes on graphene sheets is another intriguing strategy to construct 3D structure, which could offer 80 enhanced performance in many applications such as photoluminescence, solar cells, and sensors, due to its larger specific surface area and higher porosity. In Xu's group, largescale vertical ZnO nanotube arrays were directly grown on graphene/glass substrate by seedless electrochemical deposition 85 method in pure zinc nitrate solution (Fig. 9).<sup>141</sup> ZnO nanorods



Fig. 9 SEM images of 3D ZnO-graphene nano-arrays (Adapted from ref. 141 with permission).

<sup>90</sup> were initially grown on the graphene electrode and a selective self-etching approached then was adopted to generate nanotubes during the synthetic process. The depth of nanotubes can be

controlled by varying deposition time. A high optical transparency of above 75% in entire visible range was obtained in this hybrid, which was promising in the applications in various transparent optoelectronic nanodevices. To obtain the above 5 similar structure, a general approach for the growth of metal oxide nanorod arrays on graphene sheets was proposed by Hu et al..142 They successfully designed and synthesized TiO2, ZnO, MnO<sub>2</sub>, CuO, and ZrO<sub>2</sub> on both sides of flexible graphene (G) sheets to form sandwich-like MO/G/MO heterostructures. They 10 first grow seeds on the surface of graphene sheets by annealing the precursor at high temperature and in the second step more reactants are adsorbed on the substrate using a solvothermal method to form the final product. Among these 3D structures TiO<sub>2</sub>-graphene hybrid was found to exhibit much higher 15 photocatalytic activity for the degradation of methylene blue than TiO<sub>2</sub> nanorods, thus promising candidates for photocatalytic

decontamination. Other products obtained from this approach also have distinctive properties and wide applications in fieldeffect transistors, gas sensors, optoelectronic devices, and so on. Besides metal oxide arrays on graphene, theoretical studies<sup>143-</sup>

<sup>147</sup> have indicated that 3D pillared architectures, consisting of parallel graphene layers supported by vertically aligned carbon nanotubes in between, possess desirable out-of-plane transport and mechanical properties while maintaining the excellent 25 properties of their building blocks. This structure is predicted to have efficient hydrogen storage after being doped with lithium cations.<sup>144</sup> Dai's group created tunable 3D pillared CNT-graphene architectures through intercalated growth of CNTs into thermally expanded highly ordered pyrolytic graphite (HOPG) by the 30 pyrolysis of FePc.<sup>148</sup> It could be observed from the SEM images (Fig. 10) that the CNTs grew from both sides of adjacent graphene sheets in the thermally expanded HOPG, with an intimately contacted CNT-graphene interface. This 3D CNTgraphene product was demonstrated to be excellent electrode 35 materials for energy-related devices and significantly outperformed many electrode materials, including  $\text{RuO}_2$ ,<sup>149</sup>  $\text{MnO}_2$ ,<sup>150</sup> NiO,<sup>151</sup>  $\text{Mn}_3\text{O}_4$ ,<sup>152</sup> and  $\text{Ni}(\text{OH})_2$ ,<sup>153,154</sup> as well as their composites with CNTs or graphene,<sup>155-160</sup> currently used in the state-of-art supercapacitors.



40 Fig. 10 SEM images of 3D CNT-graphene structure (Adapted from ref. 148 with permission).

Since graphene possesses the typical structure of sheet-like flat substrate, its use in field emission (FE) devices is highly restricted. Modern technology generally uses the cold cathode to 45 induce flexibility in field emission devices and the cold cathode

must satisfy two major criteria: easy electron emission and no bending-generated performance failure. It is the stringent requirement for substrate organized graphene sheets to face applied electric field with vertical edges for effective field <sup>50</sup> amplification and thereby easy electron emission. Unfortunately, documented attempts<sup>161-164</sup> was found to yield continuous films with graphene lying flat over the substrate, thus devoid of any active sharp emission sites. Besides, the agglomeration tendency of individual sheets of graphene due to van der Waals forces <sup>55</sup> would also lead to inhomogeneous and irreproducible distribution of vertical edges in the electrophoretic deposition (EPD) film. To solve the above problems, Chattopadhyay *et al.*<sup>165</sup> designed hierarchical graphene nanocones over 3D platform of carbon fabrics for FE devices (Fig. 11). The nanostructure was realized



