Efficiency of zero-dimensional and two-dimensional graphene architectural nanocomposites for organic transformations in the contemporary environment: a review

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Abstract
Graphene derivatives-based nanocatalyst finds increasing utilisation in the catalysis field for organic transformations. Researchers have been working on the development of graphene oxide, reduced graphene oxide, and graphene quantum dots with metal or metal oxide nanocomposites over the last few years. These materials exhibit excellent electrical, catalytic, optical, thermal, and magnetic properties. In particular, GO/rGO/GQDs composites assisted by metal or metal oxides have attracted broad attention for their possible applications in organic compound synthesis, drug delivery, sensors, devices, and the related areas of the environment. In this review, we have summarised GO/rGO/GQDs-metal or metal oxide composites using catalyst for organic conversions and synthesis of organic compounds in accordance with the discussion on the key problems and prospects for future study. Furthermore, there is a significant function for the catalytic efficiency of composites assisted by metal or metal oxide nanocatalyst which is categorised by graphene derivatives bases.
Introduction

Carbon is the fourth abundant material in the earth’s crust, and it is known as the universally strong and thinnest material. Nowadays, it is challenging to accommodate carbon growth, although scientists have developed greener materials like graphene derivatives. Due to the structural morphology of graphene, it has gotten much attention. In 1985, carbon nanotubes were invented and characterised in 1991 for the first time [1]. In recent times, research from various fields has been fascinated by the discovery of new types of carbon allotropes, as shown in Table 1. When graphene is exposed to the van der Waals force, it transforms from single-layer graphite to multi-layer graphite [2].

Since both graphite and graphene are members of the same carbon family, graphene has piqued the interest of scientists in recent decades. It has some interesting properties, such as unique transport efficiency, extreme thermal conductivity, high mechanical power, high charge carrier mobility, and potentially high surface area performance [3–5]. Valuable graphene derivatives are graphene oxide (GO), reduced graphene oxide (rGO), and graphene quantum dots (GQDs). In this case, both GO and rGO are nanostructured two-dimensional (2-D) materials. The 2-D layers and their distribution effectiveness have a significant impact on the physiochemical characteristics of GO and rGO sheets. Individual graphene, GO and rGO were observed to aggregate on the surface due to van der Waals and stacking interactions [6]. However, GQDS is a 0-D material based on its structural morphology. Owing to the variations in their chemical compositions, GO/rGO/GQDs exhibit various structural and chemical properties. The most prominent characteristics of this graphene are categorised by their electric conductivity, mechanical strength, hydrophilic action [7], and dispensability [8]. GO/rGO/GQDs are also used in diverse applications [9].

The GO/rGO/GQDs-based nanocatalyst is the most important for the catalytic conversion of organic reactions due to its selectivity, efficiency, and stability [10]. Heterogeneous catalysts of GO and rGO are used in 2D carbon boards with atomic thickness using different functional oxygen-containing groups, and GQDs are used as 0-D.
This material is well known for its high thermal strength, massive surface, mechanical properties, etc. Specifically, the green chemistry concept has a significant impact on several aspects, which include the use of green solvents, bio-renewables, and sustainable catalyst materials [11]. Environmentally, protocols for heterocycle synthesis have been investigated because of their atom economy, efficient energy, and reaction rate [12]. In recent years, designing high-efficiency reactions that can be performed at room temperature using renewable energy has become a popular option. In synthetic organic chemistry, organic reactions are designed in such a way that the reactants are put into one-pot reaction [13]. By using the green method, researchers are focused on preparing an efficient heterogeneous catalyst to develop good reaction yields. Metal oxide nanoparticles are the most commonly used catalysts because of their good activity and stability. In heterogeneous catalysis, metal oxides are used for both acid–base, redox properties, and they represent the highest catalyst group [14]. Metal or metal oxide NPs can be decoupled with high surface area materials like montmorillonite [15], zeolite [16], metal–organic frames [17], zeolitic organic frames [18], GO, rGO [19], etc. Metal or metal oxide-supported GO/rGO/GQDs are employed as effective candidates for heterogeneous catalysts. Additionally, NPs can act as stabilisers for both GO or rGO sheet aggregation, which is typically induced by van der Waals’ powerful interaction between GO layers [20]. rGO is altered by CuO [21], ZnO [22], and TiO$_2$/Fe$_2$O$_3$ [23]. When NPs and nanomaterials are added to the surface of graphene, they improve its morphology, catalytic activity, and ability to conduct electricity [24].

Moreover, many studies have been done on these types of reviews. Here, we reported the necessity of graphene derivatives, which is increasing day by day. Graphene acts as a functional substrate to immobilise several components to form graphene-based composites by using various dimensions of carbon materials. This review is about the GO/rGO/GQDs-metal or metal oxide-based composite materials in organic conversions (like nitro phenol reduction, dehalogenation, and oxidation), organic synthesis (coupling, addition, and substitution reactions, and one-pot synthesis), and their latest developments and applications.

### Various kinds of graphene derivatives

The use of graphite as the starting material results in graphene derivatives that deal with the structural features of graphite, graphite oxide, GO, rGO, graphene quantum dots, graphene nanosheets, single-layer graphene, and graphene layers [25] as shown in Fig. 1.

#### Graphite

Graphite is made by stacking a hexagonal layer of sp$^2$-hybridised carbon from a carbon source that looks like a very thick sheet of single atoms.

#### Graphene oxide (GO)

Due to its oxygen-containing 2-D layer structure, the surface undergoes significant oxidative change in addition to oxidation and exfoliation. GO is made up of a wide variety of chemical and physical characteristics. This substance has a hydrophilic quality and a higher proportion of hydroxyl, epoxide, ketone, and carboxylic acid groups in its structure. GO undergoes a substantial transformation as a result of the oxygenation groups. At the base and corners of the GO, they make it possible for biotechnological and bioconjugation interactions to take place. The level of oxidation, however, makes it a semiconducting nanomaterial even though it has a huge surface area of 890 m$^2$g$^{-1}$ and a tough shape [26]. A flat carbon sheet randomly coupled with epoxy groups and having a C/O ratio of two is described in the initial model created by Hofmann and Holst in 1939. Then, in 1946, Ruess’ team reported 1,3-ether and hydroxyl groups to the lattice [27]. Cyclohexane rings, as opposed to Hofmann’s carbon plane that resembles benzene, make up the lattice. Model of Scholz–Boehm [28]. As a consequence, the hydroxyl groups completely replace the epoxide groups. The base plane is made up of regular holes in cyclohexane rings that are connected by a quinoidal pattern.

Nakajima and Matsuo (1994) designed a lattice structure resembling poly (C$_3$F)$_n$ in order to produce level-2 graphite intercalation molecules [29]. Unfortunately, the most recent two theories suggested by Lerf–Klinowski are inadequate [30] and Decany [31]. Due to the inclusion of SSNMR

| S. no. | Dimension | Material | Nanometre range |
|-------|-----------|----------|-----------------|
| 1     | O-D       | Onion like carbon, carbon dot, & fullerene GDQs | XYZ axis < 100 nm |
| 2     | 1-D       | Carbon nanotubes (CNT), Single-walled carbon nanotubes (SWCNT), & multi-walled carbon nanotubes (MWCNT), | X & Y axis < 100 nm |
| 3     | 2-D       | Carbon, graphene, & graphene oxide | Dimension in one direction < 100 nm |
| 4     | 3-D       | Diamond, graphite oxide & polycrystals | XYZ > 100 nm |

**Table 1 Different sources of carbon-based nanomaterials**

This table lists different sources of carbon-based nanomaterials, including their dimensions and the nanometre range.
investigation in GO structural characterisation, it has gained the greatest popularity. The efficiency of finding the structural features on GO has increased because of this novel method. Tertiary alcohols and 1,2-ethers comprise the GO texture according to the Lerf–Klinowski model [30]. The Lerf–Klinowski idea uses loosely packed oxygen molecules instead of a regularly spaced crystal lattice. Furthermore, they hypothesised that GO alkenes (C = C) are likely aromatic or conjugated, so the GO ketones are favoured at the periphery. After that, Décány came up with a design that was based on the same basic ideas as the Scholz–Boehm version, but included 1,3-ethers in cyclohexane geometries [32].

