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The Routes to Magnetic Graphene, from Decorations with Nanoparticles to the Broken Symmetry of its Honeycomb Lattice Bonds

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Abstract: Pristine graphene is nonmagnetic because the outer electrons in the rings of its honeycomb lattice are merged into sigma- and pi- bonds. To have magnetic graphene, methods have been proposed to break the bond symmetry to obtain unpaired electrons and spins, so that their interaction can turn on the graphene magnetism. These methods are therefore based on the intrinsic nature of graphene. Other methods are based on the extrinsic decoration of graphene layers with magnetic nanoparticles. Here, we discuss the routes to have graphene magnetized in intrinsic and extrinsic manners, and some of its applications. In particular, the nitrogen-doped graphene is considered. The Ruderman–Kittel–Kasuya–Yosida interaction is also proposed in a very concise manner. Short discussion about graphene substitution with nitrogen-doped biochar and iron-decorated biochar is proposed too.

Keywords: Graphene, Magnetic Graphene, Nitrogen-Doped Graphene, RKKY Interaction, Graphdiyne, Topological frustration, Clar's Goblet, Twisted Graphene, Spintronics, Nitrogen-doped Biochar, Magnetic Iron Oxide Nanoparticles, Fe₃O₄, Magnetite, Electromagnetic Interference Shielding effectiveness, EMI-SE, Microwaves Absorption

1. Introduction

Carbon is the chemical element which is the basis for organic compounds. Including itself, carbon is stable bonding with many elements, allowing the formation of key molecules for life. As pure element, we can find it in diamond, the material possessing the highest hardness and the best thermal conductivity among the natural materials (Sparavigna, 2002). In diamond, carbon arranges itself in a face centered cubic Bravais lattice. In graphite, carbon is stacked in layers of graphene, which is possessing a honeycomb lattice. Actually, the term "graphene" is coming from "graphite" and the suffix -ene, which is reflecting the abundance of double bonds according to organic chemistry nomenclature (Katsnelson, 2016). The International Union of Pure and Applied Chemistry,

IUPAC, recommends the name "graphite" for the three-dimensional material, and "graphene" only when the properties of the individual layers are considered. However, besides for the single layer, in literature we can find the term "graphene" also used for a multilayer carbon sheet, because a good single layer of graphene free from defects is hard to create and manipulate (Giorcelli & Bartoli, 2019).

In the Fig.1, cartoons are showing that each atom of a graphene layer has three nearest neighbors in the honeycomb lattice. The structure provides graphene with peculiar conduction and valence bands touching each other at Dirac points, the vertices usually labeled K and K' of its Brillouin zone, with linear massless dispersion (see Novoselov et al., 2005).

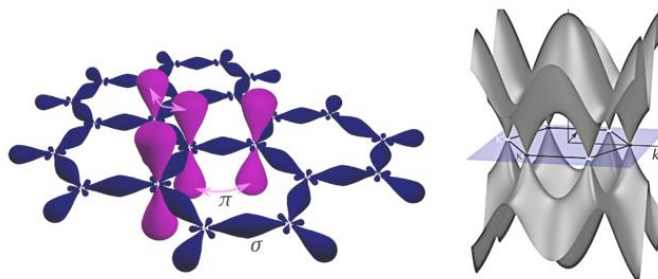


Fig.1. On the left: sigma- and pi- bonds in graphene. Sigma bonds are due to overlap of sp² hybrid orbitals (Yang et al., 2018). Pi bonds are emerging from p_z orbitals. Only a few neighboring p_z orbitals are shown, for clarity of the cartoon (courtesy Ponor, under CC BY-SA 4.0 License). On the right: the electronic band structure of graphene. The valence and the conduction bands touch themselves at the vertices of graphene hexagonal Brillouin zone. Being the dispersion linear, the valleys have the name of "Dirac cones" (courtesy Ponor, under CC BY-SA 4.0 license).



Graphene is able of conducting heat and electricity in a very good manner, of course along its plane, and has remarkable properties fundamental for several applications, ranging from electronics to biology (Avouris & Xia, 2012, Sherlala et al., 2018, Giorelli & Bartoli, 2019, Razaq et al., 2022, Zhang et al., 2022). Here we aim to consider how graphene can gain magnetic features, that is how to convert graphene into "magnetic graphene", a material suitable for spintronics (Han et al., 2014).

Pristine graphene is nonmagnetic because the outer electrons in the rings of the honeycomb lattice are merged into sigma- and pi-bonds. To obtain the magnetic graphene, methods "are carried out to break the symmetric bonds to release the unpaired electrons and generate net spins" (Tang et al., 2020). When these spins are interacting, a magnetic ordering is generated. Actually, "the coexistence of pi- and sigma-bonding in graphene is so unique that it [can provide] the possibility to simultaneously generate the localized spins and couple these spins when modifying these bonds" (Tang and coworkers are mentioning González-Herrero et al., 2016). Moreover, the magnetism studies about graphite, nanotubes and fullerenes can be joined with those regarding graphene, because all these forms of carbon have the same basic block (Tang et al., 2020). This is immediately evident in the case of carbon nanotubes, where a graphene layer is wrapped on itself. For nanotubes, we can find, as for graphite layers, a remarkable thermal conductivity (Sparavigna & Ravetti, 2005, Sparavigna, 2008).

In applications demanding lightweight magnets and for carbon-based spintronic devices, magnetic graphene assumed a specific importance (Tombros et al., 2007, Tang et al., 2020, Li et al., 2022). In agreement with Tang and coworkers, we can add that it exists an urgent need for the development of further methods for synthesizing magnetic graphene. Before addressing this material, let us add that research about magnetism in low-dimensional carbon materials is not limited to graphene. In the article by Li and coworkers, 2022, for instance, we can find discussed nanotubes and graphdiyne too. The structure of graphdiyne (GDY) is a one-atom-thick planar layer where benzene rings are connected by diacetylene bonds. The aim of the investigation by Li et al., 2022, is also that of promoting 2D carbon-based materials in spintronics and "lay a foundation for the preparation of high-performance carbon-based magnetic materials with specific magnetic properties" (Li et al., 2022).

Here, we will consider the methods based on the breaking of the bond symmetry to obtain unpaired spins, methods that we can consider based on the

intrinsic nature of graphene. Other methods are based on the extrinsic decoration of graphene layers with magnetic nanoparticles. Let us start from the decoration.

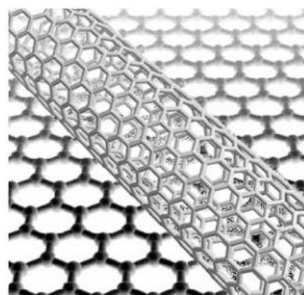


Fig.2. Nanotubes are wrapped graphene layers.

