A Platinum Open Access Journal
for Organic Chemistry

Review

Free to Authors and Readers

DOAJ Seal

Arkivoc **2023**, part v, 0-0
to be inserted by editorial office

Graphene-based materials for asymmetric catalysis

Elżbieta Wojaczyńska[a]* and Mariola Zielińska-Błajet[b]*

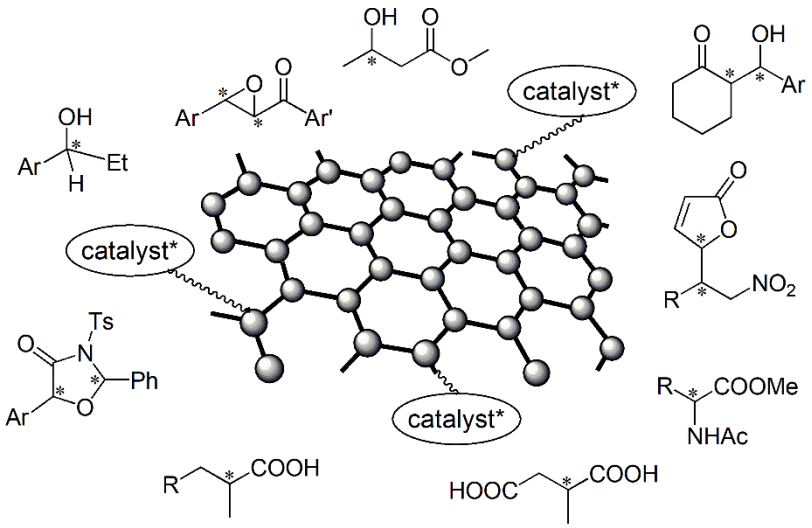
[a]*Department of Physical and Quantum Chemistry, Faculty of Chemistry,*
Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50 370 Wrocław, Poland
[b]*Department of Organic and Medicinal Chemistry, Faculty of Chemistry,*
Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50 370 Wrocław, Poland
Email: elzbieta.wojaczynska@pwr.edu.pl, mariola.zielinska-blajet@pwr.edu.pl

Dedicated to Professor Józef Drabowicz on the occasion of his anniversary

Received 09-27-2022 **Accepted** 11-10-2022 **Published on line** 11-18-2022

Abstract

A mini-review presents advances in the application of graphene-based materials in catalytic stereoselective synthesis. Examples of chiral organocatalysts and metal complexes immobilized on carbon nanosheets are discussed.



Keywords: Asymmetric synthesis, catalysis, enantioselectivity, graphene, heterogenized catalysts, organocatalysis

Table of Contents

1. Introduction

Though the story of graphene – a single layer of graphite – dates back to the 19th century,[1,2] it was in 2004 when the research conducted by Andre Geim and Konstanin Novoselov at the University of Manchester led to the discovery and isolation of a single atomic layer of carbon - a new allotropic form of this element.[3,4] In 2010, for this achievement, both scientists received the Nobel Prize in physics. To produce a single layer of graphene from graphite, they applied the "adhesive tape method" (mechanical exfoliation), a simple technique that does not require any special equipment. This was immediately adopted by other research groups which led to a fast development of research on graphene and exploration of various aspects.

Graphene and materials based on it (called GRMs – Graphene-Related Materials) show extraordinary properties which substantiate their applications in various fields – energy production and storage, sensors, building materials, medicine *etc*. A stable, two-dimensional sheet of very tightly bound sp^2 carbon atoms, with a thickness of a single layer of atoms arranged in a honeycomb pattern (hexagonal mesh), exhibits an extraordinary strength connected with high stretchability, flexibility and lightness.[5,6] Graphene is almost transparent to light, and impermeable to molecules (it represents the thinnest membrane that blocks-off all molecules).[7] It also conducts heat and electricity very well. One should remember, however, that the defects present even in high quality samples of graphene significantly alter its characteristics as compared with the theoretical predictions.

These unusual properties prompted research on potential applications of graphene and GRMs. One can expect that in the near future they will be used on a commercial scale in optoelectronics; specifically touchscreens, liquid crystal displays (LCD) and organic light emitting diodes (OLEDs). There are intense studies on the use of GRMs for energy storage – construction of new batteries and capacitors. Solar cells, fuel cells and hydrogen storage also constitute areas where these new carbon-based materials can be used to produce novel devices or significantly modify the performance of existing ones. Medical applications could involve efficient bioelectric sensory devices, tissue engineering and regeneration, drug delivery *etc*. Graphene can not only alter the properties of current coatings, but also introduce new materials characterized by extreme strength, impermeability and lightness. Composites reinforced with graphene can be used in – among others – the aviation industry, building materials, and mobile devices.[8,9]

Chemical stability and high surface area connected with diverse possibilities of structure modification roused an interest in the use of graphene-based materials as catalysts or catalyst supports. The adsorption capacity is strongly dependent on the number of layers and defects present in the sample.[10,11] The deposition is realized through physisorption or by formation of covalent bonds, which modifies the network of carbon atoms. Graphene serves as an ideal platform for the adsorption of various species, typically inorganic nanoparticles, which prevents the material from stacking and leads to the formation of functional composites bearing unique properties.[10]

For catalytic applications, mainly functionalized materials are used since graphene itself contains too few reactive sites. The majority of studies have been carried out with the relatively inexpensive graphene oxide (GO) or reduced GO (rGO) in which defects change the electrical and mechanical properties, but result in some features that improve the catalytic activity.[11] It was shown that not only surface area, but also the ability to participate in proton- and electron-transfer is very important for efficient catalytic action.[12]

Graphene-based catalysts have been employed in numerous catalytic reactions (including photocatalysis and electrocatalysis), such as oxygen reduction, CO_2 fixation, dihydrogen generation from water, hydrogenation, Fischer-Tropsch synthesis, degradation of pollutants and many others.[10,13-15] Graphene oxide was used as a selective catalyst for oxygenation/oxidation of organic substrates, but also for SO_2 to SO_3, conducted under mild conditions. Recently, GO was efficiently applied as an acidic catalyst for esterification, affording the corresponding products in good yields.[16]

Graphene layers functionalized with metals have shown their utility in various transformations, in particular Suzuki and Heck reactions. Supported palladium nanocatalysts performed much better than conventional Pd/C (a significant increase of TOF was observed).[11] For example, to construct a carbon-carbon bond in the Suzuki-Miyaura cross-coupling of potassium aryltrifluoroborates with aryl halides the authors applied palladium nanoparticles supported on graphene platelets as a very efficient catalyst (Figure 1).[17]

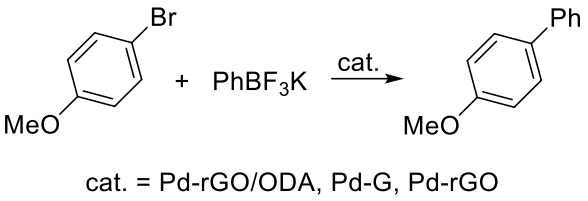


Figure 1. Suzuki-Miyaura cross-coupling catalyzed by graphene-derived Pd catalysts.

