

Synthesis of Fe⁺²/Mo:MWCNTs by CVD/Impregnation Technique and application in in Photo-Fenton Reaction to dicolorazation Methyl Orange: as a model of health water treatment

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Abstract

In this work, Fe⁺²/Mo and Fe⁺²/Mo:MWCNT were prepared as a heterogeneous Fenton bi and ti-catalyst for the decolorazation of Methyl orange (MO) dye which used the surfaces of multi walled carbon nanotubes (MWCNTs) and Mo as synergistic effect for enhance the activity of Fe⁺². The MWCNTs was prepared by CVDs method with using ethanol as source of carbon and Ferrocene as catalyst for precipitation at 600°C. The Mo was impregnated within synthesized MWCNTs and characterized by Raman spectroscopy, filed emission scanning electron microscopy FE-SEM and the elements were analyzed by EDX tectonic. The results shows that ternary catalyst Fe⁺²/Mo:MWCNT was succeed to dicolorazation of MOs dye when complete more than 98% of dicolorazation after 150 min which is best results as compare with Fe⁺² alone or with Mo.

Keywords

Fentons reaction, pH, MWCNT, Mo, Fe⁺²/Fe⁺³.

The common strategy which adopted to safe environment from variety of huge organic and inorganic pollutants is advanced oxidation processes (AOPs) when shows higher efficiency in removing from aqueous solution [1]. the AOPs behave as typical active for synthetic catalytically nanoparticles as strategy to remediate contaminants when generate hydroxyl radicals (OH[·]) that produce other reactive intermediates such as HO₂[·] and O₂^{·-} [2]. Many reported works had been used AOPs in removing many organic materials such Tetrabromobisphenol with photocatalysis solution [1] or ozone oxidation [3], and Fenton method [4]. Maybe the most characteristic feature for these methods, photocatalytic high oxidation performance with less by product as secondary pollution [5], while the disadvantage represent by technique requirement such high energy with higher cost and that limited the ability to use it[6]. One of

technical problem which may limit and reduce the activity of Fe⁺²/Fe⁺³ in Fenton reaction was the formation of Fe sludge, and that was removed by reduce the ratios of Fe salts and substituted the reduction value by zero valance Molybedenum [7].

The role of Mo was to replace the traditional Fenton reagent, strong reduction, with abilities to participate in reactions and improved the amount of Fe²⁺ for reaction [8]. heterogeneous Fenton oxidation reaction influence with many parameters, such pH, concentration of H₂O₂, temperature and the physical properties of co-catalyst, via catalyst regeneration, over homogeneous Fenton oxidation [9]. All of these parameters enhance the researchers to developing heterogeneous technology for preparing higher efficiency process, low cost, easy to re-use the catalysts, and increase the ability for use it in new applications. Homogeneous fenton oxidation required Fe²⁺ /Fe³⁺, as a catalyst which

used in an acidic environment (pH < 3), and characterized by high corrosion activity and greatly reduces the abilities of applications [10].

Many litterateurs were used specific surface as support for Fe²⁺/Fe³⁺ in fenton reaction one of the common surface was carbon nanotubes CNTs [11] such as multi-walled carbon nanotubes MWCNTs with NiFe₂O₄ in fenton reaction to remove pullutents [12] or used with fenton reaction in AOPs [13]. The most important causes that encourage to used MWCNTs in fenton reactions was the high elecron density could be separation of electron–hole pairs of and avoiding recombination on the catalyst, and that absolutely enhance to produce and increase HO[·] ratios in reaction under UV-light .

In this work malt-walled carbon nanotubes MWCNTs were synthesized by chemical vapour deposition CVD and impregnate with nano-Molibdinum which characterized by Raman spectroscopy, filed emission scanning electron microscopy with analysis the elements EDX. The synthesized materiasl were used together with Fe²⁺/H₂O₂ for photo-fenton reaction to dicolorazation methyl orange by mono and dio-cocatalyst.