2. Decoration by means of magnetic nanoparticles

To have magnetic graphene, an apparently simple route exists based on the decoration of its honeycomb lattice with nanoparticles. We have encountered decoration in a study about the magnetic iron oxide nanoparticles (Fe_3O_4) dispersed in supporting materials to produce composites that can better respond to electromagnetic wave fields, absorbing a part of their energy (Sparavigna, 2023). Using the magnetic nanoparticles and suitable dielectric properties of supporting materials, we have light weight "absorption-type" electromagnetic shields, relevant for absorbing microwaves.

To prepare an absorption-type shielding material, we need suitable permittivity and permeability, accompanied by a finite electrical conductivity. As told by Arora et al., 2014, particles with high dielectric constant or high magnetic permeability, like those of Fe_3O_4 , are used as fillers in polymeric materials to increase their shielding performance. Responding to an external magnetic field, magnetic nanoparticles are able of absorbing its energy (Ni et al., 2009). Moreover, the magnetic losses produced by nanoparticles act in a synergistic manner with the dielectric losses which are causing dissipation too (Qin et al., 2022). Particularly relevant are considered carbon porous materials, biochar, carbon nanotubes, filaments, fibers, and graphene for electromagnetic wave absorbers (Devi et al., 2022).

The manner of decorating graphene with magnetic nanoparticles is discussed, for instance, by Yao et al., 2012, but a large literature exists. Limiting ourselves to the magnetite nanoparticles, we can find the application of "magnetic graphene" to microwave absorption in Zheng et al., 2014, Zhu et al., 2017, Hu et al., 2021, Manna & Srivastava, 2021, Shu et al., 2022. Zheng et al., 2014, are proposing particles glued

on graphene nanosheets: SEM and TEM images are showing that the Fe_3O_4 nanoparticles "with relatively uniform size are well-distributed on the surface of graphene nanosheet" (Zheng et al., 2014).

About the decoration method, let us just consider that given by Shu et al., 2022. Graphene oxide is ultrasonic dispersed into N-dimethylformamide (DMF). Metal salts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 with an organic ligand, the p-phthalic acid (PTA) are added into the suspensions. Under solvothermal condition, the components react forming FeZn-MOFs/RGO precursors. The precursors are changed into $\text{Fe}_3\text{O}_4/\text{C}$ decorated graphene by a carbonization treatment at $600\text{ }^\circ\text{C}$ for 2.0 h under argon atmosphere (Shu et al., 2022). "MOFs" means "metal-organic frameworks". "RGO" is the reduced graphene oxide. In the article by Shu et al. we have in the Figure 1 some cartoons representing the fabrication process of decorated graphene. In the rightmost cartoon, the proportion between the sizes of nanoparticles and of graphene honeycomb cells is violated. The proper manner to depict the decoration of graphene by a nanoparticle is to imagine the nanoparticle as an unwrapped candy, stuck to its wrapper, that is the graphene layer.

Besides microwave absorption application, we find the use of $\text{Fe}_3\text{O}_4/\text{graphene}$ composites for storage in lithium batteries (Lian et al., 2010, Su et al., 2011), for absorption of substances (Kassaei et al., 2011, Chang et al., 2012, Guo et al., 2015), for thermal properties (Askari et al., 2017), and so on. Regarding other carbon materials, such as the carbon nanotubes for instance, let us mention Li et al., 2022, about the magnetization by means of Fe_3O_4 nanoparticles. These particles are combined with Al_2O_3 to synthesize uniform and dense vertically aligned carbon nanotubes arrays by atomic layer deposition (Wang et al., 2011). For multiwalled nanotubes decorated with Fe_3O_4 see also Fan and Li, 2012.

In conclusion, the decoration of graphene by means of magnetic nanoparticles is a method which we can define as extrinsic, being not intrinsically based on the electronic nature of graphene.

3. Nitrogen doping

Li et al., 2017, proposed nitrogen-doped (N-doped) graphene decorated by Fe_3O_4 nanoparticles. The researchers used a solvothermal method to disperse Fe_3O_4 nanocrystals on N-doped sheets. In this manner, Li and coworkers obtained "synergistic microwave absorbers". "Taking the advantage of synergistic effect between Fe_3O_4 nanocrystals with magnetic loss and nitrogen-doped graphene with dielectric loss" (Li et al., 2017), the graphene hybrids have an enhanced

microwave absorption (N-doping is reducing conductivity too). The maximum reflection loss observed is of -65.3 dB , achieved at 6.8 GHz with a matching thickness of 3.4 mm . The microwave absorption peak frequency can be tuned by changing the nitrogen-doping of graphene (Li et al., 2017).

In the proposal by Li et al. for magnetic graphene we have it given in an N-doped form. Let us concentrate on this doping, because it can be used to disrupt the bond symmetry of the honeycomb lattice, obtaining magnetism in an intrinsic manner. A defect, such as a vacancy or a dopant atom, can act "breaking the electrical symmetry of the structure", producing an induced magnetism depending on the defect concentration density (Dankworth, 2020). Defects are in fact giving "the unpaired electrons" that, with the pi-bond, "play an essential role in modifying the magnetic properties of graphene" (Yutomo et al., 2021).

The use of nitrogen N as a dopant is the route that we can find proposed by Quan et al., 2017, to have "magnetic graphene" for microwave absorbing application. The route is "transforming graphene from diamagnetic to ferromagnetic and meanwhile suppress the conductivity" (Quan et al., 2017). Quan and coworkers assert that in the nitrogen-doped graphene the magnetism is produced by the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. The N-doped graphene is obtained by means of a facile hydrothermal method from graphene oxide and urea precursors. In Shao et al., 2010, we can find references to other methods to obtain N-doped graphene, comprised the proposal of a method based on the exposition of graphene to nitrogen plasma.

Graphene is an excellent charge conductor, meaning an impedance mismatch for electromagnetic waves at the interface between this material and air, mismatch which means wave reflection. A possible strategy mentioned by Quan et al, 2017 to have microwave absorption capability is to "lower the conductivity of graphene and make it magnetic simultaneously". To turn on the magnetism in graphene, a chemical doping can be used, which is keeping the graphene structurally stable but, at the same time, is introducing the point defects. Among dopants, "N atom is considered as an ideal candidate in that it has equivalent atomic size with carbon atom" (Quan et al., 2017). The researchers are mentioning the presence of *pyrrolic* nitrogen N-5 as the main actor in magnetic graphene. In Błóński et al., 2017, it is the doping with *graphitic* nitrogen considered as the trigger of graphene ferromagnetism. For a picture of graphitic-N and pyrrolic-N, and pyridinic-N and pyrazole-N in graphene, see please the Figure 1 in Li et al., 2016, an

article about the graphitic nitrogen-doping in thermally treated graphene with ammonia, and the Figure 1, of Vesel et al., 2020, a review about the strategies for having N-doped graphene-like materials.