**Fig. 11** (a) and (b) Plasma etched hierarchical graphene nanowall at different magnification obtained with etching time 40 s. (c) and (d) 3 min <sup>75</sup> plasma etched hierarchical graphene nanocones with different magnification (Adapted from ref. 165 with permission).

through plasma treatment of graphene, coaxially deposited over individual carbon fiber by means of simple aqueous phase electrophoretic deposition technique. Outstanding FE 80 performance was observed since the electric field modification around the special woven like geometry of the underlying base fabric substrate served as the booster to the nanostructured graphene related field amplification at the electron emission site. The suppressed joule heating on behalf of higher inborn 85 accessible surface area of graphene nanocone as well as excellent electrical and thermal conductivity of both the graphene and carbon fabrics lead to the product's superb robustness in the emission stability. The superior flexibility of this highperformance graphene based 3D emitter and other similar 90 structures thus ensure their huge potential use in completely foldable and wearable field emission devices.

Graphene, unlike CNTs with limited decoration space or length, has much potential to be compounded with various materials compositionally or in different dimensions for numerous <sup>95</sup> applications in diverse fields. Stimulating fresh ideas in the design of graphene-based inorganic materials has become urgently important to develop functional derivatives of this star material in the new century.

# 100 3. Novel routes to combine graphene and inorganic materials

In the last few decades, huge efforts have been made to synthesize inorganic nanostructures with controlled shape, size, crystallinity and functionality. These materials are widely employed in various applications like electronics, optics, s electrochemical energy conversion and storage, solar energy harvesting and so on. In order to further enhance their properties, a great number of inorganic nanostructures have been composited with graphene and its derivatives. Common combining approaches include hydro/solvothermal method, electrochemical 10 deposition, gas phase deposition, chemical reduction, microwave-

assisted reduction, sonication-assisted reduction, photo-assisted reduction, thermal evaporation, sol-gel method, template method, *ex situ* assembly and so on. These synthetic methods and their advantages/disadvantages had been thoroughly summarized and <sup>15</sup> discussed in previous reviews.<sup>166,167</sup> Here we present a few newly designed inspiring approaches on the basis of original routes for better combination of inorganic nanoparticles and graphene.

#### 3.1 Gas-liquid interface method

Interface chemistry is of great interest to researchers since <sup>20</sup> numerous reactions can happen on the interface to produce materials with unique morphology because of the distinct characters of different phases. Combining the solvothermal method and interface synthesis, a "beaker in autoclave" method (Fig. 12) was recently developed by Wang's group for the <sup>25</sup> fabrication of Fe<sub>3</sub>O<sub>4</sub>-graphene nanocomposites.<sup>85</sup> In this system, a



**Fig. 12** Schematic illustration of gas-liquid interface method (Adapted from ref. 85 with permission).

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beaker with ethylene glycol (EG) was put in an autoclave containing ammonia solution. Graphene and iron nitrate were added as precursors into EG to react in the sealed autoclave at 180 °C for 12 h. Several advantages can be outlined from this <sup>45</sup> clever modification of the traditional solvothermal method. Most importantly, the reaction mainly occurred at the interface due to the poor solubility of NH<sub>3</sub> in EG at 180 °C. Therefore the particle growth is localized, which is important for synthesizing monodispersed nanoparticles with a narrow size distribution. In <sup>50</sup> addition, the convection inside the beaker will cause the graphene

- sheets to become immersed in the liquid and return back to the interface along the convection flow during the reaction process, which helps to achieve a homogeneous loading of nanoparticles on all the graphene sheets. Besides, the EG solution owns a
- <sup>55</sup> boiling point as high as 197 °C, which offers a wide range of reacting temperature for different reactions in the same system to avoid it from splashing out of the beaker. This idea was first brought up by Guo *et al.*<sup>168</sup> for the fabrication of Fe<sub>3</sub>O<sub>4</sub>

nanoparticles and was then successfully extended to synthesize <sup>60</sup> Fe<sub>3</sub>O<sub>4</sub>-graphene,<sup>85</sup> SnO<sub>2</sub>-graphene<sup>86</sup> and Fe<sub>3</sub>O<sub>4</sub>-SnO<sub>2</sub>-graphene<sup>82</sup> multicomponent materials. EG in this system can be replaced by other solutions that possess high boiling point as well as good reducibility and ammonia can be changed into other volatile liquids for the preparation of more graphene-based hybrids.