The band gap has narrowed with increase in oxygen saturation, according to Boukhvalov and Katsnelson, who hypothesised a chain-like arrangement [33]. The introduction of a single hydrogen atom through chemical adsorption led to a 5 Å (radius) deformation of the graphene sheet, indicating that graphene is very flexible [34]. The most energetically advantageous arrangement for the chemical adsorption of two hydrogen atoms is when two hydrogens are bound to nearby carbons on opposing sheet edges. Furthermore, full hydrogen atom coverage may reduce the overall energy of the graphene layer [35]. The validity of this finding was shown theoretically by Yan and Chou [36]. In their Monte Carlo simulations, Paci et al. have highlighted the significance of hydrogen bonding as an important interaction. Additionally, it was discovered that epoxide groups moved on the crystal lattice in reactions that were often catalysed via hydrogen chemical reactants between the movable epoxide oxygen and nearby chemical bonding or stabilised by hydrogen bonding [37]. According to Li et al., epoxy couples coordinating in the GO layer are more likely to produce carbonyl groups, which will cause the GO sheet to “unzip” [38]. This discovery points to a way that supervised oxidation can be used to give GO a perfect surface.

**Reduced graphene oxide (rGO)**

Thermal, chemical, microwave, photothermal, photochemical, microbiological, and bacterial techniques were utilised to reduce the oxygen functional groups in GO, resulting in the fabrication of 2-D layered rGO. The presence of residual functional groups during reduction gives rise to the term rGO. Unfortunately, because GO and RGO are rather amorphous, their precise atomic structures have yet to be discovered, despite significant spectroscopy and microscopy studies of these materials. As a result, numerous GO structural models are still being debated. The most generally accepted explanation for GO is that it is a stochastic mix of oxidised areas with oxygenated functional groups and nonoxidised regions with the bulk of carbon atoms retaining sp² hybridization. People thought that the differences between RGO and pure graphene were caused by structural flaws like those seen in carbon nanotubes and fullerenes, which are also low-dimensional carbon nanomaterials [39].

The hydrophilic role of moieties that include oxygen considerably increases the hydrophobicity of the rGO, which makes it more robust in water and sensitive to aggregating, which can modify its shape and specific area. The question of which one has a stronger antibacterial ability is still debatable. Conversely, rGO exhibits superior chemical strength and electrical conductivity, having resistance levels of between (5–500) GΩ cm and (100–1000) Ω cm for GO and rGO, respectively. These qualities have led to a never-ending
stream of research into rGO and have made it possible to find interesting new ways to use the material [40].

**Graphene quantum dots (GQDs)**

Graphene quantum dots emit light when stimulated, in addition to possessing a nonzero band gap. The size and surface chemistry of GQDs, like those of 0-D materials, should be modified. GQDs are more flexible than colloidal QDs, are toxic-free, and have advantageous electro-optical characteristics. Benzene has an eV of 7, while GQDs with 20 aromatic rings have an eV of 2. The photoluminescence (PL) of GQDs differs most noticeably from that of semiconductor QDs in two ways: the PL bandwidth is substantially wider in GQDs, and the PL maximum of GQDs moves to the red and declines with increase in excitation wavelength. Theoretically, GQDs have wide availability, low toxicity, high solubility in many solvents, and the capability of having functional groups attached to their surfaces [41].

Despite their label as “carbon nanodots” (C-dots), GQDs are distinct from their smaller cousins in a number of ways. On the other hand, GQDs are 100 nm in width and have one, two, or more thin layers of graphene sheets that are all less than ten nanometers (nm) thick. Also, they have functional groups on their corners, such as carboxyl, hydroxyl, carbonyl, and epoxide, which can act as reaction sites and change the PL emission from the dots by changing their electronic structure [42]. Due to their perfect material characteristics and dispersibility in polymeric composites, graphene analogues (GO, rGO, and GQDs) have been shown to be efficient compositions in nanocomposite materials, leading to several applications. Similarly, nanocomposites’ filler content can be fine-tuned to alter the selectivity of specific molecule sizes, leading to improved membrane technology. In addition, the one-of-a-kind hydrophilic, thermal, and electrical characteristics that GO derivatives have can be utilised to great effect in the development of carbon materials. Brønsted acid sites and Lewis’ acid–base centres are incorporated into the graphene carbocatalysts to improve its catalytic efficiency. These sites, in conjunction with electrostatic and stacking interactions, allow for greater reactant adsorption, resulting in increased organic traffic. Graphene-based carbocatalysts are renewable, need modest catalyst dosage, and are environmentally benign because of their simplicity of recovery by techniques including filtration, centrifugation, and magnetic decantation. A lot of progress has been made in the field of graphene-based carbocatalysts, but there are still some problems that need fixing. For example, the intricacy of graphene oxide and its changed forms resulting from their various functions, sites, edges, and flaws makes it difficult to pinpoint their precise functionalization. To fully understand the reaction mechanism underlying GO-based materials, detailed molecular-level models defining their structure are required. Also, methods for the production and functionalization of graphene derivatives that are both simpler and more cost-effective need to be investigated. Even though these problems will slow the progress of graphene-based materials, they will not stop them from becoming very effective carbocatalysts.

**Synthesis methods for graphene derivatives**

The first piece of graphene sheet was obtained through the manual mechanical cleavage of graphite using Scotch tape. Despite the fact that this method of manufacture is not frequently used, this exfoliated graphene has a distinctive structure and remarkable characteristics [43, 44]. Inspired by this novel breakthrough, significant attempts have been made to produce synthetic graphene, not only to reach high production but also to flourish in graphene-based composites. Methods of this type can be divided into two categories: bottom-up approaches and top-down procedures [45].

**Graphene oxide (GO) synthesis**

The most widely used approach is GO production. In this case, Hummers and his team wanted to use the traditional way to make GO. By using powerful oxidants such as HNO₃, KMnO₄, and H₂SO₄, graphite was oxidised and graphite oxide was exfoliated into water to generate stable water distribution. Following that, centrifugation is used to extract pure GO along with various inorganic contaminants, acids, and metal ions. Simultaneously, exfoliated Oxygen-containing categories can be found in GO in a variety of forms, such as carboxylic, hydroxyl, and epoxy units. The oxygen functionality of graphene oxide allows it to react with cations and creates reactive sites for the formation and synthesis of nanoparticles, which speeds up the development of different graphene-based composites [20, 46].

**Reduced graphene oxide (rGO) synthesis**

The synthesis of GO-supported metal or metal oxide nanocomposites can be achieved using solvothermal [47], sol–gel [48], or hydrothermal methods [49]. GO sheets are typically called graphene functions and can be used as graphene substitutes. When it comes to rGO, many reduction procedures are employed, including microwave treatment [50], heat treatment [51], chemical reductions [52], microwave reduction [53], laser reduction [54], photo reduction [55], electrochemical reduction [56], and hydrothermal reduction [57]. When rGO is made, its structural, optical, magnetic, electrical, and electrical properties, as well as its magnetic properties, will all be better [58].
Solvothermal method synthesis of rGO

In Fig. 2, an organic solvent is used as the reaction medium of a solvothermal synthesis process. Both the sol–gel and the hydrothermal methods have advantages. These characteristics alter when some experimental factors, such as reaction temperature, reactive time, solvent type, surfactant type, and precursor type, are changed [59]. Impurities from the rGO with metal or metal oxide medium were removed using a chemical ultrasonication method, and the metal region was rendered soluble in ethylene glycol with continuous stirring. Simultaneous addition of the metal region and the GO homogeneous mixture was employed, and the combination was transferred to the autoclave for a few hours to cool at room temperature. The precipitate region was therefore obtained using centrifugation, and the required product was obtained by vacuum drying it after washing it with water and ethanol [60].

Hydrothermal method synthesised rGO

Water’s capacity to dilute molecules that are virtually insoluble under normal conditions under high temperatures and pressures is the basis for the hydrothermal method of synthesis. The initial pH of the medium, the time, temperature, and pressure of the system, which determine the kinetic processes and the qualities of the resultant product, are the main parameters of the hydrothermal synthesis, as illustrated in Fig. 2. The synthesis was carried out in autoclaves, which have sealed steel cylinders that can withstand high heat and pressure for a longer period of time [61]. Over a sonification suspension, dissolved GO was injected into the metal region. Following the centrifugation process, to remove the precipitate, ethanol and double-distilled water were used. The collected sample was reduced to GO and decorated with nanocomposites [62].

Graphene quantum dot (GQD) synthesis

Some of the procedures used to create GQDs include acidic oxide decomposition, hydrothermal cutting, microwave-assisted cutting, electrochemical operations, and E-beam lithography. The drawbacks of top-down methods include lower yields, unexpected disruption of the graphene structure, and a less homogeneous GQD morphology. Bottom-up techniques, which are chemically more advanced, could yield GQDs with smaller and more uniform morphologies [63].