Experimental /Chemicals:

Ferrous chloride tetrahydrate (FeCl₂·4H₂O), with purity more then99% was purchased from Fluka and 99.99% purity of sulfur purchased from Sigma.hydrogen peroxide (H₂O₂, 30wt.%), and Methyl orange (C₁₄H₁₄N₃NaO₃S) from china (Sigma-Aldrich). Ferrocene, hydrochlorice acid and sulfuric acid were provided from BIO CHEM.

Catalyst synthesis

Synthesis of MWCNTs: Multi-walled carbon nanotubes MWCNT was produced by the chemical vapour deposition CVD of ethanol at 600°C with using Ferocen as source of catalyst over silica support inside tube furnace which deposited for 30 min, in nitrogen atmosphere. The product was purified by mixture of HCl/H₂SO₄ (1:3) then washed with distill water and dried at 100 C for 2h in nitrogen atmosphere. Synthesized MWCNTs was characterized by FE-SEM and Raman spectroscopy.

Synthesis of MWCNT/Mo: the synthesized MWCNTs was dispersion in 200 mL of ethanol by ultra-sonic water-bath for 30 min, before adding 250mg of MoCl₆ and 20mL of NaOH. The mixture was still in ultra-sonic water bath for 30 min., then filtered and washing by ethanol. the product was drying for 2h at 100C and calcined at 300°C for 1h in hydrogen atmosphere then characterized with Raman spectroscopy, E-SEM and EDX analysis.

Preparation of Fe²⁺ solution and Mo solution: The stock solution of Fe²⁺ (10 M) was prepared by dissolved equivalent weight from FeCl₂·4H₂O in 250 mL of 2 M H₂SO₄ which was used for preparing the required amount for all the experiments of dicolorazation. The 5M of MoCl₆ was prepared by dissolved 1.25 mole in 250 mL of absolute ethanol.

Reaction Procedures: All experiments were conducted in a jacket glass beaker Photochemical Reaction vial (100 mL) with stirring all time the reaction by magnetic stirring in an initial pH of 3 (adjusted with 0.1M of NaOH, or 0.1M of H₂SO₄) and cooled by circulating water. The 10 M as a stock solution of Fe²⁺ was prepared in 1 M H₂SO₄ as mentions previously. The source of UV-light was a supplied from Toshiba com. Japan (SHLS-1002A) with 100 W Hg lamp convenient to produce λ > 330 nm while the visible source was Light-emitting diodes (LEDs) which produce more then 400-800 nm. The dose of synthesized materials Fe²⁺, Fe²⁺/Mo, and Fe²⁺/Mo:MWCNT were kept constant at 150 mg with 60 μL, which added to 50 ppm Methyl Orange MO solution. The dicolorazation reactions were started after addition of H₂O₂ immediately which withdrawn sample from the dye to determined the concentration at 466 nm, At intervals reaction time, samples immediately analyzed after neutralized with 0.1 N NaOH to stop the reaction when prevent hydroxyl radicals generation before filtered measured absorbance on a Hitachi U-3100 UV-vis spectrophotometer at 617 nm.

Results and discussion:Characterization: The synthesized materials in this work were characterized by field-emission scanning electron microscopy (FE-SEM), with Energy Dispersive X-Ray for Analysis EDX the elements and X-ray diffraction (XRD). The XRD analysis of the nanoparticles was done by Cu Kα radiation (1.54 E) on a Philips diffractometer with a graphite monochromator. The FE-SEM microscopy were carried out on a JEOL JSM-6700F and EDX analysis with an ultrahigh resolution pole piece 4 μm were performed in 200 kV.

