Journal of Chemical Health Risks

www.jchr.org

JCHR (2023) 13(6), 1907-1912 | ISSN:2251-6727

Preparation of Copper based Composite for Catalytic Reduction of 4-Nitro Phenol in Ambient Condition

Saurabh Pandey[1], Gayatri Pandey[2], Archi Jain[3], Umesh Kmar Sharma[4], Nitesh Rajput[5], Narendra Pal Lamba[6*], Manmohan Singh Chauhan[7*]

[1,2,3,5,6,7]Amity University Rajasthan, Jaipur, India – 303002
[4]Dept. of Polymer Science, Bhaskaracharya college of Applied Sciences, University of Delhi, Delhi, India – 110075

(Received: 07 October 2023 Revised: 12 November Accepted: 06 December)

KEYWORDS
p-nitrophenol, Graphene oxide, Catalytic reduction

ABSTRACT:
A facile synthesis of copper oxide decorated reduced Graphene oxide using ultrasonication is reported here. This nanocomposite exhibit very high efficiency in the reduction of p-Nitrophenol to the corresponding Amine. Different concentrations of p-nitrophenol have been used to test the catalytic efficiency of prepared catalyst with sodium borohydride and it is found that it is successfully reducing higher concentrations of this compound.

1. Introduction

Similar to graphene, which has a hexagonal carbon structure, graphene oxide (GO) is a precursor to reduced graphene oxide. It comprises oxygen-based functional groups as hydroxyl, alkoxy, carbonyl, carboxylic acid, and others [1-6]. Furthermore, GO's surface functionalization has created a multitude of opportunities for its application in the development of nano-composite materials. Due to its high conductivity, graphene oxide (GO) has a broad variety of applications in this field, such as drug transport, electronics, anticancer properties, antibacterial coatings, solar desalination, water purification, and antibacterial coatings[7-15]. Doping graphene or graphene oxide with metals or metal oxides can improve its characteristics. In order to create an effective nanocomposite with surface area and effective catalytic activity, a variety of metal nanoparticles have been doped on nanostructers [16–17]. Furthermore, metals like Pd, Pt, Rh, and Ru are doped on surfaces like graphene oxide to effectively reduce nitroaromatic-like compounds [18–20]. However, due to their high pricing and limited availability, they are not frequently employed in the chemical industry, which is a notable issue from an economic perspective [21]. As a result, earth-abundant elements including Cu, Co, Fe, Mn, and Ni might be used in lieu of these pricey components as they are readily available, less expensive, and exhibit observable catalytic activity[22–24]. To improve their activities, hybrid catalysts with integrated nano-catalysts and susceptible supports must be made [25,26]. Increased catalytic properties are commonly the consequence of the synergistic interactions between the nano-catalysts and supports, like graphene oxide, in nano-composite catalysts[27–29]. Despite being one of the most significant raw materials utilised in many sectors, including the chemical and pharmaceutical industries, nitroaromatic compounds pose a threat to the environment due to their teratogenic, carcinogenic, and mutagenic properties[30,31, 32]. A common chemical in industrial manufacture (e.g., agrochemicals, paper, dyes, medicines, etc.) is p-nitrophenol (PNP).[33] is considered to be among the most dangerous wastes and toxic substances that might damage a living organism's kidney, liver, or central nervous system. On the other hand, PNP reduction yields p-aminophenol (PAP). The reduction of PNP to harmless p-aminophenol (PAP) using NaBH4 as the reducing agent has drawn a lot of attention among the available techniques because of its simplicity, high conversion efficiency, and significant industrial relevance (PAP is frequently used as an intermediate in the synthesis of analgesic and antipyretic drugs).[32, 33] It is important to acknowledge that the process of synthesising PAP from PNP using individual $NaBH_4$ is thermodynamically unstable and cannot proceed spontaneously in the absence of an appropriate catalyst [34, 35]. As a result, a wide range of metallic-based nanomaterials, such as non-noble metals like Cu[39] and Ni[39,40,41] and noble metals like Au[36],

Journal of Chemical Health Risks

www.jchr.org

JCHR (2023) 13(6), 1907-1912 | ISSN:2251-6727

Ag[36], Pt [37,36], and Pb [37,38], have been synthesised recently and have demonstrated outstanding catalytic activity towards the reduction of Nitro-aromatic compounds. Copper nanoparticles (CuNPs) are widely utilised in heterogeneous catalysis applications, such PNP reduction, because to their low cost, superior electrical conductivity, and enhanced stability.[42, 43, 44, 45]Yang et al. [45] state that nanoscale metal particles with high surface energy are often unstable and have a tendency to agglomerate, which significantly shortens their catalytic life. Because graphene oxide (GO) metals, such as copper and its metal oxides, have the aforementioned properties, we may utilise them to reduce a variety of water contaminants, including nitro-aromatic chemicals. In this work, the ultrasonication approach is used to synthesise a graphene oxide nanocomposite ornamented with copper oxide. Excellent catalytic activity was demonstrated by the composite in the reduction of p-nitrophenol.