Graphene oxide-mediated organic reactions

In 2021, Niakan et al. modified the suitable reaction conditions for its Heck coupling process using GO-Fe₃O₄-Cellulose-Pd catalysis between various aryl halides 1 and alkenes 2. (Scheme 1). Different varieties of alkene model styrene 2 are reacted with bromo-, iodo-, and chloro-benzene to produce the desired coupling final products 3 with high lentil yields (63–98%). Furthermore, the reactions were adjusted
by varying the styrene. Independent of the nature of any aryl halide substitution for electron-donating or electron-withdrawing, 2 with 1 yielded a high yield (79–96%). Under ideal conditions, the result shows that styrene was more reactive to the Heck reaction than another sub-rate of N-butyl acrylate. It has been demonstrated that GO-Fe₃O₄-Cellulose-Pd has improved catalytic performance (up to 98%) in the Heck coupling reaction. The same research investigation published remarkable results on the Heck reaction response in 2021, motivating us to perform extra research. In order to act as a catalyst for the Sonogashira coupling, a GO-Fe₃O₄-Cellulose-Pd composite was synthesised. In the Sonogashira reaction, one mole per cent of the catalyst was utilised under varied conditions while the optimised base was K₂CO₃, and a fine DMAC solvent was used. Gly was used as a solvent in the procedure at a temperature of 120 °C. When executed under ideal conditions, the iodobenzene 4 and phenyl acetylene 5 model reactions yield up to 96% (Scheme 2). Following that, the author proposed the use of natural Pd-modified magnetic GO as an easily recoverable catalyst for the C–C coupling reaction [64].

Choi et al. demonstrated an easy and straightforward method for integrating Au NPs on the surface of rGO nanosheets by electrostatic self-assembly. Nanocatalysts made of Au/GO composite were used to reduce nitroarenes in the presence of NaBH₄ (Scheme 3). Regardless of substituent position or type, the Au-GO hybrid has demonstrated strong reactivity and remarkable yields for various models of nitrophenols 7 and 4-aminophenols 8. Using Au-GO catalysts, for contrast, only 8 were fully converted in 30 min. Seven to 8 were significantly more effective than 4-nitrophenol 7. Assuming that the nitroarene mole consumed every 1 s by an Au/GO hybrid catalyst mole in NaBH₄ is constant. According to the study, this is the highest reduction activity of the 7 documented when Au NPs are used. This study successfully shows the effectiveness of hybrid Au/GO nanosheets, which are important for effective catalytic properties. The efficient catalytic consequence of AuNPs and GO nanosheets results in the hybrid Au/GO. Notably, the turnover frequency (TOF) in entry 2 is determined to be 2400 s⁻¹ under the observed reaction conditions. This number was found by counting how many moles of nitroarene each mole of the hybrid Au–GO catalyst used up every second [65].

In 2018, Shaabani and Afshari created a new nanocatalyst with a high affinity for complex Cu NPs, which resulted in the formation of carboxamide ligands on GO nanosheets. Carboxamide f-GO, Fe₃O₄, K₂CO₃, an amine 13, and 12 were added to the solution at 110 °C (Scheme 5). On the nanomaterial surface, the Fe₃O₄ nanoparticles (Fe₃O₄NPs) were mainly generated in order to produce Cu NPs
Additionally, there is a growing need for the usage of functional materials in a range of industries. A number of MCRs appear to be excellent material-functioning candidates. Because time-consuming and difficult purification phases and chemical exhaustion processes are not required to synthesise functional materials, even non-experts can make the transfer from laboratory to industry. Other significant drug delivery MCRs are working to functionalize carbonaceous materials and catalytic pathways. A crude product was filtered after the Cu NP-carboxamide-f-GO@Fe$_3$O$_4$ nanocatalyst was easily separated from the mixture using an external magnet. After that, the DES was recovered by evaporating water at 80 °C in a vacuum chamber, and then, it was reused with a nanocatalyst in order to carry out the subsequent experiment. At every iteration, there were a total of three separate experiments carried out [67].

The Cu(II)-Fur APTES/GO catalyst of ethanol and water solvents was used to stir the mixture of aryl aldehyde 16, carboxamide-f-GO@Fe$_3$O$_4$, a reusable nanocatalyst.
5,5-dimethylcyclohexane-1,3-dione, or 1,3-cyclohexanedione 15 for the required period at 50 °C (Scheme 6). It was found
that this nanocatalyst is an effective catalyst for the synthesis
of 17 key industrial xanthenes and their derivatives. The Cu
was loaded with 13.5% of functional GO, a level signifi-
cantly above that of metal catalysts, and its exceptional cata-
lytic activity was well known. It has been tested five times
and has shown no degradation in catalytic performance dur-
ing those cycles, indicating that it can be recycled [68]. The
CuO/GO catalyst is particularly effective in the short term
for the click reaction of phenylacetylene 18 with aryl azide
19. The reactions are faster, and 20 is isolated immediately
from the reaction bottle without any purification of the col-
umn. Reddy et al. used H2O as a solvent to establish sustain-
able reaction conditions for the click synthesis of 1,2,3-tria-
zole analogues (Scheme 7). Thus, the reactions are carried
out either in an aerobic environment with low percentage
loaded catalysts or at ambient temperature (RT) without
the usage of ligands. Additionally, catalysts were recycled,
and they can continue to function catalytically for up to five
cycles. The catalyst can be reused as it is possible to wit-
ness the catalytically active CuO NPs species stabilising on
the surface of the GO once the reaction has concluded. It is
noteworthy that this catalyst framework could be recycled at
least a few times without losing their photocatalytic activity.
Over the course of five consecutive runs, a minor decline
in activity. This occurred because some of the CuO active
species were washed away during the reaction and ended up
in the water [69].

In this Suzuki cross-coupling reaction (Scheme 8), using
21 and 22, a magnetically separable heterogeneous catalyst,
such as Co@GO/Fe3O4/L-dopa, was chosen to produce 23.
Under mild reaction conditions, this procedure produced a
respectable yield of 62–82%. Additionally, Sharma et al.
reported the oxidation of secondary alcohols and hydrocar-
bons using the above catalyst. Various oxidants, different
solvents, and different temperatures were used to study their
influences on anthrone oxidation. The temperature of the
reaction was kept constant at 80 °C, and TBHP was used as
an oxidant. A low yield was obtained when CH2Cl2, CH3CN,
and EtOH were used as solvents. At the same time, L-dopa
was developed to protect active cobalt NPs from leaching
while also being easily extracted from the reaction mixture,
allowing for the production of Co@GO/Fe3O4/L-dopa at a
cheap cost and with high efficiency in the process [70]. In
2017, Kumar and colleagues reported that they had success-
fully synthesised porous GO-CuFe2O4 by using a solution
paired with a new platform and that they had employed it
as an outstanding heterogeneous catalyst for the first time to
undertake the synthesis of xanthene 24 (Scheme 9). Under
mild conditions, the two-component coupling reactions of
aromatic aldehyde 25 and 1-Naphthol 26 were carried out
under mild conditions in the presence of GO-CuFe2O4 in the
presence of a mild catalyst. Furthermore, the nanocatalysts
were tested in a variety of xanthene derivatives, with the
resulting yield attaining more than 90%. When compared
to typical catalysts, all reactions happen in a much quicker
time frame. For up to five cycles in a solvent-free environment, the catalyst can also be used again with minimal loss of activity. This approach can provide information for the design of nanocatalysts employing combustion pathways for usage in a variety of other industrially important catalytic applications [71].

For the selective reduction of nitrogen excess compounds, a highly active Fe(0) embedded GO has been reported (Scheme 10). Fe(0) nanoparticles have morphologically shaped doughnuts that are trapped in rGO structural support, protecting the Fe(0) from rapid oxidation. With the proton source, hydrazine hydrate, the synthesised catalyst performs excellently in the conversion of nitro 27 to amino 28 compounds. The catalyst was recyclable and could be reused for four more cycles without losing catalytic performance. The greater catalyst performance is due to the synergistic interaction between the Fe(0) and rGO layers, which allows for mobile electron transfer from Fe(0) to the surface of rGO and prevents further oxidation of catalytically active species [72].