#### 65 3.2 The adoption of unique reducing agents

Chemical reduction by far is the most popular strategy for synthesis of graphene-based nanomaterials. Traditional reducing agents like hydrazine,<sup>10,16,63,64,67,169-180</sup> ascorbic acid,<sup>181,182</sup> bovine serum albumin (BSA),<sup>11</sup> bacterial respiration,<sup>183</sup> and hydriodic 70 acid<sup>184,185</sup> are widely adopted. In the first years, hydrazine was the most common reducing agent for the reduction of graphene oxide, whereas in the view of its toxicity to human health and environmental protection, it now is often replaced by hydriodic acid or acetic acid. Researchers around the world now try to 75 search for simple and cost-effective reducing agents that can simultaneously control the morphology of the products. Sun's group demonstrated an environmentally friendly, one-pot strategy toward rapid preparation of Ag-graphene nanocomposites by directly heating the mixture of GO and AgNO3 aqueous solution so in the presence of NaOH at 80 °C for 10 min under stirring, without the extra introduction of other reducing agents or surface modifiers.<sup>186</sup> In this specific reaction system, GO covered with

reducing agent and reduced Ag<sup>+</sup> from Ag(OH) intermediate into <sup>85</sup> Ag<sup>0</sup> nanoparticles accelerated by plenteous NaOH.<sup>7,187,188</sup> On the other hand, GO can be converted into graphene rapidly under strong alkaline conditions as Zhang *et al.* proved.<sup>189</sup> This fast successful approach is significant since it provides insights for other researchers to find simpler reducing agents and design less <sup>90</sup> complicated routes to obtain graphene-based materials.

hydroxyl groups on the hexagonal basal plane served as a mild

Photochemical reduction is another "green" process, which can provide a uniform reducing environment in solution and no additional reducing reagents are introduced. Most researchers chose semiconductors with wide band gaps like TiO2,41,45,190 95 ZnO,<sup>71,191</sup> WO<sub>3</sub>,<sup>66</sup> BiVO<sub>4</sub><sup>192</sup> as the decorating particles on graphene since they can generate electrons under the UV- visible irradiation and reduce GO. However, by choosing phosphotungstic acid (PTA) as assisting reductant, nonsemiconductors like Pt, Au, Ag, and Pd could also be decorated 100 on graphene sheets for better application. PTA is a switchable reducing agent that could easily be activated by a UV stimulus. It can participate in the catalytic redox process as an electron relay and can be reduced electrolytically or photochemically. Various oxidants like O2 and H2O2, could restore reduced PTA to its 105 original form, completing the photocatalytic cycle. Pasricha et al. pointed out that the reducing ability of PTA in this system can be selectively switched on and off.<sup>193</sup> These reactions happen instantly at room temperature and do not need any stabilizers since UV assisted mechanism has the advantage of immobilizing PTA on the surface of GO (Figure 13). Choi et al. also chose PTA as a photocatalyst in their study on M-graphene.<sup>194</sup> They assumed that the photoexcitation of PTA induces the electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).  $[PW_{12}O_{40}]^{4-1}$ 115 centers serve as trapping sites for photogenerated electrons during irradiation and the PTA solution usually turns blue on

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accumulation of electrons. It's noteworthy that in this system not only reduced PTA but also electrons stored on graphene sheets can reduce metal ions to generate metal nanoparticles.<sup>195,196</sup>



**Fig. 13** Schematic illustration of the PTA mediated synthesis of noble 5 metal NP decorated RGO (Adapted from ref. 193 with permission).