2. Materials and Methods

The components used are purchased from Sigma-Aldrich and are as follows: Graphite powder, Potassium Permanganate, Sulphuric acid, Phosphoric acid, Hydrogen Peroxide, Sodium Borohydride, 4-nitrophenol(PNP).

Preparation of Metal Oxide decorated reduced Graphene Oxide Nanoparticles :

200ml of distilled water and 1g of graphene oxide are combined in a beaker. It was then Sonicated for ten minutes. Subsequently, another beaker was filled with 400 mg of CuO and 100 ml of distilled water, and it was sonicated for ten minutes. Following sonication, 20 mg of sodium borohydride was added to both solutions. Almost four hours were spent stirring the reaction mixture. Following that, it underwent filtering, several ethanol washes, and 8 to 10 hours at 80°C in an oven were needed to create Copper-decorated reduced graphene oxide (rGO-CuO)(Figure-1)[46,47,48].

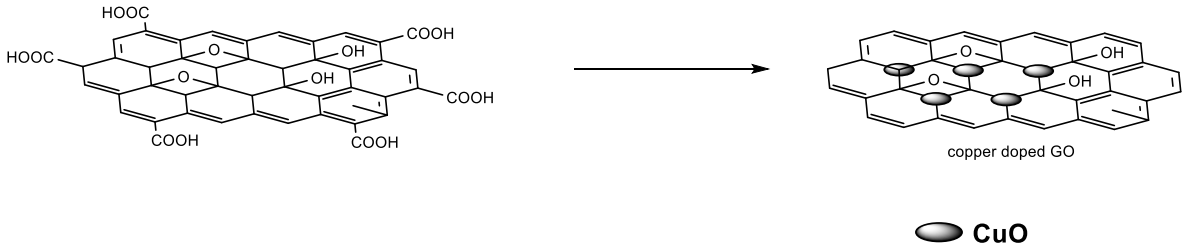


Figure 1- Synthesis of copper doped GO

Catalytic efficiency of copper doped GO: p-nitrophenol was employed as a probe to assess the synthesised material's effectiveness. In 10 millilitres of distilled water, we dissolved 0.1 millimole of PNP for the first set of catalytic reactions. Subsequently, the solution was stirred continuously for ten minutes after being mildly heated. The catalyst was then added to it. Add 1 millilitre of distilled water containing dissolved $NaBH_4$. TLC was utilised to track the response's development. There were four different amounts of catalyst loading: 5 mg, 10 mg, 15 mg, and 20 mg. In a similar vein, different amounts of sodium borohydride—9 mg, 19 mg, 28.5 mg, and 38 mg—were used. Equation 1 below was used to compute the catalytic efficiency of degradation, which is 100% when p-nitrophenol is used as 0.1 mmol and 0.25mmol.

$$\% \text{ Degradation} = 100 - \frac{A_t * 100}{A_0}$$

Where A_0 is the initial absorbance (402 for 4-NP) and A_t is the absorbance at different intervals of time (t).

3. Results and Discussion:

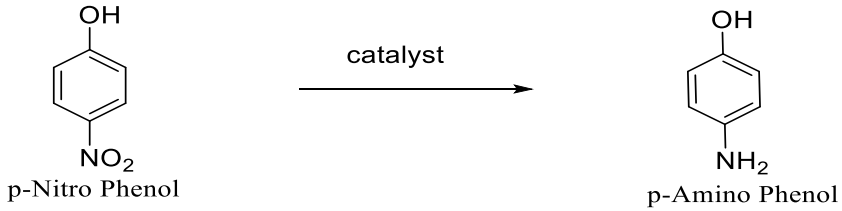
Catalytic Reduction Reaction of 4-nitrophenol

Nitrophenols can irritate eyes and cause skin necrosis. In addition to these, it also affects the liver, muscles, and kidneys. Reports state that adults who are exposed to 1 gm of nitrophenols may die. Research on how 4-NP negatively affects testicular function has also been done in birds and mammals [31, 33]. Therefore, the created catalyst rGO-CuO was used in this study to catalyse the degradation of p-nitrophenol. We employed three PNP concentrations (0.1 mol, 0.25 mol, and 0.50 mol), four sodium borohydride concentrations (9.5 mol, 19 mol, 28.5 mol, and 38 mol, respectively), and four catalyst loading levels (5 mg, 10 mg, 15 mg, and 20 mg) (fig-8). Below is the optimisation table for the same.