Asymmetric catalysis is one of the most important strategies for the synthesis of chiral enantiopure or enantiomerically enriched compounds.[18] This approach has gained great popularity in recent years due to its efficiency and environmental friendliness. In principle, a single molecule of a chiral catalyst can lead to the formation of millions of target molecules. The great importance attributed to chiral catalysts in asymmetric synthesis led to the award of the Nobel Prize in chemistry in 2001 to William S. Knowles, Ryoji Noyori and Barry K. Sharpless. Their pioneering work paved the way for the further development of asymmetric catalysis. Numerous chiral transition metal complexes have been introduced, and later, a new approach has emerged, namely the application of small chiral organic molecules (asymmetric organocatalysis), especially in the synthesis of pharmaceuticals (the final product is not contaminated with traces of heavy metals).[19-22] The development of stereoselective organocatalysis was also recognised with the Nobel Prize awarded in 2021 to Benjamin List and David MacMillan.

The dynamic development of graphene-based materials as a support for chiral metal complexes and organocatalysts has been noticed by the scientific community. Voitko reviewed the use of 1D/2D nanostructured carbon materials in asymmetric catalysis, with the focus on nanotubes.[23] In a comprehensive review by Deng and co-workers, advances in the construction and applications of chiral GRMs are gathered; catalytic applications are described rather briefly.[24]

2. Graphene-derived Materials in Asymmetric Organocatalysis

Graphene-based materials have attracted growing interest as efficient metal-free catalysts.[25,26] They have found application in carbon–carbon bond forming reactions, mainly in stereoselective aldol reactions.

2.1 Additions to carbonyl compounds

The aldol reaction represents the most versatile protocol for the preparation of optically enriched β-hydroxy ketones which have been widely used in the pharmaceutical, agrochemical and fine chemical industries.[27,28]

In 2015, Sadiq and coworkers found that the direct asymmetric aldol reaction of cyclohexanone with aromatic and aliphatic aldehydes performed in aqueous media could be catalyzed by amino acids covalently attached to graphene.[29] Heterogeneous, porous, and recyclable carbocatalysts (which can be considered organocatalysts) afforded aldol adducts with excellent yields (up to 97%) and stereoselectivity (up to 23:1 *dr* with the *anti* diastereomer predominating, and up to 99% *ee*, Figure 2). Chiral catalysts were obtained from L-alanine, L-serine, L-valine and L-arginine covalently attached to a graphene sheet in a three-step procedure initiated by Hummers' and Offeman's oxidation method.[30] They can be therefore regarded as graphene oxide derivatives. The best outcomes were observed for valine- and alanine-derived catalysts, while arginine derivative showed inferior results (only 58% yield, 1:1 *dr*, and 10% *ee* for benzaldehyde as substrate). Among aldehydes, 3-nitrobenzaldehyde led to optimal results (85-97% yield, ≥94% *ee*) in contrast to 3-methylbutanal (up to 65% yield, up to 65% *ee*).

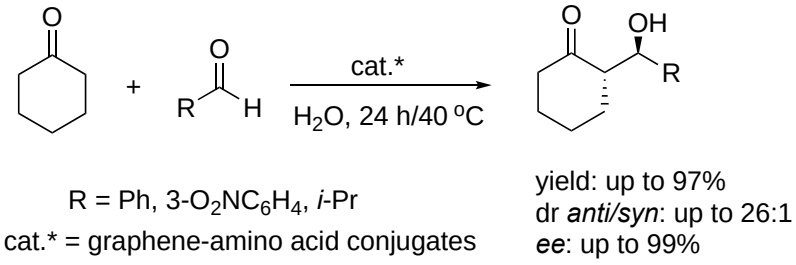


Figure 2. Stereoselective aldol reaction catalyzed by amino acids supported on graphene.

An increase in the reaction rate in the presence of water as compared to solvent-free conditions was observed. The authors suggested an enamine mechanism for the catalyzed pathway: cyclohexanone reacts with immobilized amino acid, yielding an enamine linkage (Figure 3). This is followed by the attachment of aldehyde to the chiral enamine and hydrolysis (facilitated in water). The catalyst could be reused several times without significant loss of activity or stereoselectivity.