In this reaction, different types of solvents are mixed into the reaction mixture, which includes the EtOH solvent with 2 mg of a catalytic converter, which results in a product yield of 15% in 120 min. At room temperature, an optimised solvent H2O/MeOH (1:2) catalytic converter loaded with 2 mg of product achieves greater than 99% efficiency in 8 min. From 4-chlorobenzaldehyde and malononitrile, excellent heterogeneous catalytic properties were used to synthesise 30 (Scheme 11) [73].

Nie et al. invented a MnO2/GO nanocatalyst using a novel approach, and it was a smart electrical physical...
phenomenon with a broad region in the aqueous medium (Scheme 12). They noted the TEM image with MnO₂ elemental mapping has rod morphology with a 5–20 nm diameter and a 100–600 nm length, and is evenly distributed on both sides of GO nanosheets. It was discovered that by using binary compounds and primary alcohols as starting materials, an innovative method and composite could be produced with important properties that could be recycled and used in the synthesis of amide 34. The catalytic efficiency of the MnO₂/GO composite reached up to 98.4% when used in a solvent such as water or ethanol (Scheme 12). A primary alcohol, 31, reacts with an oxygen molecule and ammonia in an aqueous medium using a MnO₂/GO catalyst to form an amide, 34. They use a variety of substrates, and the yield of the products depends on the time and substituents used. They are using water as a solvent to produce the product with a high yield of more than 97% [74].

One-pot ultrasound-assisted caff-IL-GO/Fe nanocatalysts were synthesised by Zand et al. In 2018, they substituted benzimidazole 37, 4-H pyrans, and dihydropyrimidinones. Reactants 35 and 36 are easily attached to the catalyst surface, resulting in benzimidazole 37 synthesis within 3 min (Scheme 13). Compared to other green catalysts such as ZnO, alumina, zeolite, scolecite, and Fe₂O₃/collagen, this synthesis method produced a higher yield of 93% while using a greener approach. Low reaction time, high yield, and more reproducible use are all advantages of the caff-IL-GO/Fe nanocatalyst that has been prepared [75]. Wang et al. investigated the Mannich reaction using GO doped with P3HT poly (3-hexylthiophene-2,5-diyl). By adding L-propiline to N-aryl tetrahydroisoquinoline 38, this reaction occurs via acetone 39. Using a catalyst with 2.5% of its weight in chloroform and passing it through sunlight for 3 h under mild conditions yields the products 38 and 39 (Scheme 14). They have another method of synthesis that does not involve a catalyst and yields 47%, a low yield under the same conditions. Moreover, using only P3HT as a catalyst, they achieve a 65% yield, although when using GO/P3HT as a catalyst, the reaction yields up to 93%. GO/P3HT is a more efficient catalyst [76].

Different silver nanoparticles have been employed for different applications, including catalysis, apparel, medicinal coverage, band-gap energy, photovoltaics, and sensor devices. The catalytic activity of the Ag NPs in the GO
layering materials can efficiently create organic conversions. Mandal et al. synthesised the Ag NPs GO that was employed as a catalyst for the multistep N-phenylacetamide synthesis (Scheme 15), utilising toluene 41 as the starting material and acetic acid 42. Meanwhile, acetonitrile, and dichloromethane are incorporated as solvents, but they have a poor yield. A heterogeneous catalyst was also known to be present in the absence of a solvent medium prior to the good yield of 97\% at 100 °C in 4 h. Because of the steric effect and nucleophilicity when the nitro group is placed in the ortho and para positions, the yield is poor. In this reaction, both electron-donating and -withdrawing groups have been slightly reacted to. Aniline, which acts as an electron-withdrawing group, has some difficulties in reducing the yield. Simultaneously, an electron-donating group was formed, resulting in a good yield. The mechanism underlying the N-acylation reaction (Scheme 16) in the absence of a solvent is as follows: with acetic acid and an Ag-GO nanocatalyst, the carbon atom is more sensitive to electrophilic attack, leading to the formation of C = O. Dehydration stabilises the amide bond [77].

Seyedi et al. synthesised an N-enriched GO/Cu catalyst in 2019 for use in cross-coupling reactions (Scheme 17). It comprises amines 44 via phenylboronic acid 45 as a starting material, and reaction conditions between 25 and 100 °C for 1 to 24 h. To optimise the conditions, various bases and solvents, as well as catalyst loading percentages, have been used. These processes were refluxed for 3 h with a 3 mol\% catalyst present. Water and ethanol were used as solvents in a (1:1) ratio to create an excellent yield, but other solvents such as toluene, MeCN, CH₂Cl₂, H₂O, DMF, and EtOH produced a low percentage of yield [78]. After that, Hou and colleagues in 2016 demonstrated that sulfonated graphene oxide (SGO) is a suitable catalyst for the dehydration (Scheme 18) of sucrose into 5-hydroxymethylfurfural (HMF). Employing SGO as the catalyst, a low percentage of catalyst loading resulted in high HMF 49 yields, reaching up to 94\%. Furthermore, it is in charge of converting high-concentration fructose (20\%) into a yield of 67\%, which is an appropriate yield. Aside from the availability of catalyst surface, the 2D shape improves the catalytically active efficiency of the strategy [79].

Vessally and his co-workers researched in 2016 when ethyl acetoacetate 50, an aldehyde 52, interacts with thio-urea 51 at room temperature (Scheme 19). Sulphated graphene and GO function well as heterogeneous catalysts for the high-yield production of 3,4-dihydropyrimidin-2 (1H)-ones (-thiones) 53. According to the investigations, the catalysts may be taken out of the reaction medium and recycled for at least five more instances without significantly losing...
Researchers discovered sulfonated graphene is more effective than GO [80].

In 2019, Dandia et al. devised a simple and metal-free approach for producing amides by oxidative amidation of aldehydes 55 in an aqueous phase with anilines 54 using GO as a recyclable catalyst and KBrO$_3$ as a milder oxidant under microwave irradiation. The ability of GO nanosheets to function as an acidic catalyst has been demonstrated. The reaction can take one of two possible pathways, illustrated in (Scheme 20). Following that, intermediate A is oxidised by KBrO$_3$, resulting in intermediate B, which includes oxaziridine. As a result of the intermediate, oxaziridine's temperature transition amide 56 was obtained as a result of the synthesis. Aniline reacts with benzaldehyde to make the intermediate C, which is subsequently reduced in the presence of KBrO$_3$ to yield the final product [81].

Naeimi and Kiani discovered the Sonogashira cross-coupling reaction, which was used to prepare diarylethyne compounds with widely available aryl halide derivatives and terminal alkynes in (Scheme 21). The nickel complex of N, N'-bis(2-hydroxyethyl) ethylenediamine was employed as a catalyst for coupling reaction between GO and silicon dioxide. Its thermal stability, high efficiency, and recyclability in the reaction made this catalyst a viable choice for the synthesis. Because of the absence of a sufficiently strong base owing to the copper salts, the alkyne proton cannot be eliminated. This is done by coordinating the alkyne with the ArNiX complex, which activates the terminal alkyne's C-H bond. To obtain the desired product, the C-H bond is weakened, HX is eliminated, and a base is present. Additionally, the catalyst can be detached and regenerated numerous times without causing any product loss [82].

Maleki and Rahimi reported the synthesis of different quinazoline derivatives in one-pot approach utilising graphene-based composite (Fe$_3$O$_4$@GO) as nanocatalyst with medium-to-excellent yields under ideal circumstances (Scheme 22). They carried out the reaction in a refluxing container with several solvents (water, CH$_3$CN, EtOH/H$_2$O, and ethanol) in increments of 3 mL. According to the
studies, ethanol has the highest product yield. Furthermore, they were able to monitor how the catalyst concentration affected the process’s rate of conversion by varying the concentration of Fe₃O₄@GO in refluxing ethanol. A total of 0.065 g of Fe₃O₄@GO was found to be sufficient for the effective completion of this process. Three components were combined in one pot to produce 2,3-dihydroquinazoline-4-(1H)-ones, octahydroquinazolinone, and benzimidazo[2,3-b] quinazolinone. According to the results, all of the reactants were successfully employed. The nanocatalyst may be used numerous times to obtain the reaction mixture’s result. 2-(3-nitrophenyl)-2,3-dihydro-4-(1H)-quinazolinone. After the reaction was finished under optimum conditions, the catalyst was magnetite-extracted and ethanol-washed. It was then used as a catalyst four more times in the same way, and there was no sign that its effectiveness was getting worse. [83]

Maleki and Paydar discovered a very excellent nanocatalyst for the three-component formation of trisubstituted imidazoles 74 in their graphene oxide/chitosan biocomposite employing one-pot approach (Scheme 23).