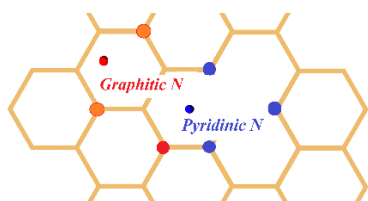


Fig.3. Graphitic and pyridinic N in graphene.

In January 2017, Błoński et al. reported "the first example of ferromagnetic graphene" obtained with a controlled doping nitrogen. The magnetic properties resulted strongly dependent on "both the nitrogen concentration and type of structural N-motifs generated in the host lattice" (Błoński et al., 2017). When the N-doping of graphene exceeds the 5%, the graphene turns from nonmagnetic to ferromagnetic at about 69 K. Simulations told that "magnetic effects were triggered by graphitic nitrogen, whereas pyridinic and chemisorbed nitrogen contributed much less to the overall ferromagnetic ground state" (Błoński et al., 2017). The researchers are also stressing that, among the strategies to have magnetic graphene, the doping of the honeycomb lattice with noncarbon atoms is relevant for "spintronic, optoelectronic, and magneto-optical applications" (Błoński et al., 2017). It is also stressed that the nitrogen doping has been extensively studied, and a long list of applications of N-doped graphenes proposed: Li-ion batteries, fuel cells, field-effect transistors, ultra- and supercapacitors, photocatalysis, electrochemical biosensing. Actually, Błoński et al. in their article reported "the emergence of a magnetically ordered state in graphene doped solely with nitrogen".

4. Missing atoms and graphite

In 2010, Ugeda and coworkers discussed the missing atoms "as a source of carbon magnetism". In graphene, there are localized electronic states at zigzag edges and vacancies (Ugeda et al., 2010), which produce "an extreme enhancement" of spin polarizability. "It seems likely that similar phenomena also take" in other carbon materials, such as graphite. Consequently, a "possibly magnetic ordering may exist in single layer graphene and graphite" (Ugeda et al., 2010).

Ugeda and coworkers are reporting two references about magnetic order in graphite with lattice defects, even at room temperature. The first is by Esquinazi, et al., 2003, where evidence is given that proton irradiation of pyrolytic graphite samples "triggers ferro- or ferrimagnetism". Experimental data give

magnetic ordering stable at room temperature. The second is by Ohldag et al., 2007, that presented a spectro-microscopic analysis, at room temperature, of proton irradiated carbon. Samples are metal-free. The researchers "demonstrate that the magnetic order in the investigated system originates only from the carbon pi-electron system" (Ohldag et al., 2007).

In the article by Ugeda et al., 2010, it is exposed that the researchers created "perfectly characterized single vacancies on a graphite surface". By means of low temperature scanning tunneling microscopy (LT-STM), they investigated the vacancies, identifying localized electronic resonances at the Fermi energy. These states can be linked to magnetic moments in an all-carbon material. "In addition, ... ferrimagnetism is favored in multilayered graphene samples" (Ugeda et al., 2010).

5. Frustration of Kekulé structure

In Dankworth, 2020, among the mentioned mechanisms to have the magnetic graphene we can find the frustration of the graphene "Kekulé structure". Graphene carbon atoms are arranged in a honeycomb Kekulé structure where, due to Pauli's exclusion principle, electron pairs which are referring to the same orbital must have opposite spin. No unpaired electrons are consequently left in the organic structure (Dankworth, 2020), and graphene turns out being non-magnetic. But, if we can have just an electron in an orbital, its spin remains unpaired. Consequently, "defying the Kekulé structure" in an approach of topological frustration that might produce magnetic graphene (Dankworth, 2020). Besides the use of vacancies and doping, it is possible to obtain magnetism at nanoscale in structures such as the "Clar's goblets" (Mishra et al., 2020). It was in 1972 that Erich Clar proposed "a bow-tie-shaped nanographene," with topological frustration in the pi-electron network. In this nanographene, it is "impossible to assign a classical Kekulé structure without leaving unpaired electrons, driving the system into a magnetically non-trivial ground state" (Mishra et al., 2020). Mishra and coworkers have reported the experimental realization and characterization of the Clar's goblet. Accordingly, the researchers claim they proved the "long-predicted paradigm where topological frustration" is producing unconventional magnetism, "with implications for room-temperature carbon-based spintronics" (Mishra et al., 2020).

6. Twisted graphene

Peng et al., 2022, are proposing a discussion about the graphene-based magnetic hybrids, to obtain high efficiency for microwave absorption. "Nitrogen doping strategies are one of the most commonly used strategies for achieving metal-free magnetic"

graphene (Peng et al., 2022), but "Recently, bilayer GE [graphene] with a magic twist angle ... is found to be ferromagnetic" (Peng et al. are mentioning the work by Sharpe et al., 2019). "When two sheets of graphene are stacked at a small twist angle, the resulting flat superlattice minibands are expected to strongly enhance electron-electron interactions" (Sharpe et al., 2019). The enhanced interaction changes the twisted bilayer graphene into a ferromagnet. Peng et al. write that, in the magic-angle twisted bilayer graphene (TBG), it is expected the generation in the superlattice of large orbital magnetic moment. The "magnetic properties of TBG are highly dependent on the lattice arrangement between the GE and the encapsulation layer (hexagonal boron nitride, hBN)" (Peng et al., 2022). Associated to the bilayer graphene encapsulated by hBN, we have the possibility to tune the properties of graphene by means of a "moiré pattern" (Bistrizter & MacDonald, 2011), according to the misalignment of top and bottom hBN layers.

7. Magnetic moment interactions

To promote spintronics, as told by Zhang et al., 2023, it is fundamental to understand the source of magnetism in magnetic materials. In fact, it is necessary to understand how the magnetic moments are each other interacting, to "trigger spontaneous magnetization" (Zhang et al., 2023). The spin magnetic moments, which are present in the system, can produce some long-range magnetic orders - ferromagnetism, antiferromagnetism, ferrimagnetism - according to the exchange interactions among them. Zhang and coworkers are proposing a classification of interactions in five types: the *direct* exchange interaction, the super-exchange interaction, the double-exchange interaction, the Ruderman-Kittel-Kasuya-Yoshida interaction, previously mentioned about Quan et al. article and known as RKKY model, and the itinerant electron model. In any case, "whatever the type of magnetic exchange interaction", the result is the order of magnetic moments "in different ways within a certain range, thus building different types of long-range magnetic orderings" (Zhang et al., 2023).