#### 3.3 Novel deposition method

Chemical vapor deposition and electrochemical deposition are two common ways to fabricate graphene-based materials with averagely distributed particles/arrays on the surface of the carbon 10 layer. For their further development in the deposition method system, Sun's group for the first time brought up an atomic layer deposition (ALD) method and prepared sandwich-like SnO<sub>2</sub>graphene hybrids containing both amorphous and crystalline SnO<sub>2</sub> phases.<sup>197</sup> Atomic layer deposition is a surface-controlled 15 and layer-by-layer process, relying on two sequential selfterminating half-reactions. It affords superior control over SnO<sub>2</sub> deposition with high flexibility and precision; specifically, ALD offers unrivaled precision in terms of controlling the ratio and morphology of the crystalline and amorphous phases of deposited 20 SnO<sub>2</sub>. It was found that the amorphous SnO<sub>2</sub>-graphene hybrid is more effective than the crystalline SnO<sub>2</sub>-graphene in overcoming electrochemical and mechanical degradation, which is consistent with the intrinsically isotropic nature of the amorphous SnO<sub>2</sub>. Therefore, the amorphous SnO<sub>2</sub>-graphene hybrid can effectively changes 25 alleviate the large volume associated with charge/discharge processes.

To attain faster deposition speed, Cho et al. introduced a rapid (10 seconds of heating) graphene growth method that can be carried out on any desired substrate, including an insulator, thus <sup>30</sup> avoiding the need for the transfer step from the metal substrate.<sup>198</sup>

- This technique is based on metal-induced crystallization of amorphous carbon (a-C) into graphene, and involves an ultra-thin metal layer that is less than 10 nm in thickness (Fig. 14). Rapid annealing of a bilayer of a-C and metal deposited on the surface
- <sup>35</sup> leads to the first formation of graphene film and subsequent breaking-up of the thin metal layer underneath the film, thus resulting in the formation of a graphene-metal hybrid film, which is both transparent and electrically conducting. The use of ultrathin metal layer in this method provides the capability of
- <sup>40</sup> enhancing the transmittance of graphene film. The thin metal layer also makes it possible to grow graphene at 400 °C, one of the lowest conversion temperatures ever reported, in a short time



**Fig. 14** (a) Schematic illustration of the formation of the graphene–metal hybrid by metal-induced crystallization of a-C and agglomeration of ultrathin metal film. (b) The obtained hybrid film (Adapted from ref. 198 with permission).

of 10 s, which is one of the shortest heating times ever for graphene formation based on dry synthesis. The shorter annealing time can be explained by similar work<sup>199</sup> that reported the <sup>50</sup> requirement of an annealing time of 15 min to form graphene with a 300 nm-thick nickel layer at 800 °C. The time needed for diffusion is proportional to the square of the diffusion length. Therefore, the diffusion time for 10 nm-thick layer is almost 1000 times shorter than that for the 300 nm-thick layer.

Through these modifications of existing methods and the alternating of conventional reacting agents, tremendous efforts in recent years have been made on the development of synthetic routes for graphene-based materials. How to effectively extract their advantages to design cost-effective, environmentally of friendly, rapidly and precisely controlled synthetic routes still remains a challenge for the fabrication of graphene-based inorganic nanomaterials.

#### 4. Broader applications

Graphene-based inorganic materials enjoy a wide range of <sup>65</sup> applications due to the favorable properties of graphene and the synergetic effect between multiple components. They are most commonly designed and used in lithium ion batteries, superconductors, fuel cells, solar cells, catalysts, sensors and other devices for energy storage and conversion, gas/bio-<sup>70</sup> detection, photocatalysis and so on, which have been reported detailedly in other reviews. In this section, we present some broader applications of these hybrid materials in military field, environmental protection and the design of smart devices.

#### 4.1 Application in military

<sup>75</sup> Electromagnetic wave absorbing materials are usually chosen as the coating of stealth aircrafts to avoid radar detection and are required to have wide absorption frequency range, strong absorption properties, low density, good thermal stability, and antioxidation capability. Compared with traditional ferrite
 <sup>80</sup> materials, carbon based composite materials with advantages like low density and high complex permittivity values<sup>200</sup> are often designed to improve the microwave absorption performance and electromagnetic interference shielding effect. Chemically reduced graphene oxide (r-GO) is then believed to exhibit microwave

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the surface of the r-GO nanosheets, which can introduce defect polarization and electronic dipole relaxation of groups.<sup>201</sup> Xu *et al.* decorated bowl-like Fe<sub>3</sub>O<sub>4</sub> hollow spheres on both sides of graphene. They found that the composites exhibited enhanced <sup>5</sup> microwave absorption property in the range of 2–18 GHz compared with graphene and pure Fe<sub>3</sub>O<sub>4</sub> nanoparticles,<sup>202</sup> which is even better than that of the reported M-type hexagonal ferrite<sup>203</sup>