These reactions occurred without the presence of a solvent. In this method, the reaction time, the yield, the ability to separate the catalyst, and the availability of the solvent are all important success factors. The author found that 0.012 g of GO/chitosan heated to 120 °C for 10 min in a solvent-free environment produced a high yield of 95%. Simply said, GO can catalyse the process, albeit at a low yield. This is due to the carboxylic acid groups 71 of GO causing an undesired amidation process when paired with the amine formed during the breakdown of ammonium acetate 73. This seems to be the first study to show that a GO/chitosan composite can be used to speed up an organic process. Because of its exceptional heat stability, this catalyst was chosen for this reaction. Furthermore, the GO/chitosan nanocomposite has high biological activity and renewability. The GO/chitosan was recovered and reused 7 times in successive runs with no notable loss of activity [84].

Maleki and colleagues used citric acid in the synthesis of a nanocomposite containing graphene oxide and citric acid. The nanocomposite was successfully developed, and
the nanocatalyst’s structure and shape were assessed. A major condensation reaction, which produces imidazole derivatives 77 in high yield and in shorter reaction times at room temperature, was employed to demonstrate the usefulness of this nanocatalyst (Scheme 24). These materials, including a novel GO/CA nanocomposite as a catalyst support, and their application in the approach to developing imidazole analogues via the interaction of benzaldehyde 75 and o-phenylenediamine 76 in an eco-friendly ethanol solvent at room temperature, were thoroughly investigated. The catalyst’s high catalytic capabilities and reusability following simple work and progress as well as uncomplicated separation demonstrate a clear immobilisation of citrate surface functional groups of graphene oxide sheets for at least 6 cycles without significant loss in performance. This study is the first to describe how a GO/CA composite is made and how it can be used as an efficient and long-lasting catalyst in chemical processes, such as the making of imidazole analogues [85].

As a novel catalytic system of furan complexes 81, graphene oxide/Schiff base N2O4 ligand-palladium was created by Noori and colleagues. In order to study the catalytic activity of GO/H2L-Pd and to ensure that the reaction was carried out in the most efficient manner possible, a range of quantities of the catalyst and a variety of solvents as well as temperatures were utilised. Applying GO/H2-L-Pd as the catalyst in a variety of solvents was the primary factor that contributed to the improvement in reaction efficiency. They made the point that ethanol was the most effective solvent, which allowed for an 85% yield of the product. After that, the temperature of the mixture was adjusted until it was perfect. It was discovered that the reaction produced the maximum yield when performed at a temperature of about 60 °C with a loading amount of 0.05 g catalyst. With dimethyl acetylene dicarboxylate 79, they looked at conditions for aromatic aldehydes 80 and aromatic amines 78 with either electron-withdrawing or electron-donating substituents (Scheme 25). Various types of aryl aldehydes and aromatic amines were all able to react well with the catalyst. Based on these numbers, using GO/H2-L-Pd as a reusable catalyst can increase the yield of product and reduce the time it takes for the reactions to occur [86].

Reduced graphene oxide-mediated organic reactions

Researchers have recently used nanoparticles as a catalyst. Metal catalysts such as palladium (Pd) are used in the oxidation, hydrogenation of olefins, and carbon–carbon cross-coupling reactions in many chemical processes. Pd, in particular, has been widely investigated as a robust and promising catalyst for optimising reaction kinetics because of its high surface-to-volume ratio. Due to heterogeneous Pd, hydrogenation has been one of the most important, innovative, and commonly used synthetic processes [87]. As reported by Kilic et al. (Scheme 26), rGO-Ni@Pd was used as an effective catalyst in the carbon–hydrogen bond arylation of pyridine 82 with aromatic halides 83. Different solvents were tested and found to be optimal for different base combinations. DMA is assumed to be a solvent under mild conditions (130 °C for 24 h), resulting in a 90% yield. Using DMF as a constant solvent, the reaction was carried out with various bases such as K2CO3, t-BuOK, NaOH, KOH, and KOAc, producing 12%, 60%, 32%, 67%, and 98%, respectively. Using both electron-withdrawing and electron-donating groups in the reactants proved to be the most effective method for converting product 84, with product yields ranging from 74 to 99%. Apart from being the first example of core@shell NPs, GO-Ni@Pd produced a significant yield
of 86% after four consecutive runs, indicating its reusability. In C-H arylation processes, the rGO-Ni@Pd catalyst has been shown to lose activity, and there may be two possible explanations. The first is that the shape of the Ni@Pd NPs changes in relation to the rGO nanosheet agglomeration, and the second is that very little of the catalyst is lost during the process of separating and purifying after catalysis [88].

Development of core–shell nanoparticles containing Pd–Pt cores embedded in rGO was developed using a simple, one-point scalable microwave-assisted method. An aromatic dehalogenation approach and olefin reduction reactions (Scheme 27) were successfully carried out using this nanocomposite as a catalyst. The synergistic effect of each component is due to the efficiency of the catalyst. The sustainable catalyst system is critical because it is very versatile and stable, and it can be easily removed and recycled without losing activity. To avoid the fire hazard during the catalytic reaction process, commercial Pd or Pt (Pd/C, Pt/C) systems require considerable caution and isolation. The development of hybrid nanostructured materials, notably catalysts such as Pd@Pt/rGO, may pave the way for more selective organic compound functionality by utilising their efficiency. Individual component yields, selectivity, recyclability, and synergistic action can be achieved in the area of nanocatalysis [14].

Carbon–carbon cross-coupling reactions (Heck and Sonogashira coupling reactions) have been reported by Moussa and co-workers using Pd/Partially rGO as a heterogeneous catalyst under an advanced non-conventional microwave (MW) irradiation method for 15 min (Scheme 28). The Heck reaction of iodobenzene 87 with styrene 88 as a model reactant and K$_2$CO$_3$ as a base was performed in the existence of water and ethanol as solvents. On MW irradiation for 10 min, Pd/rGO undergoes 100% transformation with a 95% yield. Following that, reactant 87 with phenylacetylene 90 produced the required products 91 with isolated yields of roughly 92%. Lower conversions and yields were obtained when bromobenzene and 4-nitro-1-chloro-benzene were used as reactants in the Heck and Sonogashira reactions, respectively. With a TON of 7800 and a TOF of 230,000 h$^{-1}$ over 120 $^\circ$C under microwave irradiation, the Pd/rGO catalyst exhibits excellent photocatalytic activity and remarkable reusability for the product 91. The photocatalytic process seems to play a significant role in creating defect sites on the PRGO nanosheets, which are then responsible for the catalyst’s extraordinary catalytic characteristics [89].

Silver (Ag) NPs are essential surface plasmonic compounds with a variety of applications. It is employed in a variety of sectors, including water treatment, antibacterial action, and catalyst development. Kumar et al. synthesised Ag/rGO with optical response and light absorption characteristics; photocatalyst analyses have been examined in the oxidative coupling of 70 imines with oxygen under visible light, utilising CH$_3$CN as the reaction medium at room temperature (Scheme 29). There were few by-products in the reaction, and benzylamines 92 changed into the equivalent

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Scheme 28  Pd/Partially rGO-catalysed Heck and Sonogashira coupling reaction

Scheme 29  Synthesis of N-benzylidene benzylamine under visible lightening catalyst Ag@rGO
N-benzylidenebenzylamine 93 with a high yield of 98%; the reactions were carried out with various electron-releasing and -withdrawing groups. The optimal reaction conditions and suitable reactants demonstrated efficiency and selectivity among diverse substrates, 92 of which were substituted by groups of electron donors, i.e. -OCH₃ and -CH₃ were found to be more reactive halides as compared to those with electron-withdrawing groups. For so many runs, the photocatalyst exhibited constant reuse with no significant detrimental effects. This study promotes the development of GO or rGO-based materials that can be used as solid-state catalysts for visible light-enabled organic conversions [90].