Journal of Chemical Health Risks

www.jchr.org

JCHR (2023) 13(6), 1907-1912 | ISSN:2251-6727

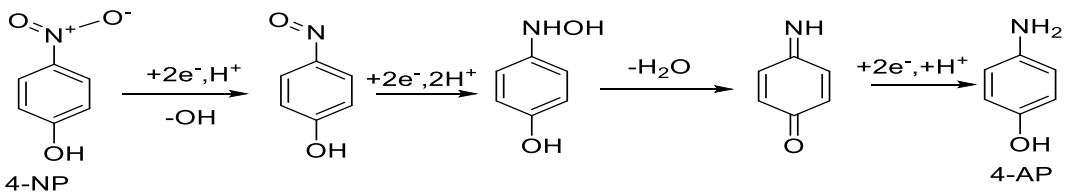


Scheme 1: Reduction of PNP

Table-1: Optimization table for reduction of PNP

p-nitrophenol	**Catalyst**	**Time**
0.1mmol	Copper doped GO	45
0.1mmol	Copper doped GO	17
0.1mmol	Copper doped GO	15
0.1mmol	Copper doped GO	10
0.1mmol	Copper doped GO	7
0.1mmol	Copper doped GO	6
0.1mmol	Copper doped GO	13
0.1mmol	Copper doped GO	11
0.1mmol	Copper doped GO	10
0.1mmol	Copper doped GO	8
p-nitrophenol	Copper doped GO	**Time**
0.25mmol	Copper doped GO	59
0.25mmol	Copper doped GO	56
0.25mmol	Copper doped GO	31
0.25mmol	Copper doped GO	17
0.25mmol	Copper doped GO	21
0.25mmol	Copper doped GO	14
0.25mmol	Copper doped GO	36
0.25mmol	Copper doped GO	21
0.25mmol	Copper doped GO	17
0.25mmol	Copper doped GO	11

The catalytic reduction of p-nitrophenol (PNP) is carried out at room temperature using the optimisation table 1 above, which includes varying PNP concentrations, catalyst loadings, and sodium borohydride concentrations. Thin Layer Chromatography (TLC) was used to analyse the results of the experiments, and we found that 0.1 mmol of PNP is efficiently reduced with all catalyst loading and all concentrations of sodium borohydride. The minimum time was found to be observed with the set 0.1 mmol of PNP, 28 mg catalyst, and 38 mg Sodium Borohydride. The reduction of 0.25 mmol of PNP was done using various catalyst and $NaBH_4$ concentrations. Using TLC, it was discovered that all PNP is reduced, and that 20 mg of catalyst and 38 mg of $NaBH_4$ resulted in the shortest reaction times in this series of reactions. When the PNP concentration was finally raised to 0.50 mmol, it was discovered that, even after 48 hours, the reduction of PNP was only 40% to 60%, as indicated by the asterisks, with 5 mg and 10 mg of catalyst and 9.5 mg and 19 mg of sodium boric acid. On the other hand, the reduction was completely realised and verified by TLC when the catalyst loading was 15 mg, 20 mg, and Sodium Borohydride 28.5 mg and 38 mg.



Scheme 2: Mechanism for PNP reduction to PAP using copper doped GO catalyst

Journal of Chemical Health Risks

www.jchr.org

JCHR (2023) 13(6), 1907-1912 | ISSN:2251-6727

4. Conclusion

p-nitrophenol is a useful but hazardous chemical. Higher concentrations of it can be toxic and hazardous for human being and environment also. Higher concentrations of p-nitrophenol are degraded successfully using the prepared catalyst copper doped GO with sodium borohydride and % degradation is also evaluated. It is found that 0.1mmol and 0.25mmol of p-nitrophenol is 100% reduced using prepared catalyst.

5. Acknowledgment:

We are highly thankful to Amity University, Jaipur, and Rajasthan for providing us laboratory facilities. The authors thank the BIRAC for providing grant BT/EF0286/02/22 as financial assistance.