Figure 1a and b include the identification for synthesized MWCNTs and that shown two peaks at 1285 cm⁻¹ and 1674 cm⁻¹ which refers to D and G band, in addition to D+G at 2959 cm⁻¹[14]. The I_D/I_G refers to to the surface composition and thickness which was more than 10 sheets of graphite with distortion on the surface and that give good reason for adsorption in the modification part with Mo [15]. Figure 1b was shown the two peaks at 24.7° and 44.6° for two planer 100, and 101 respectively which refers to MWCNTs [16].

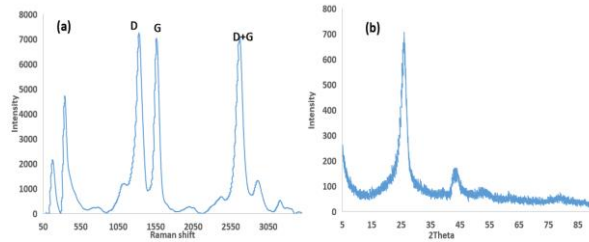


Figure 1: Skim identification for synthesized MWCNTs by (a) Raman spectroscopy and (b) X-ray diffraction

Figure 2a [16] refers to completely clean MWCNTs without impurities at the maximum limited of analysis by EDX and the oxygen mostly can be related to oxidation process during purification process. The FE-SEM image in figure 2b shows that tubular or filaments with length reach to more then 2 micro meter and average diameter (15-26 nm).

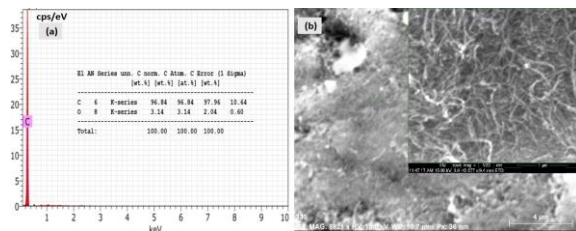


Figure 2: Skim of elements analysis and morphology for synthesized MWCNTs by (a) EDX analysis and (b) FE-SEM.

The characterized of MWCNTs after modification with Mo were analysis with the same techniques as shown in figure 3 and 4. the Raman spectroscopy in figure 3a and that include the same peaks D, G and D+G with reduce the intensities for the three peaks and shifted to about +8 cm⁻¹ due to Mo mostly adsorbed on the surface of MWCNTs [17]. The XRD patterns were reported in figure 3b and that include two parts; the first for MWCNTs at 25.8° and 45.9° which shown shift in position as compare with synthesized MWCNTs as shown in figure 1b [16]. The second part include four peaks at 37.9°, 45.1°, 64.7°, and 78.7° which refers to Mo and shown the planer 110, 200, and 211 respectively [18]. the higher crystalline for Mo were covered for the lower crystalline of carbon structure which cousins reduce the two characteristic peaks of MWCNTs.

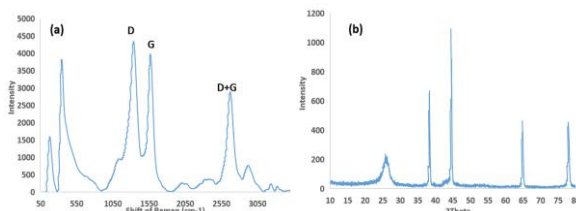


Figure 3: Skim identification for modifying Mo:MWCNTs by (a) Raman spectroscopy and (b) X-ray diffraction.

The elements analysis in figure 4a for Mo:MWCNTs was reported adsorbed of Mo with MWCNTs which mostly adsorbed with ratios reach to 0.64% . the FE-SEM images in figure 4b shown increase the agglomerations with MWCNTs due to modified with Mo which may the last make as active site for agglomerations.

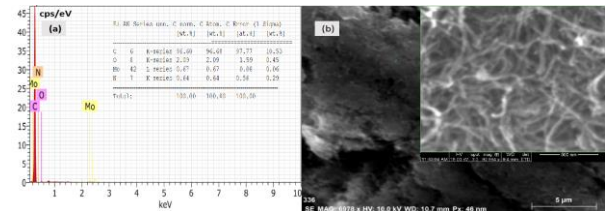


Figure 4: Skim of elements analysis and morphology for modifying Mo:MWCNTs by (a) EDX analysis and (b) FE-SEM.