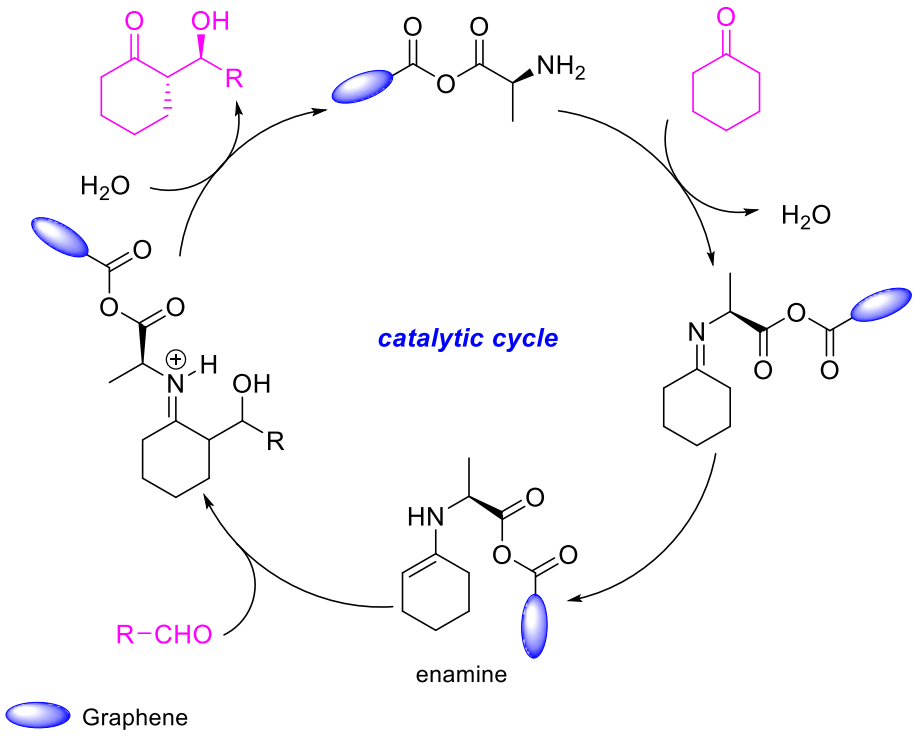


Figure 3. A proposed reaction pathway.

Szőri *et al.* used L-proline supported by graphite oxide or graphene oxide and their sulfated derivatives as chiral organocatalysts in the aldol reaction between aromatic aldehydes and acetone.[31] Proline was attached to the preorganized carbon supports in a mostly reversible manner though in the case of sulfated materials the bonding was stronger. The reaction between 2-nitrobenzaldehyde and acetone catalyzed by these catalyst systems led to variable yields of the products (11-81% conversion) with good selectivity and enantioselectivity (71-76% *ee*, values higher than 70% obtained for unsupported L-proline under identical conditions, Figure 4). Catalysts prepared from graphene exhibited higher activity as compared with those prepared from graphite. The catalytic activity decreased upon recycling due to the loss of proline from the surface.

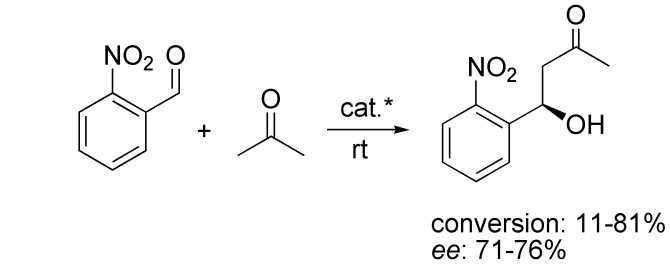


Figure 4. Enantioselective aldol reaction catalyzed by L-proline on the carbonaceous support.

Recently, Durmaz and co-workers reported the first example of preparation of recyclable graphene-supported proline-based bifunctional carbocatalysts.[32] L-Proline was attached to the graphene oxide sheets via organoamine-functionalized graphene oxide (GO-NH_2) and reduced graphene oxide (rGO-NH_2). The catalytic properties of heterogeneous catalysts (GO-Pro and rGO-Pro) were investigated in the direct asymmetric aldol

reaction. L-Proline grafted catalyst (GO-Pro) exhibited the best efficiency under mild conditions (room temperature, hexane as solvent) in the presence of benzoic acid and afforded the corresponding aldol adducts with good isolated yields (up to 88%) and enantiomeric excess (up to 85%; Figure 5).

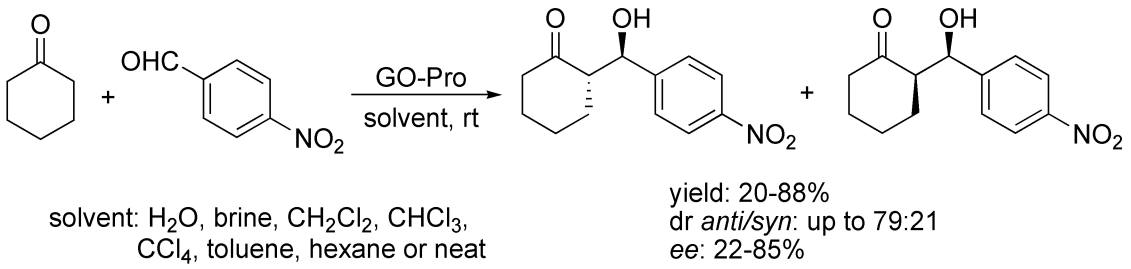


Figure 5. The direct asymmetric aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde.

A new nanocatalyst was prepared via immobilization of proline complexed to copper(II) onto the surface of magnetic graphene – a composite of silica-coated graphene and $MnFe_2O_4$ (MF).[33] The newly synthesized G/MF@SiO_2@Cu(proline)$_2$, which contains Cu(II) center as Lewis acid, was found to be an efficient catalyst for asymmetric aldol reactions of benzaldehyde with cyclohexanone under solvent-free conditions, providing appropriate aldol products in high yield and excellent enantiomeric excess (> 90 %).

2.2 Conjugate additions

The Michael addition is one of the most useful and representative methods for the formation of new C–C bonds, thus the formation of new C–C bonds via Michael addition is an important transformation in organic chemistry, and is used extensively in the synthesis of a variety of molecules, including biologically active natural products and antibiotics.

Acocella *et al.* described the use of graphene oxide-based catalysts in the diastereoselective Mukaiyama–Michael addition of 2-(trimethylsiloxy)furan (TMSOF) and *β*-nitrostyrene (Figure 6).[34] A preference for the formation of *anti* product was noteworthy, as other catalysts led mainly to *syn* diastereomer. The authors noticed that the use of the nitroalkenes with aromatic substituents in the *β*-position generated the product in moderate to good yields (65-90%). The presence of an electron-donating group in the *para* position of the aromatic ring of the *β*-nitrostyrene caused a significant decrease in efficiency (23%), while a slight lowering in the diastereoselectivity was observed with both EDG or EWG groups. The highest diastereoselectivity was observed for a naphthyl group (*syn/anti* = 15:85), whereas the lowest activity and selectivity were achieved with aliphatic nitroalkenes (yield up to 30%, dr (*syn/anti*) up to 35:65).