The *direct* exchange interactions are given in Zhang et al., 2023, in the form of the Heisenberg Hamiltonian in Heitler-London approximation, $H = -2 \sum_{i < j} J_{ij} \vec{S}_i \cdot \vec{S}_j$, where J_{ij} is the exchange integral constant between i -th and j -th spins. $J_{ij} > 0$ means ferromagnetic coupling, whereas $J_{ij} < 0$ is giving antiferromagnetic coupling. The other four interactions make the magnetic moments align in parallel or antiparallel modes through *indirect* ways. Actually, "the presence of unpaired electron spins (up or down) and ferromagnetic interaction is the key to

obtaining ferromagnetism" (Zhang et al., 2023). In the article by Zhang and coworkers we can find the strategies and experimental methods for introducing magnetism into transition metal oxides.

"It is generally accepted" that ferromagnetism in graphene is appearing because of an indirect interaction between "localized magnetic moments within the materials, mediated by the charge carriers" (Miao et al., 2016). The coupling is the RKKY interaction. Miao and coworkers prepared graphene samples with different nitrogen contents, by means of a method based on self-propagating high-temperature synthesis (SHS). The N-doped SHS produced graphene samples exhibit "both high Curie temperatures (higher than room temperature) and high coercive force. Thus, it is considered a good candidate for nanomagnetic applications" (Miao et al., 2016).

About RKKY model, let us consider Kogan, 2019, who studied the interaction in graphene at finite temperature. "More than 60 years ago it was understood that localized spins in metals can interact by means of Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism" (Eugene Kogan is mentioning also his previous contribution in the Physical Review B). Kogan explains that the *indirect* exchange coupling between two spins in a non-magnetic host, is mediated by conduction electrons. It can be calculated in second order perturbation of exchange interaction between the magnetic impurity and electrons. RKKY interaction appears in several materials: disordered conductors, superconductors, topological insulators, carbon nanotubes and so on, "but most thoroughly in graphene" (see references given in Kogan, 2019).

Let us consider two magnetic moments in the graphene; "The first moment perturbs the conduction electrons, which is seen by the second moment leading to an indirect exchange interaction as illustrated in Fig. (1)" of the article by Sherafati and Satpathy, 2012. In the discussion given by the authors, we find told that, instead of the $1/R^2$ fall-off with distance R proper of 2D metals with quadratic dispersion, the RKKY interaction in graphene has a $1/R^3$ dependence on distance, due to the linear band structure. Moreover, because of the interference between the Dirac cones in the Brillouin zone, an oscillatory behavior of the RKKY interaction is observed. In any case, the interaction is ferromagnetic when moments are located on the same sublattice, antiferromagnetic for location on opposite sublattices (Sherafati & Satpathy, 2012).

8. The Ruderman-Kittel model

The model for the coupling of nuclear magnetic moments or localized electron spins in a metal through

conduction electrons has its origin in the work by Malvin Ruderman and Charles Kittel (Ruderman & Kittel, 1954). "The interaction appears to account qualitatively for the broad nuclear spin resonance lines observed in natural metallic silver" (Ruderman & Kittel, 1954).

By means of the perturbation theory, the researchers proposed a model for an indirect exchange coupling, where the nuclear spin of one atom has a hyperfine interaction with a conduction electron, and this conduction electron, then, interacts with another nuclear spin thus creating a correlation energy between the two nuclear spins. Electrons are given as Bloch wave-functions. Therefore, - following the article by Ruderman and Kittel, 1954 - let us consider a metal crystal in which all but two of the nucleons are nonmagnetic. The electron wave functions (Block functions) are scattered by hyperfine interaction with each of magnetic nucleons. "The total wave function seen by one magnetic nucleon will depend on the spin orientation of the other, thus establishing an indirect spin-dependent coupling between the two nucleons" (Ruderman & Kittel, 1954). The calculation proceeds

$$H(R_{ij}) = \frac{\mathbf{I}_i \cdot \mathbf{I}_j |\Delta_{k_m k_m}|^2 m^*}{4 (2\pi)^3 R_{ij}^4 \hbar^2} [2k_m R_{ij} \cos(2k_m R_{ij}) - \sin(2k_m R_{ij})]$$

R_{ij} is the distance between nuclei i and j , and spins are given by $\mathbf{I}_i, \mathbf{I}_j$. $\Delta_{k_m k_m}$ is representing the strength of hyperfine interaction (Δ is the hyperfine interaction operator), and can be related to the observed atomic hyperfine structure splitting. m^* is the effective mass of the electrons in the crystal, and k_m the Fermi momentum. Then, the interaction between nucleon spins in metals assumes a final form as (Ruderman & Kittel, 1954), $H = \sum_{i>j} \sum_i A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$, after summation on all the spins in the lattice. Coefficient A_{ij} is representing the expression given above.

This is the base model. Kogan, 2013, considered a toy model of graphene, with free electrons, described by the 2D Dirac Hamiltonian, giving an effective exchange RKKY interaction between $\mathbf{S}_1, \mathbf{S}_2$ spins of magnetic impurities, positioned at relative radius vector R ; then $H = -\frac{1}{4} J^2 \chi(R) \mathbf{S}_1 \cdot \mathbf{S}_2$, where J is the contact exchange interaction between spins and graphene electrons. $\chi(R)$ is the free electrons charge susceptibility. The susceptibility depends on the sublattices A and B of graphene. In fact, the honeycomb lattice of graphene is based on a unit cell containing the two atoms (see Kavitha & Jaiswal 2016). The susceptibility is given by Eq.30 in Sherafati & Satpathy, 2011.

by means of second-order perturbation theory. The final form $\vec{I}_i \cdot \vec{I}_j$ is that of an exchange operator.

Let us assume first an electron moving in a perfect periodic lattice. The interactions with nuclear spins and lattice vibrations are neglected. The electron is described by Bloch function $\phi_{\mathbf{k}}(\mathbf{r})$, conveniently normalized to 1. "The interaction between nuclear and electron spins is manifest in hyperfine structure. This same interaction will of course couple Bloch functions of different \mathbf{k} , i.e., scatter conduction electrons" (Ruderman & Kittel, 1954). The scattering matrix element from \mathbf{k} to \mathbf{k}' by the moment $\boldsymbol{\mu}$ on the nucleus at $\mathbf{r} = \mathbf{R}_i$ is based on \mathbf{S} and \mathbf{I} , the spin operators for electron and nucleus. Being the hyperfine interaction weak compared to the electron-lattice coupling, we can assume it as a perturbation. Then, assuming the interaction between the spins of nuclei i and j at the lattice positions $\mathbf{r} = \mathbf{R}_i$ and \mathbf{R}_j , through a double scattering of electrons ($\mathbf{k} \rightarrow \mathbf{k}' \rightarrow \mathbf{k}$), after perturbative calculation we arrive at interaction:

9. Graphene, pristine graphene and graphene oxide

We have mentioned the "pristine graphene", meaning the graphene in its ideal condition, without defect. But, as told by Taylor-Smith, 2022, "more often than not, when we mention graphene, we are actually referring to graphene oxide which has been reduced either chemically or thermally to yield graphene". And also "The presence of oxygen can make the material easier to work with, but this graphene is not pure, or 'pristine'" (Taylor-Smith, 2022).