Dicolorization of Methyl orange MOs: previously the activity of catalysts without H₂O₂ or light and H₂O₂ without light and catalysts, were did not witnessed any decolorization results. The experiments of dicolorization of MOs were include three catalysts which tested at first in visible -light reaction as shown in figure 5a and that shown weak activity for remove 50 ppm MOs in 225 min.,of reaction. The influence of visible light was shown very limited range when appeared less less then 24% after 223 min with Fe⁺²/Mo:MWCNT and that can be related to unable to absorb the light in this region from catalyst. The activity in UV-light were shown great enhancement when the dicolorazaton increase to remove the color after 150 min. , with the ternary composite of Fe⁺²/Mo:MWCNT. The results of reactions is related to synergistic influence for three parameters catalyst/H₂O₂ /visible light (photo-Fenton process).

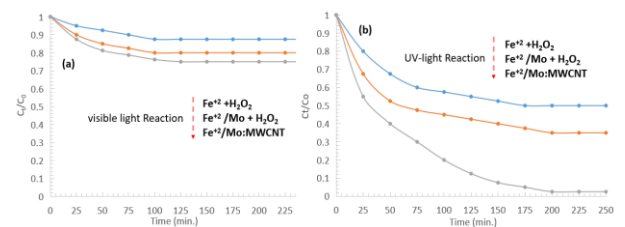


Figure 5: Skim for dicolorization of MOs by Fe⁺², Fe⁺²/Mo, and Fe⁺²/Mo:MWCNT (Fentons reaction) in (a) visible light reaction and (b) UV-light reaction

Table 1 reported the compare for the reactivity in dark and UV-light irradiation which shown enhancement in activity reach to 78 for Fe⁺²/H₂O₂ system while the ether was 72% and 75% for Fe⁺² /Mo+H₂O₂ and Fe⁺² /Mo: MWCNT+H₂O₂ respectively. The higher activity was still for the two types after marbled with Mo and MWCNTs. According to figure 5a and 5b the best catalyst for Fentons reaction was reported as shown below:



Table 1: Summary for dicoloraztion of MOs by different catalysts with Fentons reaction in dark and UV-light conditions.

Catalysts	Removal at dark Reaction %	Removal at UV-light Reaction %	Synergistic effect of UV-light in Fenton
Fe ²⁺ + H ₂ O ₂	10%	47%	78%
Fe ²⁺ /Mo+ H ₂ O ₂	17%	61%	72%
Fe ²⁺ /Mo:MWCNT+ H ₂ O ₂	24%	98%	75%

Effect of pH on the activity of catalyst in Fenton reaction

the influence of acidity were studied for the best two systems which shown the higher activity and that represent by Fe²⁺/Mo and Fe²⁺/Mo:MWCNT as shown in figure 5a and b. The change of activities for Fe²⁺/Mo was shown the lowest value when change the pH of solution which reduce to 39% at pH=12 while the maximum value of dicoloraztion was 61% at pH= 3. The reduce activity under higher value of pH > 7 can be related to insufficient concentration of H₂O₂ which causing inhibition the generated OH which failed to continues

degradation of MOs.

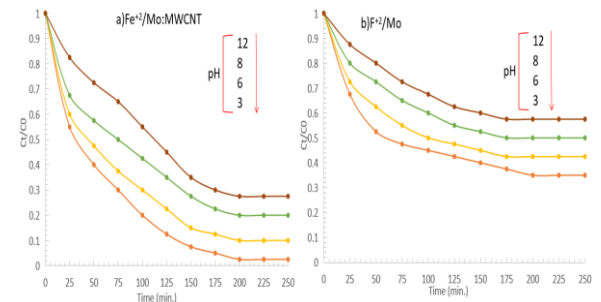


Figure 5: Skim of effect of pH for dicoloraztion of MOs by (a) Fe²⁺/Mo:MWCNT and (b) Fe²⁺/Mo (Fentons reaction) in UV-light reaction .