- with the same coating thickness of 2 mm. The possible reason is that the decoration of  $Fe_3O_4$  hollow spheres on both sides of the 10 graphene nanosheets greatly enhances the dielectric loss and
- magnetic loss of the materials, thus resulting in the enhanced microwave absorption properties. Substituting Fe<sub>3</sub>O<sub>4</sub> with nitrile butadiene, Kumar's group also found significantly enhanced properties in microwave absorption of the as synthesized <sup>15</sup> graphene-based material.<sup>204</sup> It is predictable that by choosing proper magnetic components compounding with the highly conductive graphene substrate, excellent microwave absorbing material with substantial electric as well as magnetic loss will be achieved.
- <sup>20</sup> Ammonium perchlorate (AP) as the most common oxidant in composite solid propellants is often used in rockets or other related equipment. Its reaction rate, activation energy, and temperature of the thermal decomposition are closely related to the properties of solid propellants. The lower its pyrolysis
- <sup>25</sup> temperature gets, the higher the combustion rate can be.<sup>205-207</sup> Certain nanoscale transition metals and their oxides have been proved to have catalytic effect on the thermal decomposition of AP.<sup>208-211</sup> However, these nanomaterials are easy to agglomerate due to their small size, large surface area, and high surface
- <sup>30</sup> activity, which greatly affect their catalytic properties. Moreover, the agglomeration leads to an inhomogeneous dispersion of the nano-catalysts, and therefore the catalysts can not fully come into contact with the media, resulting in a decreased catalytic efficiency. Cao *et al.* fabricated Ni-graphene nanocomposites
- <sup>35</sup> with nickel particles uniformly distributed on the graphene substrate, which significantly lowered the decomposition temperature of AP.<sup>28</sup> In this catalytic process, Ni nanoparticles on graphene sheets can decrease the activation energy of decomposition of AP, while the graphene can accelerate the
- <sup>40</sup> flow of electrons, which further enhance the rate of heterogeneous decomposition of deprotonized HClO<sub>4</sub> gas on the surfaces of catalyst particles.

#### 4.2 Application in environmental protection

- <sup>45</sup> Since graphene bears high sensitivity to electrical perturbations from the surrounding environment due to its ultrasmall thickness, it has been integrated into novel sensors for detecting gas molecules and biomolecules with such advantages as small device size, low energy consumption, fast response, and a user-
- <sup>50</sup> friendly analytical platform.<sup>45,212-214</sup> Although graphene has huge potential for sensor applications, there are only a few reports on graphene sensors for online chemical detection in the aqueous environment. Access to clean water now is one of the grand challenges for people who live near factories or highly polluted
- <sup>55</sup> areas. Mercury and its compounds are among major aqueous contaminants due to their high toxicity and risk to human health.<sup>215</sup> Even a trace amount of mercury intake can lead to acute or chronic damage to the human body. In view of this urgent

problem, Chen and his group designed field-effect transistor sensors based on thermally reduced graphene oxide with thioglycolic acid (TGA) functionalized gold nanoparticles for detecting mercury ions in aqueous solutions.<sup>216</sup> The lowest mercury ion concentration detected by the sensor is  $2.5 \times 10^{-8}$  M. The drain current shows rapid response within less than 10 s after 65 the solution containing Hg<sup>2+</sup> ions was added to the active area of the Au-TGA-graphene hybrid sensors. Zhang *et al.*<sup>217</sup> also showed noncovalent surface modification of graphene for mercury detection by taking advantage of the interactions between 1-octadecanethiol and graphene; however, the resulting

To detection limit was relatively low. For the same purpose of detecting Hg<sup>2+</sup>, Chen *et al.*<sup>218</sup> functionalized graphene with metallothionein type II protein via the precoated pyrene linker molecules, which reacted with protein on one end and attached to graphene on the other end through the strong  $\pi$ - $\pi$  stacking 75 covalent bonding, and excellent results were achieved. These examples suggest that graphene-based hybrid structures are promising for low-cost, portable, real-time, heavy metal ion detectors.