Could we here consider "magnetic graphene oxide"? Yes. A discussion of it is proposed by He et al., 2021. In its extrinsic form, it is a composite with magnetic nanoparticles and graphene oxide (GO). In Liu et al., 2018, for instance, "a direct, ultrafast, green and non-toxic strategy for scalable production of GO-Fe₃O₄ hybrids" is proposed, that is we have GO with Fe₃O₄ nanoparticles.

Besides GO, we have also the reduced graphene oxide (RGO). RGO is GO processed by chemical, thermal and other treatments to reduce the oxygen content (Papageorgiou et al., 2015). And magnetic RGO exists, in an N-doped form too. Hu et al., 2021, produced an RGO@Fe₃O₄/silicone rubber composite for microwave absorption, with minimum reflection loss RL of -59.4 dB at 8.0 GHz, in a thin layer of 1.2 mm. In Wang et al., 2020, we can find the embedding

of CoFe_2O_4 nanoparticle into an N-doped reduced graphene oxide (N-RGO) aerogel. This material is, according to Wang and coworkers, a unique microwave absorber. It is observed that RL reaches -60.4 dB at 14.4 GHz, thickness of 2.1 mm, filler loading ratio of 20 wt%. "Notably, at only 3 mm, its effective absorption bandwidth can completely cover X-band" (Wang et al., 2022).

The graphene oxide and the reduced GO, also in their N-doped forms, deserve a separate discussion.

10. Graphene vs Biochar

N-doped graphene has been extensively studied theoretically and experimentally for its wide range of applications and for improvement of spintronics. However, graphene has a relevant cost. "Despite its exciting applications, graphene is not currently widely used, and cost is a key reason why", as told by Pistilli, 2022, who is proposing a discussion about the factors impacting graphene cost. In 2010, the cost was of "tens of thousands of dollars" to have "a piece of high-quality graphene the size of a postage stamp" (Pistilli, 2022). The cost decreased but it is still expensive, with pricing oscillating according to its quality.

In the case of magnetic N-doped graphene, and due to the cost of graphene, a reasonable question could be: is it possible to find a significantly cheaper substitute? We have also seen that Li et al., 2017, proposed the nitrogen-doped graphene decorated by Fe_3O_4 nanoparticles. Is an alternative existing?

For the microwave absorption the answer is positive as discussed recently (Sparavigna, 2023), and it is provided by biochar, the solid residue of pyrolysis of biomass obtained by thermochemical decomposition at moderate temperatures under oxygen-limiting conditions (Brassard et al., 2019, Han & Kim, 2008, Ok et al., 2015, 2018, Giorcelli et al., 2021, Das et al., 2021, Yasim-Anuar et al., 2022, Bartoli et al., 2023). As catalyst, biochar is discussed by Lee et al., 2017. But several other applications are possible. In the case of catalysis for instance, we can find the approach by Yu et al., 2019, based on the magnetic nitrogen-doped biochar (XRD and magnetic characterization demonstrated the magnetic component as $\gamma\text{-Fe}_2\text{O}_3$).

Biochar is among the carbon materials that emerged as sustainable alternatives in catalysis. In Chu et al., 2022, we find the magnetic nitrogen-doped biochar used for the removal of antibiotics from aqueous solutions. The composite is a nickel-containing and nitrogen-doped biochar (Ni@NBC), synthesized via polymer-assisted metal deposition and pyrolysis. "The as-prepared Ni@NBCs can adsorb different antibiotics due to their N-doped graphitic structure"

(Chu et al., 2022). The XPS spectroscopy reveals for the composite prepared by Chu and coworkers peaks corresponding to pyridinic N, pyrrolic N, and graphitic N, "indicating the formation of N-doped carbon layers" (Chu et al., 2022).

11. Green graphene from biochar

The first route to magnetic graphene that we have discussed was based on the decoration of graphene with nanoparticles. We have also described the decoration by a nanoparticle as an unwrapped candy, stuck to its wrapper, the graphene layer. Here, let us consider the article by Ghogia et al., 2022, where we can find the candy as wrapped in many graphene layers. The subject of the article is the synthesis and growth of a "green graphene" from biochar. The method is based on the iron-catalyzed graphitization of biomass. The biochar produced by Ghogia and coworkers is coming from pyrolysis of iron-impregnated cellulose, at different high temperatures.

"Biomass precursors, which are complex mixtures of cellulose, hemicellulose, lignin, and inorganic elements, can be used as *alternative sources to synthesize highly graphitic carbon*" (Ghogia et al., mentioning Yoo et al., 2018). According to Ghogia and coworkers, Major, et al., 2018, have shown that iron-catalyzed graphitization of biomass is suitable for producing highly graphitic biochar; consequently, the presence of iron offers a method to obtain graphitic carbon and graphene. The biochar produced by Ghogia et al. is a "magnetic" biochar. The ferromagnetic character of the iron@biochar obtained at different pyrolysis temperature (1000 , 1400 , and 1800 °C) is given in the Figure 3 of the mentioned article. The researchers conclude that "both particle size and degree of reduction of the iron catalyst positively impacts biochar graphitization ... Encapsulation of iron particles by *graphene sheets* is more pronounced for large particles, which are prevalent at higher temperatures due to more extensive sintering" (Ghogia et al., 2022). The researchers have produced a magnetic composite, where we can find iron@graphene particles in the form of core-shell nanoparticles. In Sparavigna, 2023, we have discussed the relevance of magnetic core-shell particles in producing synergistic magnetic and dielectric losses for microwaves absorption. It would be interesting to investigate microwave absorption features and reflection loss attitude also for the composite produced by Ghogia and coworkers.

12. Perspective

Among the magnetic graphenes, created intrinsically by breaking the honeycomb lattice symmetry, we have discussed the nitrogen-doped graphene. We have also mentioned N-doped biochar as alternative material,

suitable for catalysis. But why is N-doping of carbon forms so important? We can find an answer in the article by Lv et al., 2018, where selectively nitrogen-doped carbon materials are proposed as metal-free catalysts in oxygen reduction reaction (ORR). Carbon-based metal-free catalysts are considered for ORR instead of platinum-based catalysts, because of the exorbitant cost of this metal (Wang et al., 2019). For ORR, heteroatom-doped carbon materials have been investigated and, among them, "nitrogen (N)-doped carbon materials are some of the most efficient metal-free catalysts" (Lv et al., 2018). And ORR is just one of the several applications of N-doped carbon materials.