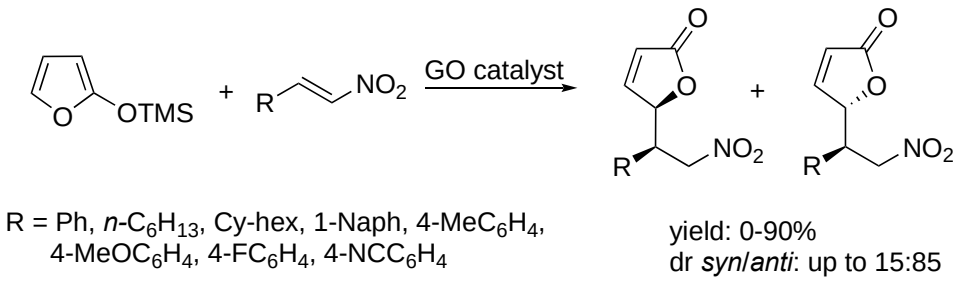


Figure 6. Diastereoselective Mukaiyama−Michael addition of TMSOF to variously substituted *β*-nitroalkenes.

Schulz and coworkers reported the synthesis of a catalyst *pyr*-hyperBTM@rGO by the immobilization of the pyrene-tagged hyperBTM ((2*R*,3*S*)-(−)-3,4-dihydro-3-(isopropyl)-2-phenyl-2*H*-pyrimido[2,1-b]benzothiazole) onto the reduced graphene oxide (rGO) surface.[35] The catalytic efficiency and the recyclability of this catalyst was tested on the asymmetric formal [3+2] cycloaddition of arylacetic anhydrides and *rac*-3-phenyl-2- tosyl-1,2-oxaziridine (Figure 7).

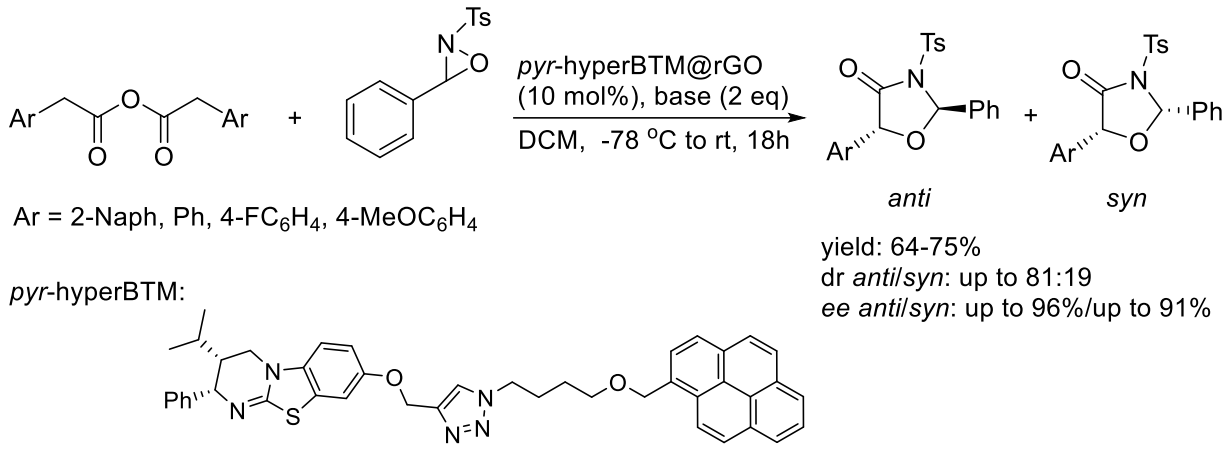


Figure 7. Asymmetric cycloaddition of aromatic anhydride and oxaziridine derivative catalyzed by *pyr*-hyperBTM@rGO.

The pyr-hyperBTM@rGO under optimized reaction conditions displayed good catalytic activity and the products were obtained in high yields and with good-to-excellent enantioselectivity values. Recovery of the active species was possible by simple filtration and after 7 cycles no decrease in the efficiency of the catalyst was observed.

3. Graphene-supported Chiral Metal Catalysts

Several examples of immobilization of chiral transition metal complexes on graphene-based support have been reported yielding heterogenized catalysts, mainly for asymmetric epoxidation and hydrogenation.

A stereoselective epoxidation is an important method to transform electron-deficient olefins into enantiomerically pure epoxides, valuable intermediates in organic synthesis.[36-38] In the last decade, chiral salen manganese(III) complexes were one of the most efficient catalytic systems used for obtaining chiral epoxides.[39,40] Tan and co-workers developed an enantioselective epoxidation of nonfunctionalized olefins catalyzed by chiral salen Mn(III) derivatives supported by graphene oxide.[41] The metal complex was covalently attached to the GO sheet through an imidazolium-based ionic liquid (IL) linker (Figure 8).

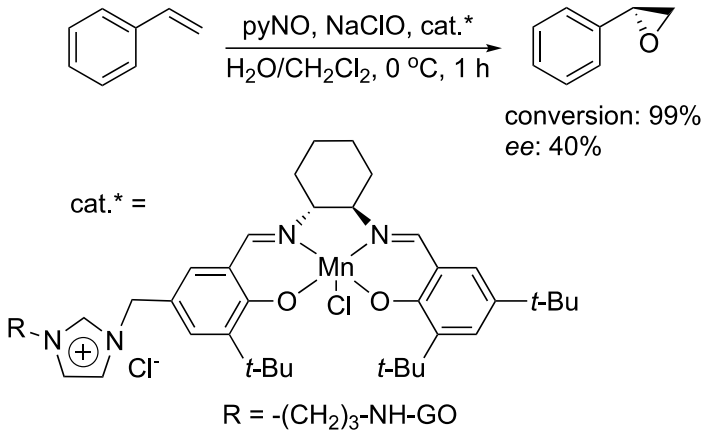


Figure 8. Epoxidation of styrene catalyzed by Mn(III) salen complex-ionic liquid conjugate.

The flexible layer-structure, and the active role of the IL linker in the reaction, make the novel heterogeneous catalyst efficient for the enantioselective epoxidation of unfunctionalized olefins in a biphasic system (aqueous NaClO was used as an oxidant), affording the products in moderate to high yields (53-95%) and enantioselectivity (73-93%), except for styrene and α-methylstyrene (40% and 44% *ee*, respectively). A significant increase of the reaction rate was observed for various alkenes such as styrene derivatives, indene, 1,2-dihydronaphthalene, 6-cyano- and 6-nitro-2,2-dimethylchromene, both in comparison with GO-free and IL-free complexes. It is worth mentioning that the catalyst was perfectly stable and could be reused several times without remarkable loss of activity and enantioselectivity.