Certain chemical reagents like hydrazine are known as highly <sup>80</sup> poisonous and pose danger to human health and other creatures in the nature. However, they are still commonly used in the laboratories for the synthesis of various materials and the residues remain a major problem. Rh-Ni-graphene hybrid material was recently found to exert 100% selectively and exceedingly high <sup>85</sup> activity to complete the decomposition reaction of hydrous hydrazine at room temperature owing to the role of graphene role as a communicating platform in facilitating the electron transfer and mass transport kinetics during the catalytic reaction process.<sup>219</sup> The same material may be further applied in <sup>90</sup> decomposition of other hazardous reagents and minimize their harmful effects on human body and the environment.

Greenhouse effect is another major environmental problem that people face in the twenty first century. It is urgently important to reduce the excessive carbon dioxide produced by human 95 activities in the atmosphere and stop its negative effect to the world climate or to other aspects. Lately, a high conversion of CO<sub>2</sub> into renewable fuels was realized by Zhou et al. using Ti<sub>0.91</sub>O<sub>2</sub>-graphene composites as catalyst.<sup>220</sup> They pointed out that upon band gap excitation of Ti0.91O2 nanosheets, holes and 100 electrons are generated in the valence band and the conduction band, respectively. The electrons and holes either take part in redox reactions at the surface or recombine, and the recombination process generally has faster kinetics than the redox reactions. Graphene nanosheets compactly stacking with Ti0.91O2 105 nanosheets allows the photogenerated electron to migrate fast from Ti0.91O2 nanosheets into graphene, leading to the spatial separation of the electrons and holes. It thus enhances lifetime of the charge carriers and therefore improves the efficiency of the photocatalytic process. The efficient charge transfer in the case of 110 Ti0.91O2-graphene may originate from the surface conjugation (d- $\pi$  conjugate) of titania with graphene.

#### 4.3 Application in smart devices

One unique property of the two-dimensional honeycomb lattice <sup>115</sup> of graphene is the linear energy dispersion relationship around the Dirac point where the carriers behave like relativistic

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particles.<sup>1, 213</sup> Recently, novel nanoscale electronic devices in this region have been systematically investigated. Xu *et al.* demonstrated that the metal/graphene contact can be switched between 'ohmic-like' and 'space charge region-limited' states and <sup>5</sup> robust bistable memory cells were achieved by properly applying electric bias when low work function metal electrodes, graphene active layer, and self-assembled monolayers (SAM) modified substrate were used in combination.<sup>221</sup> The memory elements exhibited high performance in terms of on-off ratio of current, <sup>10</sup> cycling endurance and retention time. They interpreted the bistable contact states with a density-of-states (DOS) limited space-charge region model and the mechanism is qualitatively substantiated by Kelvin Probe Force Microscopy (KPFM). The results illustrate the great potential of graphene in future high-

<sup>15</sup> efficiency low-cost memories and the strategy of utilizing the small DOS of graphene around its Dirac point provides an effective route for improving the on/off ratio in graphene devices. The combination of the high transparency, wideband tunability,

and excellent mechanical properties of graphene makes graphene very promising candidate for flexible electronics, 20 a optoelectronics, and phonotics.<sup>222-224</sup> The technical breakthrough of large-scale graphene synthesis in the past few years has further accelerated the use of graphene films as transparent electrodes.<sup>225,</sup> <sup>226</sup> Hong et al. presented a new route to achieve low sheet 25 resistance values in large-scale single-layer graphene by introducing a transparent thin ferroelectric polymer coating.<sup>227</sup> The as-obtained graphene-ferroelectric transparent conductors (GFeTC) exhibited a low sheet resistance value at ambient conditions due to a large electrostatic nonvolatile doping from 30 ferroelectric dipoles. Beyond having low sheet resistance values, the GFeTCs are also highly transparent (>95%) in the visible wavelength range, making them suitable for optoelectronics applications where a combination of both is required. With the excellent mechanical support the hybrid GFeTCs fabrication can 35 also easily be integrated with industrial-scale fabrication processes such as roll-to-roll techniques.