Due to the importance of such a doping in applications, a survey of literature can be relevant too. However, the amount of literature regarding the N-doped forms of carbon is extremely large. A possible perspective is that of considering them only in the magnetic form, so that to collect information about nanotubes, graphene, graphene oxide, ribbons, fullerenes and other forms, such as graphdiyne, in a comprehensive review.

References

- Arora, M., Wahab, M. A., & Saini, P. (2014). Permittivity and electromagnetic interference shielding investigations of activated charcoal loaded acrylic coating compositions. *Journal of Polymers*, 2014.
- Askari, S., Koolivand, H., Pourkhalil, M., Lotfi, R., & Rashidi, A. (2017). Investigation of Fe₃O₄/Graphene nanohybrid heat transfer properties: Experimental approach. *International Communications in Heat and Mass Transfer*, 87, 30-39.
- Avouris, P., & Xia, F. (2012). Graphene applications in electronics and photonics. *Mrs Bulletin*, 37(12), 1225-1234.
- Bartoli, M., Jagdale, P., Giorcelli, M., Rovere, M., & Tagliaferro, A. (2023). Overview of Nanostructured Carbon-based Catalysts. *Nanochemistry: Synthesis, Characterization and Applications*, 313.
- Bartoli, M., Giorcelli, M., & Tagliaferro, A. (Eds.). (2023). *Biochar - Productive Technologies, Properties and Applications*. doi: 10.5772/intechopen.100763
- Bistrizter, R., & MacDonald, A. H. (2011). Moiré bands in twisted double-layer graphene. *Proceedings of the National Academy of Sciences*, 108(30), 12233-12237.
- Black-Schaffer, A. M. (2010). RKKY coupling in graphene. *Physical Review B*, 81(20), 205416.
- Błoński, P., Tucek, J., Sofer, Z., Mazanek, V., Petr, M., Pumera, M., Otyepka, M., & Zboril, R. (2017). Doping with graphitic nitrogen triggers ferromagnetism in graphene. *Journal of the American Chemical Society*, 139(8), 3171-3180.
- Brassard, P., Godbout, S., Lévesque, V., Palacios, J. H., Raghavan, V., Ahmed, A., Hogue, R., Jeanne, T., & Verma, M. (2019). Biochar for soil amendment. In *Char and carbon materials derived from biomass* (pp. 109-146). Elsevier, 2019
- Chang, Y. P., Ren, C. L., Qu, J. C., & Chen, X. G. (2012). Preparation and characterization of Fe₃O₄/graphene nanocomposite and investigation of its adsorption performance for aniline and p-chloroaniline. *Applied Surface Science*, 261, 504-509.
- Chu, Z., Zheng, B., Wang, W., Li, Y., Yang, Y., & Yang, Z. (2022). Magnetic Nitrogen-Doped biochar for adsorptive and oxidative removal of antibiotics in aqueous solutions. *Separation and Purification Technology*, 297, 121508.
- Dankworth, J. (2020). Is magnetic graphene possible? Available <https://nanografi.com/blog/is-magnetic-graphene-possible/>, archived [WaybackMachine](https://www.archive.org/web/20200808100000/https://nanografi.com/blog/is-magnetic-graphene-possible/)
- Das, C., Tamrakar, S., Kiziltas, A., & Xie, X. (2021). Incorporation of biochar to improve mechanical, thermal and electrical properties of polymer composites. *Polymers*, 13(16), 2663.
- Devi, G., Priya, R., Tapas Babu, B. R., Thandaiah Prabu, R., Sathish Kumar, P. J., & Anusha, N. (2022). Role of carbonaceous fillers in electromagnetic interference shielding behavior of polymeric composites: A review. *Polymer Composites*, 43(11), 7701-7723.
- Fan, X. J., & Li, X. (2012). Preparation and magnetic property of multiwalled carbon nanotubes decorated by Fe₃O₄ nanoparticles. *New Carbon Materials*, 27(2), 111-116.
- Ghogia, A. C., Romero Millán, L. M., White, C. E., & Nzihou, A. (2022). Synthesis and growth of green graphene from biochar revealed by magnetic properties of iron catalyst. *ChemSusChem*, 16(3), e202201864.
- Giorcelli, M., & Bartoli, M. (2019). Carbon nanostructures for actuators: An overview of recent developments. *Actuators*, 8(2), 46.
- Giorcelli, M., Das, O., Sas, G., Försth, M., & Bartoli, M. (2021). A review of bio-oil production through microwave-assisted pyrolysis. *Processes*, 9(3), 561.
- González-Herrero, H., Gómez-Rodríguez, J.M., Mallet, P., Moaied, M., Palacios, J.J., Salgado, C., Ugeda, M.M., Veuillen, J.Y., Yndurain, F., & Brihuega, I. (2016). Atomic-scale control of graphene magnetism by using hydrogen atoms. *Science*, 352(6284), pp.437-441.
- Guo, L., Ye, P., Wang, J., Fu, F., & Wu, Z. (2015). Three-dimensional Fe₃O₄-graphene macroscopic composites for arsenic and arsenate removal. *Journal of Hazardous Materials*, 298, 28-35.
- Han, J., & Kim, H. (2008). The reduction and control technology of tar during biomass gasification / pyrolysis: an overview. *Renewable and sustainable energy reviews*, 12(2), 397-416.
- Han, W., Kawakami, R. K., Gmitra, M., & Fabian, J. (2014). Graphene spintronics. *Nature nanotechnology*, 9(10), 794-807.
- He, Y., Yi, C., Zhang, X., Zhao, W., & Yu, D. (2021). Magnetic graphene oxide: Synthesis approaches, physicochemical characteristics, and biomedical applications. *TrAC Trends in Analytical Chemistry*, 136, 116191.
- Hu, W., Zhang, J., Liu, B., Zhang, C., Zhao, Q., Sun, Z., Cao, H., & Zhu, G. (2021). Synergism between lignin, functionalized carbon nanotubes and Fe₃O₄ nanoparticles for electromagnetic shielding effectiveness of tough lignin-based polyurethane. *Composites Communications*, 24, p.100616.
- Hu, J., Liang, C., Li, J., Liang, Y., Li, S., Li, G., Wang, Z., & Dong, D. (2021). Flexible reduced graphene oxide@Fe₃O₄/silicone rubber composites for enhanced microwave absorption. *Applied Surface Science*, 570, 151270.
- IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. <https://doi.org/10.1351/goldbook>.
- Kassae, M. Z., Motamedi, E., & Majidi, M. (2011). Magnetic Fe₃O₄-graphene oxide/polystyrene: fabrication and characterization of a promising nanocomposite. *Chemical Engineering Journal*, 172(1), 540-549.
- Katsnelson, M. I. (2016). "graphene". *Encyclopedia Britannica*, 8 Jan. 2016, Available link: <https://www.britannica.com/science/graphene>. Accessed 19 February 2023.
- Kavitha, M. K., & Jaiswal, M. (2016). Graphene: A review of optical properties and photonic applications. *Asian J. Phys*, 25(7), 809-831.
- Kogan, E. (2011). RKKY interaction in graphene. *Physical Review B*, 84(11), 115119.