Sun and co-workers demonstrated the first example of manganese complexes of N_4 ligands and graphene oxide catalyzing the highly enantioselective epoxidation of olefins (up to 99% *ee*) with aqueous H_2O_2 as a green oxidant (Figure 9).[42] Six chiral Mn(II) complexes containing N_4 coordination core were tested as catalysts for chalcone epoxidation. It was shown that the addition of a small amount of GO improved enantioselectivity (up to 99% *ee*) as compared with the traditional carboxylic acid additives. The reaction showed wide substrate scope, giving reasonable yields and high asymmetric induction for various chalcones, chromenes, cinnamates and styrenes. Lower enantioselectivity was observed for substrates bearing electron-donating groups. The catalyst could be easily separated from the reaction mixture by centrifugation. In a proposed mechanism, a formation of an intermediate containing the oxidized manganese ion bound to carboxylic groups of graphene oxide was included.

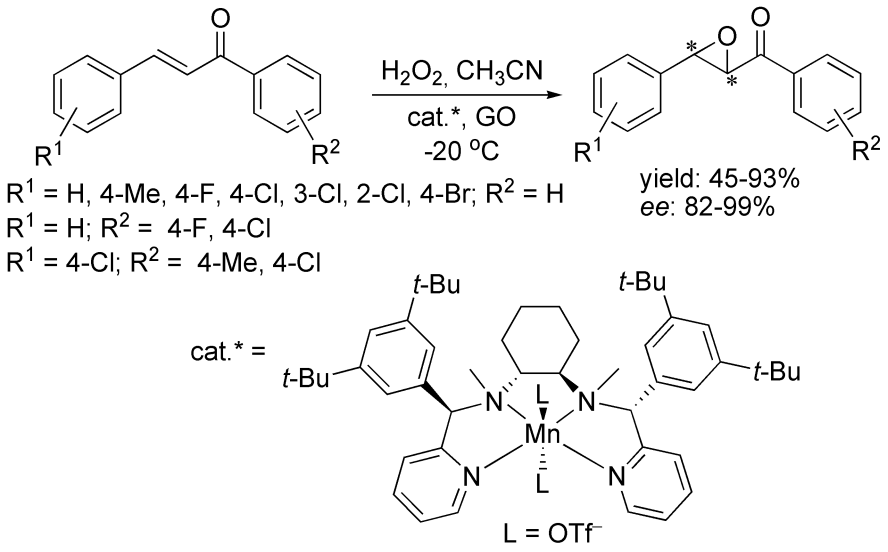


Figure 9. Asymmetric epoxidation of chalcone derivatives catalyzed by a manganese(III) complex in the presence of GO additive.

Hosseini-Monfared and Abbasi successfully employed the manganese(III)-salan complex immobilized on a modified reduced graphene oxide in the aerobic enantioselective epoxidation of non-functionalized olefins (Figure 10).[43] The chiral Mn(III) salan complex was covalently grafted onto rGO sheets decorated with magnetic Fe_3O_4 nanoparticles (GFC). High activity and enantioselectivity for the epoxidation of styrene, α-methyl styrene and *trans*-stilbene were observed. The catalyst was stable and could be reused at least five times with no significant change of its activity.

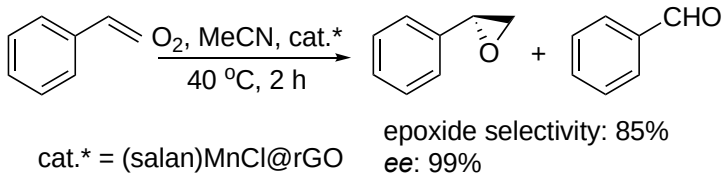


Figure 10. Oxidation of styrene with O_2 catalyzed by Mn(III) complex attached to a modified reduced graphene.

Highly effective heterogeneous hydrogenation ranks among the most important reactions in organic synthesis, used to produce a variety of functional compounds, including chiral derivatives. Among many methods, the reduction of β-keto esters over tartrate-modified Raney nickel catalyst and the hydrogenation of α-keto esters over *Cinchona* alkaloid-modified platinum catalyst (Orito reaction) are of particular significance. The catalytic systems involve an achiral activator, responsible for the reduction, and a chiral modifier, responsible for enantioselectivity, and a support.[44]

Palladium nanoparticle-graphene catalysts modified by cinchonidine were applied by Szöri *et al*. for the stereoselective hydrogenation of α,β-unsaturated carboxylic acids (Figure 11).[45] Three types of hybrid materials were prepared from graphene and palladium using various synthetic approaches, resulting in slightly different palladium content, reduced to oxidized Pd ratio and particle size. Their performance in the asymmetric hydrogenation was found to be better than for the commercial Pd/C with cinchonidine added. The observed

conversions were in most cases high (quantitative in some examples), and the enantiomeric excess was in the range of 3-49%. The optimized conditions included the use of achiral amine additive, H_2 pressure was 2-5 MPa.

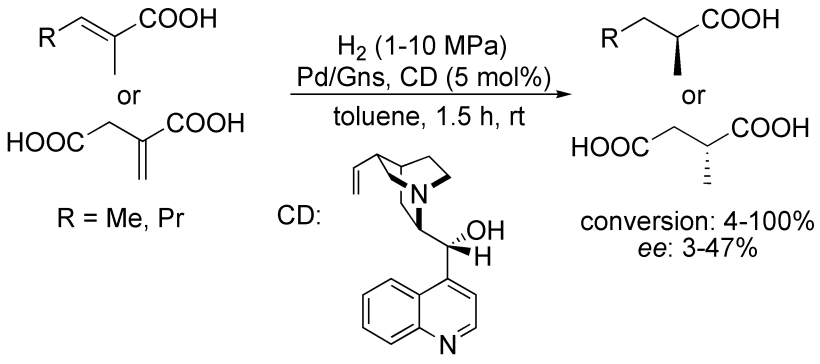


Figure 11. Hydrogenation of unsaturated amino acids catalyzed by palladium nanoparticle-graphene catalyst modified with cinchonidine.