6. References

1. Ranjan, P., Agrawal, S., Sinha, A., Rao, T. R., Balakrishnan, J., & Thakur, A. D. (2018). A low-cost non-explosive synthesis of graphene oxide for scalable applications. Scientific reports, 8(1), 12007.
2. Smith, A. T., LaChance, A. M., Zeng, S., Liu, B., & Sun, L. (2019). Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites. Nano Materials Science, 1(1), 31-47.
3. Ban, F. Y., Majid, S. R., Huang, N. M., & Lim, H. N. (2012). Graphene oxide and its electrochemical performance. Int. J. Electrochem. Sci, 7(5), 4345-4351.
4. Alam, S. N., Sharma, N., & Kumar, L. (2017). Synthesis of graphene oxide (GO) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rGO). Graphene, 6(1), 1-18.
5. Liu, Y., Dong, X., & Chen, P. (2012). Biological and chemical sensors based on graphene materials. Chemical Society Reviews, 41(6), 2283-2307.
6. Kavinkumar, T., Varunkumar, K., Ravikumar, V., & Manivannan, S. (2017). Anticancer activity of graphene oxide-reduced graphene oxide-silver nanoparticle composites. Journal of colloid and interface science, 505, 1125-1133.
7. Chen, Y., Xu, P., Shu, Z., Wu, M., Wang, L., Zhang, S., ... & Shi, J. (2014). Multifunctional graphene oxide-based triple stimuli-responsive nanotheranostics. Advanced Functional Materials, 24(28), 4386-4396.
8. Hu, W., Peng, C., Luo, W., Lv, M., Li, X., Li, D., ... & Fan, C. (2010). Graphene-based antibacterial paper. ACS nano, 4(7), 4317-4323.
9. Ghosh, D., Dhibar, S., Dey, A., Mukherjee, S., Joardar, N., Babu, S. S., & Dey, B. (2019). Graphene oxide dispersed supramolecular hydrogel capped benign green silver nanoparticles for anticancer, antimicrobial, cell attachment and intracellular imaging applications. Journal of Molecular Liquids, 282, 1-12.
10. Singh, P., Shandilya, P., Raizada, P., Sudhaik, A., Rahmani-Sani, A., & Hosseini-Bandegharaei, A. (2020). Review on various strategies for enhancing photocatalytic activity of graphene based nanocomposites for water purification. Arabian Journal of Chemistry, 13(1), 3498-3520.
11. Safarpour, M., & Khataee, A. (2019). Graphene-based materials for water purification. Nanoscale materials in water purification, 383-430.
12. Li, X., Zhu, B., & Zhu, J. (2019). Graphene oxide based materials for desalination. Carbon, 146, 320-328.
13. Sharma, S., Prakash, V., & Mehta, S. K. (2017). Graphene/silver nanocomposites-potential electron mediators for proliferation in electrochemical sensing and SERS activity. TrAC Trends in Analytical Chemistry, 86, 155-171.
14. Chen, J., Sun, L., Cheng, Y., Lu, Z., Shao, K., Li, T., ... & Han, H. (2016). Graphene oxide-silver nanocomposite: novel agricultural antifungal agent against Fusarium graminearum for crop disease prevention. ACS applied materials & interfaces, 8(36), 24057-24070.
15. Fu, X., Wang, Y., Liu, Y., Liu, H., Fu, L., Wen, J., ... & Chen, L. (2019). A graphene oxide/gold nanoparticle-based amplification method for SERS immunoassay of cardiac troponin I. Analyst, 144(5), 1582-1589.
16. Baig, R. N., & Varma, R. S. (2013). Organic synthesis via magnetic attraction: benign and sustainable protocols using magnetic nanoferrites. Green chemistry, 15(2), 398-417.
17. Verho, O., Gustafson, K. P., Nagendiran, A., Tai, C. W., & Bäckvall, J. E. (2014). Mild and Selective Hydrogenation of Nitro Compounds using Palladium Nanoparticles Supported on Amino-Functionalized Mesocellular Foam. ChemCatChem, 6(11), 3153-3159.
18. Dong, Z., Le, X., Dong, C., Zhang, W., Li, X., & Ma, J. (2015). Ni@ Pd core–shell nanoparticles modified fibrous silica nanospheres as highly efficient and recoverable catalyst for reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol. Applied Catalysis B: Environmental, 162, 372-380.