31. Kogan, E. (2013). RKKY Interaction in Gapped or Doped Graphene, *Graphene*, 2(1), 8-12.
32. Kogan, E. (2019). RKKY interaction in graphene at finite temperature. *Journal of Carbon Research C*, 5(2), 14.
33. Kogan, E. (2022). Graphene for Electronics. *Nanomaterials*, 12(24), 4359.
34. Lee, J., Kim, K. H., & Kwon, E. E. (2017). Biochar as a catalyst. *Renewable and Sustainable Energy Reviews*, 77, 70-79.
35. Li, X.F., Lian, K.Y., Liu, L., Wu, Y., Qiu, Q., Jiang, J., Deng, M., & Luo, Y. (2016). Unraveling the formation mechanism of graphitic nitrogen-doping in thermally treated graphene with ammonia. *Scientific Reports*, 6(1), 23495.
36. Li, Z., Li, X., Zong, Y., Tan, G., Sun, Y., Lan, Y., He, M., Ren, Z., & Zheng, X. (2017). Solvothermal synthesis of nitrogen-doped graphene decorated by superparamagnetic Fe₃O₄ nanoparticles and their applications as enhanced synergistic microwave absorbers. *Carbon*, 115, pp.493-502.
37. Lian, P., Zhu, X., Xiang, H., Li, Z., Yang, W., & Wang, H. (2010). Enhanced cycling performance of Fe₃O₄-graphene nanocomposite as an anode material for lithium-ion batteries. *Electrochimica Acta*, 56(2), 834-840.
38. Liu, Y., Huang, H., Gan, D., Guo, L., Liu, M., Chen, J., Deng, F., Zhou, N., Zhang, X., & Wei, Y. (2018). A facile strategy for preparation of magnetic graphene oxide composites and their potential for environmental adsorption. *Ceramics International*, 44(15), pp.18571-18577.
39. Lv, Q., Si, W., He, J., Sun, L., Zhang, C., Wang, N., Yang, Z., Li, X., Wang, X., Deng, W., & Long, Y. (2018). Selectively nitrogen-doped carbon materials as superior metal-free catalysts for oxygen reduction. *Nature Communications*, 9(1), p.3376.
40. Major, I., Pin, J. M., Behazin, E., Rodriguez-Uribe, A., Misra, M., & Mohanty, A. (2018). Graphitization of Miscanthus grass biocarbon enhanced by in situ generated FeCo nanoparticles. *Green Chemistry*, 20(10), 2269-2278.
41. Manna, R., & Srivastava, S. K. (2021). Reduced graphene oxide/Fe₃O₄/polyaniline ternary composites as a superior microwave absorber in the shielding of electromagnetic pollution. *ACS omega*, 6(13), 9164-9175.
42. Miao, Q., Wang, L., Liu, Z., Wei, B., Xu, F., & Fei, W. (2016). Magnetic properties of N-doped graphene with high Curie temperature. *Scientific reports*, 6(1), 1-10.
43. Mishra, S., Beyer, D., Eimre, K., Kezilebieke, S., Berger, R., Gröning, O., Pignedoli, C.A., Müllen, K., Liljeroth, P., Ruffieux, P., & Feng, X. (2020). Topological frustration induces unconventional magnetism in a nanographene. *Nature nanotechnology*, 15(1), pp.22-28.
44. Ni, S., Lin, S., Pan, Q., Yang, F., Huang, K., & He, D. (2009). Hydrothermal synthesis and microwave absorption properties of Fe₃O₄ nanocrystals. *Journal of Physics D: Applied Physics*, 42(5), 055004.
45. Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Katsnelson, M.I., Grigorieva, I.V., Dubonos, S., & Firsov, A. (2005). Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, 438(7065), 197-200.
46. Ohldag, H., Tylliszczak, T., Höhne, R., Spemann, D., Esquinazi, P., Ungureanu, M., & Butz, T. (2007). π -electron ferromagnetism in metal-free carbon probed by soft x-ray dichroism. *Physical review letters*, 98(18), 187204.
47. Ok, Y. S., Uchimiya, S. M., Chang, S. X., & Bolan, N. (Eds.). (2015). *Biochar: Production, characterization, and applications*. CRC press.
48. Ok, Y. S., Tsang, D. C., Bolan, N., & Novak, J. M. (Eds.). (2018). *Biochar from biomass and waste: fundamentals and applications*. Elsevier.
49. Papageorgiou, D. G., Kinloch, I. A., & Young, R. J. (2015). Graphene/elastomer nanocomposites. *Carbon*, 95, 460-484.
50. Peng, F., Dai, M., Wang, Z., Guo, Y., & Zhou, Z. (2022). Progress in graphene-based magnetic hybrids towards highly efficiency for microwave absorption. *Journal of Materials Science & Technology*, 106, 147-161.
51. Pistilli, M. (2022). What Factors Impact Graphene Cost? Published in *Investingnews.com*, at link <https://investingnews.com/daily/tech-investing/nanoscience-investing/graphene-investing/graphene-cost/> and archived [WaybackMachine](#).
52. Quan, L., Qin, F. X., Estevez, D., Wang, H., & Peng, H. X. (2017). Magnetic graphene for microwave absorbing application: Towards the lightest graphene-based absorber. *Carbon*, 125, 630-639.
53. Qin, M., Zhang, L., & Wu, H. (2022). Dielectric loss mechanism in electromagnetic wave absorbing materials. *Advanced Science*, 9(10), 2105553.
54. Razaq, A., Bibi, F., Zheng, X., Papadakis, R., Jafri, S. H. M., & Li, H. (2022). Review on graphene-, graphene oxide-, reduced graphene oxide-based flexible composites: From fabrication to applications. *Materials*, 15(3), 1012.
55. Ruderman, M. A., & Kittel, C. (1954). Indirect exchange coupling of nuclear magnetic moments by conduction electrons. *Physical Review*, 96(1), 99.
56. Shao, Y., Zhang, S., Engelhard, M.H., Li, G., Shao, G., Wang, Y., Liu, J., Aksay, I.A., Lin, Y. (2010). Nitrogen-doped graphene and its electrochemical applications. *Journal of Materials Chemistry*, 20(35), pp.7491-7496.
57. Sharpe, A.L., Fox, E.J., Barnard, A.W., Finney, J., Watanabe, K., Taniguchi, T., Kastner, M.A., & Goldhaber-Gordon, D. (2019). Emergent ferromagnetism near three-quarters filling in twisted bilayer graphene. *Science*, 365(6453), 605-608.
58. Sherafati, M., & Satpathy, S. (2011). Analytical expression for the RKKY interaction in doped graphene. *Physical Review B*, 84(12), 125416.
59. Sherafati, M., & Satpathy, S. (2012). On the Ruderman-Kittel-Kasuya-Yosida Interaction in Graphene. In *AIP Conference Proceedings* (Vol. 1461, No. 1, pp. 24-33). American Institute of Physics.
60. Sherlala, A. I. A., Raman, A. A. A., Bello, M. M., & Asghar, A. (2018). A review of the applications of organofunctionalized magnetic graphene oxide nanocomposites for heavy metal adsorption. *Chemosphere*, 193, 1004-1017.
61. Shu, R., Li, X., Tian, K., & Shi, J. (2022). Fabrication of bimetallic metal-organic frameworks derived Fe₃O₄/C decorated graphene composites as high-efficiency and broadband microwave absorbers. *Composites Part B: Engineering*, 228, 109423.
62. Sparavigna, A. (2002). Influence of isotope scattering on the thermal conductivity of diamond. *Physical Review B*, 65(6), 064305.
63. Sparavigna, A., & Ravetti, A. (2005). Thermal conductivity in nanotubes and nanotube bundles. In *Recent research developments in physics* (Volume 6 part I (2005)) (pp. 173-183).
64. Sparavigna, A. (2008). Lattice specific heat of carbon nanotubes. *Journal of thermal analysis and calorimetry*, 93(3), 983-986.
65. Sparavigna, A. C. (2023). Iron Oxide Fe₃O₄ Nanoparticles with ICPs and Biochar to Improve Electromagnetic Shielding Performance. SSRN: Social Science Research Network Journal. DOI 10.2139/ssrn.4331866
66. Su, J., Cao, M., Ren, L., & Hu, C. (2011). Fe₃O₄-graphene nanocomposites with improved lithium storage and magnetism properties. *The Journal of Physical Chemistry C*, 115(30), 14469-14477.
67. Tang, N., Tang, T., Pan, H., Sun, Y., Chen, J., & Du, Y. (2020). Magnetic properties of graphene. In *Spintronic 2D Materials* (pp. 137-161). Elsevier.
68. Taylor-Smith, K. (2022). The difference between rebar and pristine graphene. AZoM. Retrieved on February 15, 2023 from <https://www.azom.com/article.aspx?ArticleID=17133>.
69. Tombros, N., Jozsa, C., Popinciuc, M., Jonkman, H. T., & Van Wees, B. J. (2007). Electronic spin transport and spin precession in single graphene layers at room temperature. *Nature*, 448(7153), 571-574.