Au NPs and their support form have recently been discovered to be more efficient catalysts for a variety of heterogeneous reactions. According to the study, new catalytic norms of the oxidation process analogous to the oxygen act were utilised to produce aminophenol, aldehydes, carboxylic acids, and other widely used organic reactions in the pharmaceutical industry, as established in a number of organic transformations. For their eco-friendly procedure, Pocklanova and her team have developed a new approach to nanocatalysts. The nanocomposite of Au and rGO was used to oxidise 94 to produce 95 and 96 (Scheme 30); in comparison with pure Au NPs and rGO, the author suggests that Au on the rGO substrate has a significantly higher catalytic performance. The alkene oxidation and aerobic oxidation reactions with nanocomposite are excellent. Nanocomposite materials have such high performance that they can be recycled an unlimited number of times without losing any of their original properties [91]. A new Au NPs-rGO-catalysed Ullmann homocoupling reaction has been reported by Movahed and co-workers (Scheme 31). Base and solvent effects on 97, a reactant in a bimolecular coupling process, were optimised under NMP at 100 °C for 6 h. At 94% efficiency, this base outperforms all other bases tested, including K₂CO₃, Cs₂CO₃, and potassium hydroxide (KOH), which each yield 67%, 84%, and 39%, respectively, when the technique was implemented. NMP was also found to be a good coupling reaction that yielded 97% of the desired product. According to the reaction mechanism proposed by the author, an aryl halide 97 band fragment is observed to form on the stage or surface of Au inside the Au NPs-rGO catalyst. The final product, 98 was produced by coupling aryls after homocoupling gold-attached aryl compounds. The recovery was finally found to be successful after six repeated reaction cycles [92].

| Aryl Halide | Yield |
|------------|-------|
| I          | 97%   |
| O Ar     | 94%   |
| Br        | 88%   |
| O Ar     | 81%   |
| Br        | 80%   |
| O OH     | Trace |
| Br        | Trace |
| O H      | 68%   |
| Br        | 41%   |

\[
\begin{align*}
\text{Au NPs-rGO, K}_2\text{PO}_4, \text{NMP, } 100 \, ^\circ\text{C, 6h} \Rightarrow & \quad \text{X} = -I, -Br \\
& \quad \text{R} = -\text{CHO}, -\text{H}_2, -\text{COCH}_3
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 31} \quad \text{Ullmann homocoupling reaction using Au NPs-rGO catalyst}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 30} \quad \text{Au/rGO-catalysed oxidation of ethyl benzenes}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 32} \quad \text{Synthesis of N-arylation of N-heterocycles}
\end{align*}
\]
Movahed et al. demonstrated in 2014 that Cu@Cu2O-rGO nanocomposite is an efficient heterogeneous catalyst for C-N generation in Ullmann cross-coupling reaction exhibiting good yields of up to 98%. Under aerobic circumstances Cs2CO3 as base and DMSO as solvent, the starting materials are aryl halide 99 and n-dodecane 100 (Scheme 32). Several parameters, including base, solvent, temperature, and duration, were used to optimise the reaction conditions. It was discovered that aerobic conditions produced 98% of the target product 101. The advantages of reactions are that they can be carried out in short periods of time without the usage of external ligands or inhibitors as promoters. The catalyst has been reused for a number of cycles, each separated by simple filtration [93].

Moghanlou et al. developed aromatic amine 103 by reducing the nitro aromatic group 102 in 2021 in the presence of hydrazine hydrochloride, copper oxide-reduced graphene oxide (Cu2O/rGO) as photocatalyst (Scheme 33). The photocatalytic material Cu2O/rGO was created by reducing Cu(OAC)2 and GO at the same time, resulting in Cu2O-rGO bonded nanosheets. Various conversions of nitro aromatic compounds were created utilising this catalyst at Cu2O/rGO in the presence of monohydrate hydrazine mixture (1:1:1), dichloromethane, methanol, and acetonitrile under visible light medium at room temperature. The yield was 100% after 150 min. This research has demonstrated that the nanoparticles construct a two-dimensional structure of rGO and that they will be very well decorated with Cu2O in these frameworks. The recyclability of the catalyst has been confirmed six times, and no significant variations in the reaction conversion have been observed [94].

In 2019, Rana et al. reported on the fabrication of Ni NPs supported by rGO with an average particle size of 12 nm, utilising a straightforward technique. Using the prototype reactants iodoanisole 104 and aryl magnesium chloride 105 in the presence of THF at 60 °C, the Kumada–Corriu cross-coupling reaction produces biphenyl as an end product (Scheme 34). This nanomaterial has exhibited great catalytic performance, yielding % and exhibiting good stability. XRD analysis confirmed the presence of Ni(OH)2 and NiO particles. The Ni nanoparticles, with a particle size of 11 nm, were designed to be equally distributed all over the rGO surface. The catalyst showed better stability during reuse trials [95]. Rajesh et al. investigated various 3-substituted indoles 110 with synthesis methods. Benzaldehyde 108 and malononitrile 109 react with indole 107 in the presence of rGO/ZnO composites to produce 3-amino alkylated indole 110 (Scheme 35). In the presence of organic solvents, the reaction takes a prolonged 120 min to generate product 110 at a low percentage of yield. However, water was utilised as an optimum solvent by the author, and the product was procured in a significant yield of 90% within 20 min, indicating its efficiency. The high catalytic activity and reusability of rGO/ZnO in this reaction are particularly remarkable [96].

In 2018, Bahuguna and colleagues described the production of bisindoles 113 by combining indole with aldehyde while using a ZnO-rGO as a catalyst

**Scheme 33** Reduction of nitroaromatic compounds

**Scheme 34** Ni(0)/rGO-catalysed C–C cross-coupling reaction

**Scheme 35** Synthesis of 3-amino alkylated indoles using rGO/ZnO
Furthermore, the author expanded on their invention by experimenting with indole 111 and unsaturated ketones 112. On the other hand, monoindole with three substituents was produced instead of bisindole 113. When 5-nitro indole was used, the same reaction was not enhanced. This study looked into the possibility of recycling catalysis. The catalyst’s capacity to withstand repeated uses was tested by conducting a recyclability experiment, which revealed that the nanohybrid catalyst can be regenerated numerous times, thereby maintaining its initial performance. There may have been some minor catalyst loss during the recovery phase, which could explain the 4.49% decrease in product yield that was measured between the first and fifth cycles [97].

Aghayan et al. have examined the copper catalyst mediated reduced GO with titanium dioxide as a photocatalyst for azide and alkyne cycloaddition click reactions (Scheme 37). Cu$_2$O/rGO/TiO$_2$ nanocomposites were observed in CuAAC cycloaddition when irradiated to visible light at about 254 nm. Various solvents, including CH$_3$CN, CH$_3$OH, H$_2$O, and DMF, were tried in this cycloaddition procedure, producing a low yield of 40% in 1–2 h. The author then improved the solvent mixtures while employing a DMF/H$_2$O (2/1) concentration, which increased the yield to approximately 66%, and then slightly increased the solvent concentration to complete the process. The DMF/H$_2$O (3/1) reaction was performed in 1 h with an 80% yield. The analysis indicated that the compounds were dispersible and had a high collision rate. The final product was formed after 120 min of light radiation with 2-(phenoxy)methyl oxirane 114 and 4-(prop-2-yn-1-yl-oxy) benzaldehyde 115. Cyclic epoxide reaction, which included 7-oxabicyclo [4.1.0] heptane employing phenyl acetylene 117 and NaN$_3$ 116, as well as the addition of triethylamine in the presence of the catalyst, resulted in a considerable yield of 80%. Even 1 h of 450 nm irradiation yielded 80% of triazole 118 and 119 derivatives from 4-(prop-2-yn-1-yl-oxy) benzaldehyde and 1-bromo-4-(bromomethyl) benzene [98].

The fabrication of AgPd nanoparticles supported on rGO was studied by Liu et al. They found that a straightforward non-noble metal catalytic approach was used. Co$_3$(BO$_3$)$_2$ & AgPd nanoparticles has been code posited on rGO, and

(Scheme 36). Aghayan et al. have examined the copper catalyzed reduced GO with titanium dioxide as a photocatalyst for azide and alkyne cycloaddition click reactions (Scheme 37). Cu$_2$O/rGO/TiO$_2$ nanocomposites were observed in CuAAC cycloaddition when irradiated to visible light at about 254 nm. Various solvents, including CH$_3$CN, CH$_3$OH, H$_2$O, and DMF, were tried in this cycloaddition procedure, producing a low yield of 40% in 1–2 h. The author then improved the solvent mixtures while employing a DMF/H$_2$O (2/1) concentration, which increased the yield to approximately 66%, and then slightly increased the solvent concentration to complete the process. The DMF/H$_2$O (3/1) reaction was performed in 1 h with an 80% yield. The analysis indicated that the compounds were dispersible and had a high collision rate. The final product was formed after 120 min of light radiation with 2-(phenoxy)methyl oxirane 114 and 4-(prop-2-yn-1-yl-oxy) benzaldehyde 115. Cyclic epoxide reaction, which included 7-oxabicyclo [4.1.0] heptane employing phenyl acetylene 117 and NaN$_3$ 116, as well as the addition of triethylamine in the presence of the catalyst, resulted in a considerable yield of 80%. Even 1 h of 450 nm irradiation yielded 80% of triazole 118 and 119 derivatives from 4-(prop-2-yn-1-yl-oxy) benzaldehyde and 1-bromo-4-(bromomethyl) benzene [98].