Enantioselective heterogeneous hydrogenation of β-keto esters in the presence of chiral modified Ni catalysts supported with reduced graphene oxide (rGO) was reported by Ding *et al.*[46] The hybrid catalyst was prepared *via* chelation of $NiCl_2$ with graphene oxide and subsequent reduction, followed by treatment with L- or D-tartaric acid (TA) as a chiral modifier. Examination of the obtained composite indicated that nickel was 60% Ni^0 and 40% (Ni^{2+} + Ni^{3+}) and the part of TA carboxylic groups were coordinated. The obtained catalytic system used for hydrogenation of methyl acetylacetonate afforded β-hydroxyesters with excellent enantioselectivity (98.5-98.6% *ee*) and conversion (>99%, Figure 12). The performance was significantly better than for TA-modified Raney Ni (79% conversion, 63% *ee*). In addition, the system exhibited a high turnover frequency of ca. 20,000 h^{-1}. The excellent catalytic activity and asymmetric induction could be attributed to the unique properties of the modified rGO, *i.e.* a large surface area to stabilize Ni particles and enhance the adsorption of the reactant, and to the ability of transfer electrons in catalytic process. The ferromagnetism of Ni made the catalyst easy to magnetically separate and reuse, though a slight decrease of yield and enantioselectivity was observed after the five repetitions attributed to the size increase of Ni nanoparticles and leaching of TA.

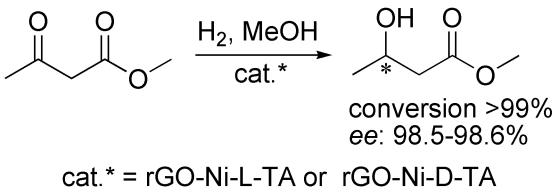


Figure 12. Asymmetric hydrogenation of methyl acetylacetonate by the modified rGO.

In a recent paper, Shi and co-workers reported the use of a multicomponent catalyst immobilized on the surface of graphene via π-π interactions.[47] A rhodium(I) complex with two axially chiral MonoPhos ligands tagged with pyrene moieties was prepared in three steps from commercially available reactants, 1-pyrenebutyric acid, (*R*)-[1,1'-binaphthalene]-2,2'-dimethoxy-6-butanol, hexamethyltriamidophosphite, and $[Rh(COD)_2]BF_4$. Adsorption of the complex onto graphene was manifested by a disappearance of the orange color of its solution. The authors used the obtained hybrid material as a heterogeneous catalyst of asymmetric hydrogenation of unsaturated amino acid derivatives (Figure 13). The reaction was performed in ethyl acetate

with 20 atm hydrogen pressure for two hours; catalyst loading of 1% allowed >99% conversion for eight substrates studied, and enantioselectivity was also high (91-96% *ee*). The activity and selectivity of the homogeneous system were fully retained, while the heterogenization allowed easy reuse of the catalyst: 13 cycles were checked with no change of conversion and a very slight decrease of stereoselectivity, although an increase of reaction time to ten hours was necessary due to the observed Rh leaching.

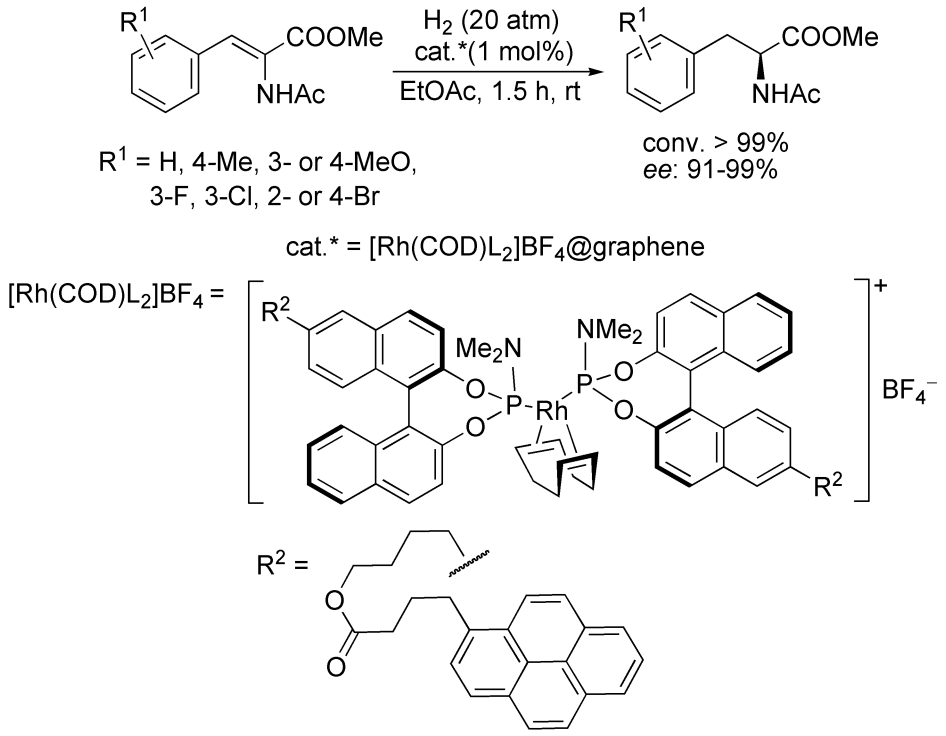


Figure 13. Hydrogenation catalyzed by rhodium(I) complex of MonoPhos derivative with graphene support.

Other types of reactions can also be catalyzed by metal complexes supported with graphene derivatives. The chiral BINOL-functionalized nanoporous graphene oxides-catalyzed conjugate addition of diethylzinc to aromatic aldehydes was performed by Yan and co-workers.[48] To prepare GO-BINOL-Ti catalyst, a commercial GO was first oxidized in an acidic environment to make nano-porous GOs and then enantiopure (*R*)- or (*S*)-NH_2-BINOLs were covalently attached to the nanoporous GOs, and this GO-BINOL was subsequently treated with Ti(O*i*-Pr)$_4$. Applied in asymmetric addition of $ZnEt_2$, the GO-BINOL-Ti catalyst displayed a very good activity (resulting in 99% conversion), but relatively low enantioselectivity (up to 45% *ee*, Figure 14) as compared with the use of *R*-BINOL as catalyst (90% *ee*).