In the medical field, photothermal therapy (PTT) employs photo-absorbing agents to generate heat from optical energy, leading to the 'burning' of cancer cells. Graphene with strong <sup>40</sup> optical absorbance in the NIR tissue transparency window, have been proposed as photothermal agents for PTT treatment of cancer.<sup>228,229</sup> Liu *et al.* designed a novel probe based on Fegraphene nanocomposite, which was noncovalently functionalized with a biocompatible polymer, polyethylene glycol <sup>45</sup> (PEG), for applications in multimodal imaging guided

- <sup>45</sup> (PEO), for applications in infinitinodal inflaging glided photothermal therapy of cancer.<sup>230</sup> The as obtained Fe-PEGgraphene product with intrinsic high NIR optical absorbance and strong magnetic property revealed high tumor uptake of the nanocomposite in a 4T1 murine breast tumor mouse model. In the
- <sup>50</sup> designed in-vivo photothermal therapy (PTT) study, the tumors of mice treated with Fe-PEG-graphene were effectively ablated by irradiation with an 808 nm NIR laser at a low power density than usually applied gold nanomaterials.<sup>231-234</sup> Importantly, no noticeable in-vitro toxicity or in-vivo side effects were observed <sup>55</sup> at the tested doses. These data greatly promise future explorations
- of graphene-based functional nanocomposites for cancer theranostic applications.

#### **5.** Conclusions and outlook

Driven by the constant demand for optimization of graphenebased inorganic composite properties, particular efforts are directed towards the design and formation of specially constructed hybrid architectures rather than the random mixtures. The roles of graphene sheets in these designs could be 65 summarized as follows: act as a substrate for supporting more than one kind of inorganic nanomaterials or other materials; form soft covers to enwrap the inorganic nanoparticles; uniformly disperse in inorganic matrices or stack with ultrathin inorganic nanoplates alternately to form multilayer films. Diverse new 70 approaches and techniques, such as gas-liquid interface reactions, chemical reduction with special reducing agents, modified deposition methods have been developed for fabricating graphene-inorganic nanocomposites different from traditional synthetic routes including direct decomposition of precursors, 75 hydrothermal/solvothermal techniques, sol-gel processing or template methods. These newly designed nanocomposites exhibit excellent properties and improved functionalities due to the synergetic effects between graphene and the inorganic components, which thus have been explored to broader so applications in the fields of military, smart devices and environmental protection (Figure 15). It is expected that the development of practical and convenient intelligent devices to improve the quality of people's daily life is one of the most promising directions in the progress of graphene-inorganic 85 nanocomposites.



Fig.15 Illustration of new trends in the structure, synthetic method and application designs of graphene-based materials.

With the rapid development of graphene–inorganic <sup>90</sup> nanocomposites, more kinds of inorganic materials will be blended with these special carbon sheets, and numerous applications in various fields are arising. However, despite all of the promising results obtained so far, further effort for graphene– based inorganic nanocomposites is still needed to realize their <sup>95</sup> practical applications. For example, strictly high-quality graphene as the core component of the hybrid material is often hard to attain. It greatly affects the reinforcement of graphene in the

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novel properties and potential applications. To date, it is still difficult to synthesize graphene with controllable size, layer number, composition and defect level in a cost-effective and environmentally friendly manner, although promising steps in

- 5 this direction have been witnessed. At the same time, it is of great importance to improve the adhesion between graphene and inorganic components, which is especially important for applications that involve charge transfer processeses. A poor interfacial contact will destroy the synergetic effects, and thus
- 10 weaken the performance of the nanocomposites. To avoid these drawbacks various surface functionalization methods, synthesis techniques, and novel structures should be developed to make sure a large interfacial area between graphene and inorganic components. A bigger challenge involves the exact mechanism
- 15 study of assembly behaviors of graphene sheets with inorganic building blocks. How these synthetic methods precisely correlate with inorganic nanostructures stabilized on graphene is still rarely known. Therefore successful design of the material requires improvements in methodology to ensure better understanding of
- 20 interaction mechanism of the components and structure-property relationship in the nanocomposites. Finally, the successful application and further development of graphene-based inorganic nanocomposites in broader fields can not be realized without the multidisciplinary efforts from math, physics, chemistry, biology,
- 25 medical and materials science. Therefore more versatile fabrication/synthesis strategies are expected to be developed in future for the continuous advancement of graphene-based functional composites.

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### **Graphical** Abstract

#### Review on latest design of graphene-based inorganic materials

Na Li, Minhua Cao\* and Changwen Hu



This review presents an overview of the latest design of structure, synthetic methods and applications of graphene-based inorganic nanocomposites.