Table 2: summary for the effect of pH on the dicoloraztion MOs by Fe²⁺/Mo:MWCNT and Fe²⁺/Mo with H₂O₂+UV-light

Dicoloraztion % of MOs in UV-light			
Fe ²⁺ /Mo:MWCNT		Fe ²⁺ /Mo	
pH		pH	
12	67%	12	39%
8	72%	8	43%
6	77%	6	51%
3	98%	3	61%

Mechanism: The details of Fenton reaction mechanism required Equations in figure 6, firstly [19.]which could be occurred in a homogeneous or heterogeneous solution, with the first active species hydroxyl radicals (-OH) from H₂O₂ by strong electron-capturing Fe²⁺ as shown in equations first part. The first active species can attack without any selectivity most organic groups was represent in figure 6 for the second part.

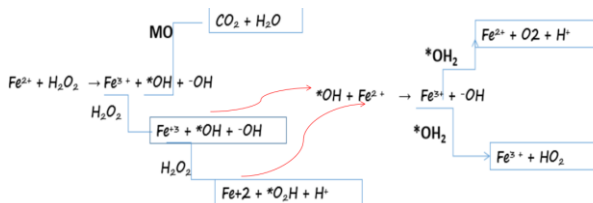


Figure 6: Skim for suppose mechanism of Fenton reaction

Equation figure 6 included the process [20]of re-activation for Fe²⁺ by the reduction of Fe³⁺ by H₂O₂ to continue the work of activating H₂O₂, while the reduction of Fe³⁺ is very slow and the generated

hydroperoxyl radicals (*O₂H) have weaker oxidation ability than *OH . All of the equations in figure 6 refers to the reactivity for Fe²⁺ with H₂O₂ which completely depend on the abilities for convert Fe³⁺ to Fe²⁺ and Fe³⁺ to Fe²⁺ .

the Fe³⁺ cannot be converted into Fe²⁺ for a continuous stream of the reaction, which means the limiting step for the entire Fenton reaction. The mechanism of Fe²⁺/Fe³⁺ with Mo will change when Mo act as activation species to re-convert Fe³⁺ to Fe²⁺ as shown in equation 9 and that enhance to produce more active free radical with with O₂ and -OH. The reactivation were reported in figure 7, which complete the recycle with Mo and Mo+6 as shown below :

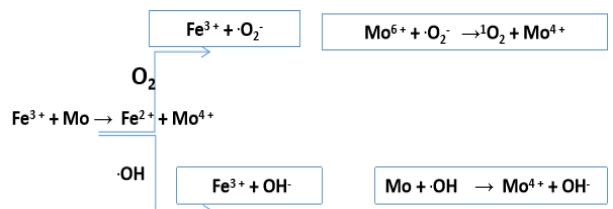


Figure 6: skim for enhancement the activity of fenton reaction by Mo

The ability of Mo was shown to increase the activity for Fe^{+2} in the Fenton reaction, which has more activity compared with Fe^{+2} when it exists alone in the reaction. When impregnated Mo on the surface of MWCNTs, the role of MWCNTs can be related in two sections: the surface of MWCNTs was characterized with charge transfer surface, which acts as an inhibition for recombination of the electrons in Fe after activation by UV-light [17]. The second section for MWCNTs with Mo and Fe can be due to its high surface area, dispersion, and species of Mo and Fe, with a value of agglutination that increases the chance to create more and more active sites for reaction [12, 21]. According to the results of pH influence in the reactivity of species, it could be seen that a lower value of pH succeeded in enhancing and stabilizing Fe^{+2} , which makes it more active, while at a higher value of pH, causing a reduction in the ratios of Fe^{+2} in solution and that would be expected in lower activities for the Fenton reaction [22].