Journal of Chemical Health Risks

www.jchr.org

JCHR (2023) 13(6), 1907-1912 | ISSN:2251-6727

19. Kim, A., Rafiaei, S. M., Abolhosseini, S., & Shokouhimehr, M. (2015). Palladium nanocatalysts confined in mesoporous silica for heterogeneous reduction of nitroaromatics. Energy and Environment Focus, 4(1), 18-23.
20. Lee, I., Joo, J. B., & Shokouhimehr, M. (2015). Graphene derivatives supported nanocatalysts for oxygen reduction reaction. Chinese Journal of Catalysis, 36(11), 1799-1810.
21. He, S., Niu, H., Zeng, T., Wang, S., & Cai, Y. (2016). A Facile and Efficient Method for Continuous Reduction of Nitroaromatic Compounds Through the Cyclic Transformation Between Fe (II)-complexes and Nano Zero–valent Iron. ChemistrySelect, 1(11), 2821-2825.
22. Karthik, M., & Suresh, P. (2017). Greener Synthesis of Reduced Graphene Oxide-Nickel Nanocomposite: Rapid and Sustainable Catalyst for the Reduction of Nitroaromatics. ChemistrySelect, 2(23), 6916-6928.
23. Wu, Y. G., Wen, M., Wu, Q. S., & Fang, H. (2014). Ni/graphene nanostructure and its electron-enhanced catalytic action for hydrogenation reaction of nitrophenol. The Journal of Physical Chemistry C, 118(12), 6307-6313.
24. Tang, B., Song, W. C., Yang, E. C., & Zhao, X. J. (2017). MOF-derived Ni-based nanocomposites as robust catalysts for chemoselective hydrogenation of functionalized nitro compounds. RSC advances, 7(3), 1531-1539.
25. Zhang, N., & Xu, Y. J. (2013). Aggregation-and leaching-resistant, reusable, and multifunctional Pd@ CeO2 as a robust nanocatalyst achieved by a hollow core–shell strategy. Chemistry of Materials, 25(9), 1979-1988.
26. Kadam, R. G., Rathi, A. K., Cepe, K., Zboril, R., Varma, R. S., Gawande, M. B., & Jayaram, R. V. (2017). Hexagonal mesoporous silica-supported copper oxide (CuO/HMS) catalyst: Synthesis of primary amides from aldehydes in aqueous medium. ChemPlusChem, 82(3), 467-473.
27. Wu, Z. S., Yang, S., Sun, Y., Parvez, K., Feng, X., & Müllen, K. (2012). 3D nitrogen-doped graphene aerogel-supported Fe3O4 nanoparticles as efficient electrocatalysts for the oxygen reduction reaction. Journal of the American Chemical Society, 134(22), 9082-9085.
28. Liang, Y., Li, Y., Wang, H., Zhou, J., Wang, J., Regier, T., & Dai, H. (2011). Co3O4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. Nature materials, 10(10), 780-786.
29. Shi, J. (2013). On the synergetic catalytic effect in heterogeneous nanocomposite catalysts. Chemical reviews, 113(3), 2139-2181.
30. Wu, Z., Yuan, X., Zhong, H., Wang, H., Zeng, G., Chen, X., ... & Shao, J. (2016). Enhanced adsorptive removal of p-nitrophenol from water by aluminum metal–organic framework/reduced graphene oxide composite. Scientific Reports, 6(1), 25638.
31. (31)Khaleghi, N., Forouzandeh-Malati, M., Ganjali, F., Rashvandi, Z., Zarei-Shokat, S., Taheri-Ledari, R., & Maleki, A. (2023). Silver-assisted reduction of nitroarenes by an Ag-embedded curcumin/melamine-functionalized magnetic nanocatalyst. Scientific Reports, 13(1), 5225.
32. (32) Tuo, Y., Liu, G., Dong, B., Zhou, J., Wang, A., Wang, J., ... & Huang, W. (2015). Microbial synthesis of Pd/Fe3O4, Au/Fe3O4 and PdAu/Fe3O4 nanocomposites for catalytic reduction of nitroaromatic compounds. Scientific reports, 5(1), 13515.
33. (33) Ma, H., Wang, H., Wu, T., & Na, C. (2016). Highly active layered double hydroxide-derived cobalt nano-catalysts for p-nitrophenol reduction. Applied Catalysis B: Environmental, 180, 471-479.
34. (34) Bai, X. J., Chen, D., Li, Y. N., Yang, X. M., Zhang, M. Y., Wang, T. Q., ... & Qi, W. (2019). Two-dimensional MOF-derived nanoporous Cu/Cu2O networks as catalytic membrane reactor for the continuous reduction of p-nitrophenol. Journal of Membrane Science, 582, 30-36.
35. (35) Wi-Afedzi, T., Kwon, E., Tuan, D. D., Lin, K. Y. A., & Ghanbari, F. (2020). Copper hexacyanoferrate nanocrystal as a highly efficient non-noble metal catalyst for reduction of 4-nitrophenol in water. Science of the Total Environment, 703, 134781.
36. (36) Misra, M., Chowdhury, S. R., & Lee, T. I. (2020). Sunlight driven decomposition of toxic organic compound, coumarin, p-nitrophenol, and photo reduction of Cr (VI) ions, using a bridge structure of Au@ CNT@ TiO2 nanocomposite. Applied Catalysis B: Environmental, 272, 118991.
37. (37) Khodadadi, B., Bordbar, M., & Nasrollahzadeh, M. (2017). Achillea millefolium L. extract mediated green synthesis of waste peach kernel shell supported silver nanoparticles: application of the nanoparticles for catalytic reduction of a variety of dyes in