The fabrication of AgPd nanoparticles supported on rGO was studied by Liu et al. They found that a straightforward non-noble metal catalytic approach was used. Co$_3$(BO$_3$)$_2$ & AgPd nanoparticles has been code posited on rGO, and
subsequently, the $\text{Co}_3(\text{BO}_3)_2$ was sacrificed using acid etching (Scheme 38). Cobalt was employed as a sacrificial agent to prohibit AgPd nanoparticles from aggregating, which resulted in well-dispersed AgPd nanoparticles. The discovered catalyst has excellent photocatalytic activity and good selectivity for the ambient temperature mechanical switch hydrogenation of nitroarenes comprising formic acid and ammonium formate. Nevertheless, the sacrificially produced $(\text{Co}_6)_\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{RGO}$ and $(\text{Co}_6)_\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{XH}-72\text{C}$ exhibited excellent catalytic activity. After 20 min and otherwise 40 min at 25 °C, nitrobenzene could be transformed onto aniline with a high yield (>99%) and excellent selectivity. The high number of dispersed AgPd nanoparticles and the synergistic connection between AgPd nanoparticles and the RGO assistance are to blame for their remarkable catalytic activity [99].

For the transfer hydrogenation of nitroarenes, scientists have also produced a wide range of mono & polymetallic nanoparticles, such as palladium, gold, silver, and various elements fabricated on graphene, metal–organic scaffold, and so on is shown in Table 2.

**Graphene quantum dots for organic reactions**

The $\text{Fe}_3\text{O}_4@\text{GOQD-O-(propane-1-sulfonic acid)}$ catalyst (Scheme 39) was used to hold a suitable mixture of aldehyde 122, malononitrile 123, and 3-methyl-1H-pyrazole-5(4H)-one hundred in DI water at RT for a suitable period. Consequently, in the presence of 126, the author performed the reaction with starting materials 122 and 123. In order to obtain the desired products, 125 and 127, the reaction mixture was dissolved in ethanol and stirred for 5 min. Finally, the magnetic nature of the catalyst was separated using an alternating electromagnetic source. As a result of this, the author proved that the catalyst has strong magnetic performance, increases reaction rate, and is easy to recycle [110].

In 2018, Mahyari et al. developed a simple method for producing benzaldehyde 128 by incorporating a recyclable heterogeneous photocatalyst. A cobalt porphyrin-supported nitrogen and phosphorous co-doped graphene quantum dot/graphene (CoPP@N,P: GQD/G) was used under visible light. These photocatalysts are used in organic reactions to achieve selective oxidation and reduction steps. As a precursor, benzyl alcohol was used, and $\text{H}_2\text{O}$ functioned as the solvent in this reaction (Scheme 40). The photocatalytic

![Scheme 38](image-url) Conversion of nitro compounds into subsequent amines

![Table 2](image-url) Different types of aniline synthesis catalysed graphene oxide composites
properties of various aromatic alcohols 129 have been tested under optimal conditions. In the reaction environment of water, this catalyst spreads efficiently due to ionic interactions, resulting in high transformations and specificity for different alcohols under milder conditions. It achieved an outstanding yield of 92%. Photocatalyst performance is greatly enhanced by the graphene quantum dots on graphene’s broad absorption spectrum when activated by visible light [111].

According to the latest findings by Tu et al., GQD-DMA can be used as a photocatalyst for the oxidative coupling of amines. The oxidative coupling of amines was successfully completed after 15 h in an O₂ medium with different reaction conditions. The GQD-DMA scattered well in solvents such as diethyl ethers, dimethyl sulfoxide, and dichloromethane while the catalyst was combined with H₂O and CH₂Cl₂. Following that, GQD-DMA established the oxidation state between the suitably oxidised benzylamine and the visible light medium (Scheme 41), the