Conclusion

Fe^{+2} /Mo:MWCNTs was prepared using a simple impregnation method and tested to make the best efficiency in the Fenton reaction to remove MOs as dyes. The characterization showed dispersion of Mo on the surface of MWCNTs, which makes an ideal hybrid with Fe^{+2} . The ternary catalyst was shown to be a more efficient catalyst compared with the pure Fe^{+2} or with Mo under two conditions in visible light and UV-light. The results show that an acidic solution succeeded in producing the best efficiency for decolorization of the dye and that was more clear and higher in value with Fe^{+2} /Mo:MWCNT and that can be related to the ideal influence of Mo and MWCNT. The hybridization for high charge transfer to surface area and electron density for MWCNT with conversion of Mo from valence oxidation +4 and +6 was the best choice for the best enhancement in this work. Therefore, the combined effect between Mo and MWCNTs with Fe^{+2} shows improvement in the Fenton reaction.

References

- Zhou Q., Xing A., Zhao D., Zhao K., "Tetrabromobisphenol A photoelectrocatalytic degradation using reduced graphene oxide and cerium dioxide modified TiO₂ nanotube arrays as electrode under visible light", *Chemosphere*, 165, pp. 268-276, 2016.
- Garrido, E., Theng, B. and Mora, M., "Clays and Oxide Minerals as Catalysts and Nanocatalysts in Fenton-Like Reactions—A Review", *Applied Clay Science*, 47, pp.182-192, 2010.
- Jéssica M., Carla A. Orge, Joaquim L. Faria, M. Fernando R. Pereira and O. Salomé G. P. Soares, "Catalytic Advanced Oxidation Processes for Sulfamethoxazole Degradation", *Appl. Sci.*, 9(13), pp.2652-2670, 2019.
- Qiu L., Jing S., Lian G., "Degradation of phenol by heterogeneous Fenton reaction using multi-walled carbon nanotube supported Fe₂O₃ catalysts", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 345(1–3), pp. 95-100, 2009.
- Jiali P., Yongli H., Chenying Z., Shijun S., Bo L., "The carbon nanotubes-based materials and their applications for organic pollutant removal: A critical review", *Chinese Chemical Letters*, 32(5), 2021, pp.1626-1636, 2021.
- Xin L., Hu J., Xiang Y., Li C., Fu L., Li Q., Wei X., "Carbon-Based Nanocomposites as Fenton-Like Catalysts in Wastewater Treatment Applications: A Review", *Materials (Basel)*, 18;14(10), pp.2643-2654, 2021.
- Qiuying Y., Jiahui J., Bin S., Chencheng D., Jun L., Jinlong Z., and Mingyang X., "Singlet Oxygen Triggered by Superoxide Radicals in a Molybdenum Cocatalytic Fenton Reaction with Enhanced REDOX Activity in the Environment", *Environmental Science & Technology*, 53 (16), pp.9725-9733, 2019.
- Yi, Q., Liu, W., Tan, J., Yang, B., Xing, M., and Zhang, J., "Mo⁰ and Mo⁴⁺ bimetallic reactive sites accelerating Fe²⁺/Fe³⁺ cycling for the activation of peroxymonosulfate with significantly improved remediation of aromatic pollutants", *Chemosphere*, 244, 125539, 2020.
- Lai C., Shi X., Li L., Cheng M., Liu X., Liu S., et al., "Enhancing Iron Redox Cycling for Promoting Heterogeneous Fenton Performance", *A Review. Sci. Total Environ.* 775, 145850. 2021.