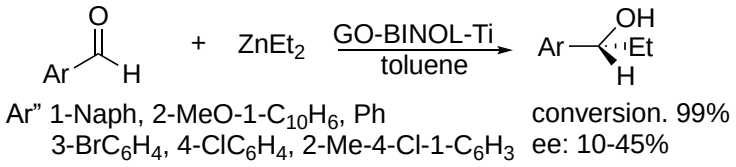


Figure 14. GO-BINOL-Ti catalyzed $ZnEt_2$ additions to aromatic aldehydes.

4. Conclusions

The presented studies show the potential of graphene-based chiral catalysts in asymmetric synthesis. High activities and stereoselectivities observed in aldol reactions, epoxidation and hydrogenation prompt further studies in the field, and perhaps in the future the extraordinary properties of carbon nanosheets will be fully utilized, as well as the wide possibility of their modifications. In particular, asymmetric variants of numerous processes which take advantage of the active participation of the carbon matrix in the catalytic cycle should be developed. The possible drawbacks are connected with the high price and limited availability of graphene, although this situation should gradually improve. In addition, in most cases the catalyst can be recycled several times, which is beneficial from both economic and environmental points of view.

In the future, more catalytic applications of graphene-based hybrid materials (nanocomposites) can be expected. One can also predict the development of systems involving enzymes. They can be directly attached to the carbon monolayer; as an example, dehydrogenase was covalently bound to graphene and applied in the electroconversion of carbon dioxide into methanol.[49] Another possibility is illustrated by the work of Baeg and co-workers who developed a protocol for solar light-driven highly enantioselective system for enzyme-catalyzed reduction of prochiral ketones.[50] They applied BODPY-modified graphene for the photocatalytic regeneration of NADPH mediated by a Rh(I) complex. The excellent enantioselectivities were accompanied with yields up to 74%. This example of asymmetric artificial photosynthesis demonstrates the versatility of graphene-based systems.

References

1. Geim, A. K. *Phys. Scr.* **2012**, T146, 014003 (and references cited therein). https://doi.org/10.1088/0031-8949/2012/T146/014003
2. Ciesielski, A.; Samori, P. *Chem. Soc. Rev.* **2014**, *43*, 381-398 (and references cited therein). https://doi.org/doi:10.1039/c3cs60217f
3. Novoselov, K. S; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I.V.; Firsov, A. A. *Science* **2004**, *306*, 666–669. https://doi.org/10.1126/science.1102896
4. Meyer, J. C.; Geim, A. K.; Katsnelson, M. I.; Novoselov, K. S.; Booth, T. J.; Roth, S. *Nature* **2007**, *446,* 60–63. https://doi.org/10.1038/nature05545 .
5. Allen, M. J.; Tung, V. C.; Kaner, R. B. *Chem. Rev.* **2010**, *110*, 132−145. https://doi.org/10.1021/cr900070d
6. Cooper, D. R.; D'Anjou, B.; Ghattamaneni, N.; Harack, B.; Hilke, M.; Horth, A.; Majlis, N.; Massicotte, M.; Vandsburger, L.; Whiteway, E.; Yu, V. *ISRN Condens. Matter Phys.* **2012**, *2012*, 501686. https://doi.org/10.5402/2012/501686
7. Berry, V. *Carbon* **2013**, *62*, 1-10. https://doi.org/10.1016/j.carbon.2013.05.052
8. Bai, S.; Shen, X. *RSC Adv.* **2012**, *2*, 64–98. https://doi.org/10.1039/C1RA00260K
9. Huang, X.; Qi, X.; Boey, F., Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 666-686. https://doi.org/10.1039/C1CS15078B
10. Machado, B. F.; Serp, P. *Catal. Sci. Technol.* **2012**, *2*, 54-75.

https://doi.org/10.1039/C1CY00361E
11. Fan, X.; Zhang, G.; Zhang, F. *Chem. Soc. Rev.* **2015**, *44*, 3023-3033. https://doi.org/10.1039/C5CS00094G
12. Radovic, L. R.; Mora-Vilches, C.; Salgado-Casanova, A. J. A. *Chin. J. Catal.* **2014**, *35*, 792-797. https://doi.org/10.1016/S1872-2067(14)60130-3
13. Su, C.; Loh, K. P. *Acc. Chem. Res.* **2012**, *46*, 2275–2285. https://doi.org/10.1021/ar300118v
14. Hu, M.; Yao, Z.; Wang, X. *Ind. Eng. Chem. Res.* **2017**, *56*, 3477-3502. https://doi.org/10.1021/acs.iecr.6b05048
15. Ahmad, M. S.; Nishina, Y. *Nanoscale* **2020**,*12*, 12210-12227. https://doi.org/10.1039/D0NR02984J
16. Chen, Z.; Wen, Y.; Fu, Y.; Chen, H.; Ye, M.; Luo, G. *Synlett* **2017**, *28*, 981-985. https://doi.org/10.1055/s-0036-1588399
17. Gómez-Martínez, M.; Buxaderas, E.; Pastor, I. M.; Alonso, D. A. *J. Mol. Catal. A: Chem.* **2015**, *404-405*, 1-7. https://doi.org/10.1016/j.molcata.2015.03.022
18. Nogradi, M. *Stereoselective Synthesis*. *A practical approach.* Wiley-VCH: Weinheim, Germany, 1994.
19. Dalko, P. I.; Moisan, L. *Angew. Chem. Int. Ed.* **2004**, *43*, 5138-5175. https://doi.org/10.1002/anie.200400650
20. Seayad, J.; List, B. *Org. Biomol. Chem*. **2005**, *3*, 719-724. https://doi.org/10.1039/B415217B
21. Dondoni, A.; Masi, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 4638-4660. https://doi.org/10.1002/anie.200704684
22. Xiang, S. H.; Tan, B. *Nat. Commun.* **2020**, *11*, 3786. https://doi.org/10.1038/s41467-020-17580-z
23. Voitko, K. V. *J. Nanosci. Nanotechnol.* **2019**, *19*, 5074-5088. https://doi.org/10.1166/jnn.2019.16897
24. Zhao, B.; Yang, S.; Deng, J.; Pan, K. *Adv. Sci.* **2021**, *8*, 2003681. https://doi.org/10.1002/advs.202003681
25. Hu, H.; Xin, J.H.; Hu, H.; Wang, X.; Kong, Y. *Appl. Catal. A: Gen.* **2015**, *492*, 1-9. https://doi.org/10.1016/j.apcata.2014.11.041
26. Navalon, S.; Dhakshinamoorthy, A.; Alvaro, M.; Antonietti, M.; García, H. *Chem. Soc. Rev.* **2017**, *46*, 4501–4529. https://doi.org/10.1039/c7cs00156h
27. Palomo, C.; Oiarbide, M.; García, J. M. *Chem. Soc. Rev.* **2004**, *33*, 65–75. https://doi.org/10.1039/B202901D
28. Sukumaran, J.; Hanefeld, U. *Chem. Soc. Rev.* **2005**, *34*, 530–542. https://doi.org/10.1039/b412490a
29. Sadiq, M.; Aman, R.; Saeed, K.; Ahmad, M. S.; Zia, M. A. *Mod. Res. Catal.* **2015**, *4*, 43–49. https://doi.org/10.4236/mrc.2015.42006
30. Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339-1339. https://doi.org/10.1021/ja01539a017.
31. Szőri, K.; Réti, B.; Szőllősi, G.; Hernádi, K.; Bartók, M. *Top. Catal.* **2016**, *59*, 1227–1236. https://doi.org/10.1007/s11244-016-0643-6.
32. Azlouk, M.; Durmaz, M.; Zor, E.; Bingol, H. *Mater. Chem. Phys.* **2020**, *239*, 122298.