water. Journal of colloid and interface science, 493, 85-93.

38. (38) Zhang, X.F., Zhu, X.Y., Feng, J.J., Wang, A.J., 2018. Solvothermal synthesis of N-doped graphene supported PtCo nanodendrites with highly catalytic activity for 4-nitrophenol reduction. Applied Surface Science 428, 798-808.
39. (39)Zhu, X.Y., Lv, Z.S., Feng, J.J., Yuan, P.X., Zhang, L., Chen, J.R., Wang, A.J., 2018. Controlled fabrication of well-dispersed AgPd nanoclusters supported on reduced graphene oxide with highly enhanced catalytic properties towards 4-nitrophenol reduction. Journal of Colloid and Interface Science 516, 355-363
40. (40) Liu, J.M., Feng, Y., Yin, J.J., Jiao, T.F., 2020. Preparation of Functional CNT-COOH-Cu Nanocomposites Using Carbon Nanotubes and Application for Reduction of p-Nitrophenol. Integrated Ferroelectrics 208(1), 97-103.
41. (41)Li, Y.G., Quan, X.J., Hu, C.Y., Li, C.P., 2020. Effective Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol over Etched Halloysite Nanotubes@alpha-Ni(OH)(2). Acs Applied Energy Materials 3(5), 4756-4766.
42. (42) Gawande, M.B., Goswami, A., Felpin, F.-X., Asefa, T., Huang, X., Silva, R., Zou, X., Zboril, R., Varma, R.S.J.C.r., 2016. Cu and Cu-based nanoparticles: synthesis and applications in catalysis. Chemical Reviews 116(6), 3722-3811.
43. (43) Kawakami, T., Murakami, K., Itami, K.J.J.o.t.A.C.S., 2015. Catalytic C–H imidation of aromatic cores of functional molecules: Ligand-accelerated Cu catalysis and application to materials-and biology-oriented aromatics. Journal of the American Chemical Society 137(7), 2460-2463.
44. (44) Tlahuext-Aca, A., Candish, L., Garza-Sanchez, R.A., Glorius, F.J.A.C., 2018. Decarboxylative olefination of activated aliphatic acids enabled by dual organophotoredox/copper catalysis. AS Catalysis 8(3), 1715-1719.
45. (45) Yang, H., Bradley, S.J., Chan, A., Waterhouse, G.I., Nann, T., Kruger, P.E., Telfer S.G.J.J.o.t.A.C.S., 2016. Catalytically active bimetallic nanoparticles supported on porous carbon capsules derived from metal–organic framework composites. Journal of the American Chemical Society 138(36), 11872-11881.
46. (46) Dixon, D.J. (2014). Recent Developments in the Reduction of Nitro and Nitroso Compounds. Comprehensive Organic Synthesis 8.13 , (), 479–492.
47. (47) Zhou, T., Chen, F., Liu, K., Deng, H., Zhang, Q., Feng, J., & Fu, Q. (2010). A simple and efficient method to prepare graphene by reduction of graphite oxide with sodium hydrosulfite. Nanotechnology, 22(4), 045704.
48. (48) Al-Nafiey, A., Kumar, A., Kumar, M., Addad, A., Sieber, B., Szunerits, S. & Jain, S. L. (2017). Nickel oxide nanoparticles grafted on reduced graphene oxide (rGO/NiO) as efficient photocatalyst for reduction of nitroaromatics under visible light irradiation. Journal of Photochemistry and Photobiology A: Chemistry, 336, 198-207.