- Cheng G., Wan J., Li Q., Sun L., Zhang Y., Li Z., Dang C., Fu J., "Degradation of Reactive Brilliant Red X-3B by Photo-Fenton-like Process: Effects of Water Chemistry Factors and Degradation Mechanism", *Water*, 14, 380, 2022.
- Peña R. C., Silva V. O., Quina F. H., Bertotti M., "Hydrogen peroxide monitoring in Fenton reaction by using a ruthenium oxide hexacyanoferrate/multiwalled carbon nanotubes modified electrode", *Journal of electroanalytical chemistry*, 686(1), pp.1-6, 2012.
- Caroline R., Eric da Cruz S., Marcio A. M., Guilherme L. D., Sérgio L. J., André G., Márcia M. L., Osvaldo C. F., Edson L. F., "Preparation of Nickel Ferrite/Carbon Nanotubes Composite by Microwave Irradiation Technique for Use as Catalyst in Photo-Fenton Reaction", *Materials Research*. 20(2), pp.311-316, 2017.
- Flávia G. P., Alexandre A.C. C., Honória F. G., Adelina P. S., Waldemar A.A. M., Cláudia A. F., "Comparative temporal analysis of multiwalled carbon nanotube oxidation reactions: Evaluating chemical modifications on true nanotube surface", *Applied Surface Science*, 357, pp.1015–1023, 2015.
- Bagotia N., Mohite H., Tanaliya N., Sharma D., "A Comparative Study of Electrical, EMI Shielding and Thermal Properties of Graphene and Multiwalled Carbon Nanotube Filled Polystyrene Nanocomposites", *Polymer Composites*, pp.-1041-1051, 2018.
- Deepak A., Ramya S., Vaidehi G., Shankar P., "non destructive analysis of carbon nanotubes based strain sensor using Raman analysis and Raman mapping", *Advanced Composites Letters*, 23, (2), pp.27-31, 2014.
- Abdulrazzak F. H., Alkiam A. F., Hussein F. H., 2019, 'Behavior of X-Ray Analysis of Carbon Nanotubes', in H. E. Saleh, S. M. M. El-Sheikh (eds.), *Perspective of Carbon Nanotubes*, IntechOpen, London. 10.5772/intechopen.85156.
- Sofia Gómez, Nicolas M. Rendtorff, Esteban F. Aglietti, "Surface modification of multiwall carbon nanotubes by sulfonitric treatment", Yoshio Sakkac, Gustavo Suárez, "Applied Surface Science 379, pp.264–269, 2016.
- Keerthi M., Boopathy G., Chen S.M. et al., "A core-shell molybdenum nanoparticles entrapped f-MWCNTs hybrid nanostructured material based non-enzymatic biosensor for electrochemical detection of dopamine neurotransmitter in biological samples", *Sci Rep* 9, 13075, 2019.

- Bautista P., Mohedano A.F., Casas J.A., Zazo J.A., and Rodriguez, J.J.”
An overview of the application of Fenton oxidation to industrial waste waters treatment”, *Chem. Technol. Biotechnol.* 83,pp. 1323–1338, 2008.
- Liu, W., Zhang, W., Liu, M., Du, P., Dang, C., Liang, J., and Li, Y.,”
Fabrication of niobium doped titanate nanoflakes with enhanced visible-light-driven photocatalytic activity for efficient ibuprofen degradation’, *Chin. Chem. Lett.* 30, pp.2177–2180, 2019.
- Garlet T.B., Weber C.T., Klaić R., Foletto E.L., Jahn S.L., Mazutti M.A., et al.,”Carbon Nanotubes as Supports for Inulinase Immobilization”, *Molecules*,19(9),pp.14615-14624, 2014.
- Wang, Y., Qi, K., Yu, S., Jia, G., Cheng, Z., Zheng, L., Wu, Q., Bao, Q., Wang, Q., Zhao, J., et al.,” Revealing the intrinsic peroxidase-like catalytic mechanism of heterogeneous single-atom Co–MoS₂”, *NanoMicro Lett.* 11, 102, 2019.