Scheme 39 Synthesis of pyrano [2, 3-c] Pyrazo and 4H-chromenes

Scheme 40 Synthesis of benzaldehyde

Scheme 41 GQD-DMA photocatalyst using oxidative coupling of benzylamide

Scheme 42 Synthesis of tetra-substituted propargylamine

Scheme 43 Synthesis of furocoumarin natural products
| S.NO | Graphene derivatives | Synthesis method | Applications | Results | Year | References |
|------|---------------------|------------------|--------------|---------|------|------------|
| 1    | Polyaniline @ reduced graphene oxide | In situ polymerization of aniline on pre-formed rGO foam | Flexible supercapacitors | after 1000 charge–discharge cycles, it retains 92% of its initial capacitance | 2015 | [115] |
| 2    | Carbon dots-labelled oligodeoxyribonucleotide and graphene oxide | Hydrothermal | Fluorescent biosensor | Hg^{2+} has a detection limit of 2.6 nM and can detect a wide spectrum of metal ions | 2015 | [116] |
| 3    | Silver@graphene oxide nanocomposite | Chemical method | Amalgamation-based detection of Hg(II) ions with Ag@GO nanocomposite | Selective 338 nM 10–200 μM Tap water recovers 97.62%, whereas lake water recovers 105.75% | 2015 | [117] |
| 4    | Graphene quantum dot/AgVO₃ nanoribbons | Facile hydrothermal and sintering technique | Photocatalytic degradation | In 180 min, the degradation rate of IBP is controlled at 98% | 2016 | [118] |
| 5    | Graphene–organic composite | Hydrothermal method | Fluorescent chemo sensor | In aqueous media, Ag⁺ selectivity is good | 2016 | [119] |
| 6    | Iron(III) porphyrin supported on S and N co-doped graphene quantum Dot | Ultrasonicated | Photocatalytic aerobic oxidation of alcohols | Under visible light irradiation, a photocatalyst with good selectivity and activity for aerobic oxidation of alcohols | 2016 | [120] |
| 7    | N-doped Bi₂O₂CO₃/graphene quantum dot | Ultrasonication | Photocatalysis applications | The use of GQDs in the composite increases the system’s light harvesting and charge separation efficiency | 2017 | [121] |
| 8    | Nitrogen-doped graphene quantum dots | Thermal pyrolysis technique | Detection of carcinogenic and toxic organic compound | 0–4 μM, with a 420 nM detection limit | 2017 | [122] |
| 9    | Mn₃O₄/reduced graphene oxide nanocomposite | Simple physical mixing method | Supercapacitor applications | After 5000 cycles, 95% of the original capacitance is preserved | 2017 | [123] |
| 10   | Graphene oxide and reduced graphene oxide | Hummer’s method & reduced graphene oxide (rGO) by using Zn metal powder | Super capacitor | Spectroscopy revealed that the RCT values for rGO and GO are 21.84 and 30.54 Ω, correspondingly | 2018 | [124] |
| 11   | Double-layer film composed of reduced graphene oxide and Rose Bengal dye | Ultrasonic-spin coating method | Chemo sensor for silver(I) detection | The measured Ag⁺ concentration is 98.5–104.2% | 2018 | [125] |
| 12   | Reduced graphene oxide/C₃N₄/Ag₂O/ | Simple chemical method | Electrochemical capacitors | After 1000 cycles, the composite electrode was examined and the bindings revealed that it is quite stable | 2018 | [126] |
| 13   | ZnO–Graphene quantum dots | Hydrothermal synthesis method | Photocatalyst | Photocatalysts with high efficiency for purification of water | 2018 | [127] |
| 14   | BiO/I/Fe₃O₄@graphene oxide | Co-precipitation | Photocatalyst | DNP photodegradation in visible light took 2 h to destroy the % of DNP | 2019 | [128] |
| 15   | Graphene quantum dot appended terpyridine | Ultrasonication & reflux condition | Fluorescence enhanced probe for Zn²⁺ | With detection limits of ~1.43 × 10⁻⁷ M chemosensory | 2019 | [129] |
| 16   | TiO₂-decorated graphene | Chemical reflux method | Fluorescent chemo sensor | Ag⁺ is very selective, and other metal ions have little effect on it | 2019 | [130] |
| 17   | Manganese nitride stabilised on reduced graphene oxide | Modified Hummers’ method | Sodium ion batteries, supercapacitors, and EMI shielding | Even after 180 cycles, the sodium storage capacity is still 716 mAhg⁻¹ | 2019 | [131] |
| S.NO | Graphene derivatives | Synthesis method | Applications | Results | Year | References |
|------|----------------------|------------------|--------------|---------|------|------------|
| 19   | rGO-BiVO₄-ZnO        | Hydrothermal method | Photocatalyst | Ciprofloxacin breakdown is efficient | 2020 | [132] |
| 20   | Graphene oxide-HoVO₄-TiO₂ | Hydrothermal method | Photocatalyst for degradation of ibuprofen | Ibuprofen photocatalytic degradation and excellent stability | 2020 | [133] |
| 21   | Poly-alanine/chitosan/reduced graphene oxide | Ultrasonication | Photocatalysis degradation | Excellent nano-photocatalyst advancement in industrial wastewater treatment | 2020 | [134] |
| 22   | Alkylamine-rGO       | Solid-phase reduction | Photocatalysis | Photocatalyst with high efficiency derived from organic materials | 2020 | [135] |
| 23   | CNT/ZnO/MoS₂ nanocomposite | Hydrothermal method | Photocatalytic degradation of aniline | Wastewater containing various types of organic contaminants need to be treated | 2020 | [136] |
| 24   | Silver nanoparticles coated by green graphene quantum dots | Green synthesis method | Antibacterial activity | Enhanced ability to destroy MRSA and hasten the healing of MRSA-infected wounds | 2020 | [137] |
| 25   | Silver/reduced graphene oxide | Co-precipitation method | Antibacterial activity and catalytic reduction of organic dyes | Bactericidal rates of 89.35, 95.67, and 99.99% for Pseudomonas aeruginosa | 2020 | [138] |
| 26   | Graphene quantum dot/Au | Pyrolysis | Calorimetric detection of imidacloprid with a LOD of 0.007 ppm, the linear range is 0.01–1 ppm | | 2020 | [139] |
| 27   | Polypyrrole/graphene heterostructures | Universal soft template method | NH₃-based sensing | (ΔR/R₀ = 45% for 10 ppm NH₃ and LOD of 41 ppb) against 0.2–40 ppm vapour NH₃ | 2020 | [140] |
| 28   | Graphene-quantum-dots-induced MnO₂ | Simple hydrothermal method | Supercapacitors | After 25 2,000 cycles, there was 95.3% retention rate | 2020 | [141] |
| 29   | Nitrogen-doped-graphene quantum dots | Hydrothermal method | Supercapacitors | Upon 5000 charging-discharging cycles, the capacitance stability was 98.91% | 2020 | [142] |
| 30   | Reduced graphene oxide | Chemical reduction | Antibacterial activity | Antibacterial vs. growth-promoting | 2021 | [143] |
| 31   | Poly (n-vinylpyrrolidone-co-acrylonitrile-co-methacrylic acid)–graphene quantum dot | Ultrasonication | Chemical sensing ammonia vapour | At 90 °C, the current density of the detector increased fivefold for ammonia vapour | 2021 | [144] |
| 32   | Fe₃O₄-rGO Nanocomposite | Ultrasonication, Chemical reduction | Electrochemical detection methods to detect trace amounts of arsenic in water | Arsenic has a lower limit of detection (1.19 ppb) and a higher sensitivity (2.15 A/ppb) | 2021 | [145] |
| 33   | Bi₂S₃/rGO composite | Hydrothermal method | Electrochemical sensor for ascorbic acid detection | There was a good rebound 97.1–101.55% | 2021 | [146] |
| 34   | Reduced graphene oxide | Reduction of ginger extract | Supercapacitor | Over 1000 cycles, there was 98% cycling stability | 2021 | [147] |
| 35   | Reduced graphene oxide supported PbTiO₃ nanospheres | Sol–gel method | Photocatalyst | 60 min of mild contact with 2.0 g.L⁻¹ solution resulted in the removal of 600 ppm sulphur contained ThP | 2020 | [148] |
molecules in a sequential manner. Substituents have a minor impact on phenyl rings, whether electron-donating (methyl and methoxy) or electron-withdrawing (halides and trifluoromethyl). Secondary amines such as indoline, 1,2,3,4-tetrahydroquinoline, and 1,2,3,4-tetrahydroisoquinoline, as well as other secondary amines, were tolerated with moderate to high selectivity. As expected, thiophen-2-ylmethylamine can be detected with amazing accuracy, as well as a great conversion rate of 88% and selectivity of 99%. By simply bubbling CO₂ into the reaction, this photocatalyst can be easily removed from the reaction mixture [112].

In 2020, Kharkwal et al. investigated the synthesis of tetra-substituted propargylamine 135 using ZnO with GQDs nanocomposites as a model reaction (Scheme 42). Among the starting materials for this reaction are cyclohexanone 132, morpholine 133, and phenylacetylene 134. In this reaction’s catalysts and substrates, there was little to no conversion of product when acetonitrile, DMF, DMSO, or H₂O was used as a solvent. Toluene, despite being a non-polar solvent, proved to be an effective solvent in the production of the desired product. At 80 °C for 4.5 h, a solvent-free condition was achieved, resulting in a 100% conversion rate. A yield of 85% was achieved using secondary amines such as morpholine, piperidines, and pyrrolidine to make the required tetra-substituted propargylamine product. If aryl-o-alkynes or secondary amine groups are allowed, propargylamine with four substituents can be synthesised. Some 85–94% of propargylamine was separated from a wide range of aromatic-alkynes and secondary amines with 5/6-membered carboxylic acids in this reaction [113].

Babaei and Ghomi developed a hydrothermal method for fabricating N-GQDs/ZnO/CuO heterojunction nanocomposites. Additionally, using chiral recoverable L-proline-connected N-GQDs/ZnO/CuO nanocomposites as catalysts, 4-bromophenacyl bromide 138, aromatic aldehydes 136, and 4-hydroxy coumarin are converted into furocoumarin synthetic compounds (Scheme 43). The results showed that changing the solvent, temperature, and pH level might change the form of the nanocatalyst. The developed heterostructure’s catalytic effectiveness was tested utilising a one-pot diastereoselective production of novel as well as established furocoumarin analogues 139 from natural sources. The total catalytic efficiency of developed heterojunction nanocomposites has been investigated employing one-pot diastereoselective manufacture of diverse and recognised furocoumarin analogues of organic components. Excellent yields of 86–96% were achieved in a short period of time as a result of the formation of 3 new sigma bonds, 2 C–C and 1 C–O, all through the three-component reaction development. Furthermore, the basic characteristics of the nanocomposites, such as heat, solvent, and molarity, were optimised to achieve the greatest catalytic efficiency. This method is also different because it has a high diastereoselective, moderate to excellent atom economy, less reaction time of only 35 min, a catalyst that can be reused for almost 7 times, and a very small amount of catalyst loading without loss of activity [114].

**Quick summary**

Table 3 provides an overview of graphene and its derivatives synthesised from different sources and prepared using a variety of procedures, as well as their catalytic applications in a wide range of different research areas.

**Conclusions and prospects**

These results reported above show that the GO/rGO/GQDs-assisted metal or metal oxide nanocomposites are useful heterogeneous catalysts for simple organic conversion and one-pot synthesis. The study looks at the different types of heterocyclic synthesis and emphasises the importance of different catalyst carriers and inhibitors. Palladium, silver, gold, copper, iron, and other metals are supported on the graphene’s surface, reduced graphene, and graphene quantum dots. This review includes cross-coupling processes, oxidation, reduction reactions, and one-pot multi-component synthesis. Because of their wide surface area, mild acidity, thermal-resistant, and the possibility of reusability, GO/rGO/GQDs have been proposed as heterogeneous nanocatalyst in organic processes. Owing to the existence of oxygen functions, GO can be easily distributed in water and other organic solvents. In the future, a variety of organic reactions such as etherification, dehydrogenation, addition, oxidation, hydrolysis, ring opening, cyclization, and esterification can be carried out using GO/rGO/GQDs-supported metal or metal oxide nanocomposites, and various heterocyclic compounds can be synthesised easily, at low cost, and eco-friendly. In the coming decades, high-stability supports such as GO or rGO-based nanocatalyst will become more common. As a result, extensive studies on the synthesis of nanophotocatalysts and the emergence of new approaches that avoid the use of hazardous chemicals in organic synthesis are required.

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