70. Ugeda, M. M., Brihuega, I., Guinea, F., & Gómez-Rodríguez, J. M. (2010). Missing atom as a source of carbon magnetism. *Physical Review Letters*, 104(9), 096804.
71. Vesel, A., Zaplotnik, R., Primc, G., & Mozetič, M. (2020). A review of strategies for the synthesis of N-doped graphene-like materials. *Nanomaterials*, 10(11), 2286.
72. Wang, X., Krommenhoek, P.J., Bradford, P.D., Gong, B., Tracy, J.B., Parsons, G.N., Luo, T.J.M., & Zhu, Y.T. (2011). Coating alumina on catalytic iron oxide nanoparticles for synthesizing vertically aligned carbon nanotube arrays. *ACS applied materials & interfaces*, 3(11), 4180-4184.
73. Wang, X., Lu, Y., Zhu, T., Chang, S., & Wang, W. (2020). CoFe₂O₄/N-doped reduced graphene oxide aerogels for high-performance microwave absorption. *Chemical Engineering Journal*, 388, 124317.
74. Yang, G., Li, L., Lee, W. B., & Ng, M. C. (2018). Structure of graphene and its disorders: a review. *Science and technology of advanced materials*, 19(1), 613-648.
75. Yao, Y., Miao, S., Liu, S., Ma, L. P., Sun, H., & Wang, S. (2012). Synthesis, characterization, and adsorption properties of magnetic Fe₃O₄@ graphene nanocomposite. *Chemical engineering journal*, 184, 326-332.
76. Yasim-Anuar, T. A. T., Yee-Foong, L. N., Lawal, A. A., Farid, M. A. A., Yusuf, M. Z. M., Hassan, M. A., & Ariffin, H. (2022). Emerging application of biochar as a renewable and superior filler in polymer composites. *RSC advances*, 12(22), 13938-13949.
77. Yoo, S., Chung, C. C., Kelley, S. S., & Park, S. (2018). Graphitization behavior of loblolly pine wood investigated by in situ high temperature X-ray diffraction. *ACS Sustainable Chemistry & Engineering*, 6(7), 9113-9119.
78. Yutomo, E. B., Noor, F. A., & Winata, T. (2021). Effect of the number of nitrogen dopants on the electronic and magnetic properties of graphitic and pyridinic N-doped graphene—a density-functional study. *RSC advances*, 11(30), 18371-18380.
79. Yu, J., Tang, L., Pang, Y., Zeng, G., Wang, J., Deng, Y., Liu, Y., Feng, H. Chen, S., & Ren, X. (2019). Magnetic nitrogen-doped sludge-derived biochar catalysts for persulfate activation: Internal electron transfer mechanism. *Chemical Engineering Journal*, 364, 146-159.
80. Wang, X., Li, Z., Qu, Y., Yuan, T., Wang, W., Wu, Y., & Li, Y. (2019). Review of metal catalysts for oxygen reduction reaction: from nanoscale engineering to atomic design. *Chem*, 5(6), 1486-1511.
81. Zhang, F., Yang, K., Liu, G., Chen, Y., Wang, M., Li, S., & Li, R. (2022). Recent Advances on Graphene: Synthesis, Properties, and Applications. *Composites Part A: Applied Science and Manufacturing*, 107051.
82. Zhang, H., Xia, B., & Gao, D. (2023). Recent advances of ferromagnetism in traditional antiferromagnetic transition metal oxides. *Journal of Magnetism and Magnetic Materials*, 170428.
83. Zheng, J., Lv, H., Lin, X., Ji, G., Li, X., & Du, Y. (2014). Enhanced microwave electromagnetic properties of Fe₃O₄/graphene nanosheet composites. *Journal of alloys and compounds*, 589, 174-181.
84. Zhu, L., Zeng, X., Li, X., Yang, B., & Yu, R. (2017). Hydrothermal synthesis of magnetic Fe₃O₄/graphene composites with good electromagnetic microwave absorbing performances. *Journal of Magnetism and Magnetic Materials*, 426, 114-120.