https://doi.org/10.1016/j.matchemphys.2019.122298.
33. Kooti, M.; Kooshki, F.; Nasiri, E. *Res. Chem. Intermed.* **2019**, *45*, 2641–2656. https://doi.org/10.1007/s11164-019-03755-x.
34. Acocella, M. R.; Mauro, M.; Falivene, L.; Cavallo, L.; Guerra, G. *ACS Catal.* **2014**, *4*, 492-496. https://doi.org/10.1021/cs401053t
35. Yuan, Y. C.; Abd El Sater, M.; Mellah, M.; Jaber, N.; David, O. R. P.; Schulz, E. *Org. Chem. Front.* **2021**, *8*, 4693–4699. https://doi.org/10.1039/d1qo00646k
36. Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, *103*, 2457-2473. https://doi.org/10.1021/cr020471z
37. Xia, Q. H.; Ge, H. Q.; Ye, C. P.; Liu, Z. M.; Su, K. X. *Chem. Rev.* **2005**, *105*, 1603-1662. https://doi.org/10.1021/cr0406458
38. Wong, O. A.; Shi, Y. *Chem. Rev.* **2008**, *108*, 3958-3987. https://doi.org/10.1021/cr068367v
39. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801-2803. https://doi.org/10.1021/ja00163a052
40. Liao, S.; List, B. *Angew. Chem. Int. Ed.* **2010**, *49*, 628-631. https://doi.org/10.1002/anie.200905332
41. Zheng, W.; Tan, R.; Yin, S.; Zhang, Y.; Zhao, G.; Chen, Y.; Yin, D. *Catal. Sci. Technol.* **2015**, *5*, 2092-2102. https://doi.org/10.1039/C4CY01290A
42. Miao, C.; Yan, H.; Xu, D.; Xia, C.; Sun, W. *Adv. Synth. Catal.* **2017**, *359*, 476-484. https://doi.org/10.1002/adsc.201600848
43. Hosseini-Monfared, H.; Abbasi, V. *Trends Green Chem.* **2017**, *3*, 98. https://doi.org/10.10.21767/2471-9889-C1-003
44. Blaser, H.-U.; Jallet, H.-P.; Müller, M.; Studer, M. *Catal. Today* **1997**, *37*, 441-443. https://doi.org/10.1016/S0920-5861(97)00026-6
45. Szöri, K.; Puskás, R.; Szöllösi, G.; Bertóti, I.; Szépvölgyi, J.; Bartók, M. *Catal. Lett.* **2013**, *143*, 539-546. https://dx.doi.org/10.1007/s10562-013-1006-6
46. Ding, C.; Wei, W.; Sun, H.; Ding, J.; Ren, J.; Qu, X. *Carbon* **2014**, *79*, 615-622. https://doi.org/10.1016/j.carbon.2014.08.022
47. Hao, E.-J.; Li, G.-X.; Lv, Z.-Z.; Li, F.-S.; Chen, Y.-Q.; Lin, S.-J.; Shi, C.-Z.; Shi, L. *Org. Chem. Front.* **2020**, *7*, 345-349. https://doi.org/10.1039/C9QO01331H
48. Wang, X.; Guo, J.; Qie, F.; Yan, Y. *J. Mater. Sci.* **2019**, *54*, 6908–6916. https://doi.org/10.1007/s10853-018-03230-9
49. Seelajaroen, H. ; Bakandritsos, A.; Otyepka, M. ; Zbořil, R. ; Sariciftci, N. S. *ACS Appl. Mater. Interfaces* **2020**, *12*, 250-259. https://doi.org/10.1021/acsami.9b17777
50. Choudhury, S.; Baeg, J.-O.; Park, N.-J.; Yadav, R. K. *Green Chem.*, **2014**, 16, 4389-4400. https://doi.org/10.1039/c4gc00885e

Authors' Biographies

Elżbieta Wojaczyńska received her M.Sc.Eng. degree in organic chemistry from the Wrocław University of Science and Technology in 1997. Her doctoral thesis on the enantioselective synthesis and application of chiral sulfoxides was completed in 2001. Her research at the Department of Physical and Quantum Chemistry of the Wrocław University of Science and Technology focusses on the synthesis of new chiral heteroorganic compounds for asymmetric synthesis and biomedical applications.

Mariola Zielińska-Błajet received her PhD in chemistry at the Wrocław University of Science and Technology under the supervision of Professor Bożena Bujnowska. After a period as post-doctoral fellow (STA fellowship) at the National Institute for Resources and Environment (NIRE) in Tsukuba, Japan she joined the Department of Organic Chemistry of the Wrocław University of Science and Technology. Her research interests include asymmetric synthesis, organocatalysis, heteroorganic compounds and chemistry of Cinchona alkaloids.