Research Article

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Synthesis of Co$_3$O$_4$ Nano Aggregates by Co-precipitation Method and its Catalytic and Fuel Additive Applications

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Abstract: The nano aggregates of cobalt oxide (Co$_3$O$_4$) are synthesized successfully by adopting simple a co precipitation approach. The product obtained was further subjected to the calcination process that not only changed it morphology but also reduces the size of individual particles of aggregates. The prepared nano aggregates are subjected to different characterization techniques such as electron microscopies (scanning electron microscopy and transmission electron microscopy) and X-ray diffraction and results obtained by these instruments are analyzed by different software. The characterization results show that, although the arrangement of particles is compact, several intrinsic spaces and small holes/ pores can also be seen in any aggregate of the product. The as synthesized product is further tested for catalytic properties in thermal decomposition of ammonium perchlorate and proved to be an efficient catalyst.

Keywords: Nano-aggregates; Cobalt oxide; Calcination; Thermal decomposition; Fuel additives.

1 Introduction

Nanomaterials are divided into different types based on their dimensions. They are classified as 0 D, 2 D and 3 dimensional. Nanoparticles can be crystalline and amorphous. They exhibit different morphology according to the dimensions as hollow sphere, nanocubes, nanofibers, nanofilms, nanowires and nanoplates [1-5].

There are various physical and chemical techniques that are being employed for the fabrication of nanoparticles. Physical techniques constitute ball milling, ion ejection, lithography and laser ablation methods [6] and chemical methods involve sol-gel method, thermal decomposition, salt reduction, reverse micelles approach, hydrothermal method and co-precipitation techniques [7]. Many groups of researchers have synthesized transition metal oxide nanoparticles and reported their characterization and the applications. Titania (TiO$_2$) nanoparticles are being used as dye sensitized solar cells and material for electronic circuits [8-12], ZnO nanostructures also have unique optoelectronics and electronic properties, therefore, used in laser and light emitting diodes [13-21]. CuO is being employed in dry cell as well as wet cell batteries [22]. Among all these metal oxides, cobalt oxide (Co$_3$O$_4$) nanoparticles have engrossed emergent attention because of its magnetic and catalytic properties. These fascinating properties of cobalt oxide nanoparticles have made it important in hi-tech applications [23].

This preference is due to hexagonal close-packed structure (HCP) known as α-cobalt and face-centered cubic structure (FCC) known as h-cobalt, in bulk, while metastable structure ε-cobalt in nanometer ranges [24]. Cobalt formulate a very defined binary compound with O as 2- are; tricobalt tetraoxide (Cobalt (III) oxide) and cobaltous oxide (Cobalt (II) oxide) [25]. Cobalt (III) oxide with +8/3 oxidation state and cobalt (II) oxide with +2 oxidation state are most stable Cobalt (III) oxide is an (intrinsic) p-type semiconductor having optical band gap of 1.48 and 2.19 eV. It shows large mechanical strength with 116 to 160 GPa young’s modulus [26].

Therefore, considerable attention has been given to the fabrication of cobalt (III) oxide nanostructures in order to utilize its properties by preparing nanofilms, nanotubes and nanorods. Many methods of synthesis for cobalt oxide nanoparticles have been reported by various researchers. Coprecipitation, sol-gel, solvothermal, reverse microemulsion, thermal decomposition and...
chemical vapor deposition methods have been used for synthesis of cobalt oxide nanoparticles [1-5,23,27]. So, it is applicable in different fields like electrochemistry [28], catalysis [29], energy storage [30] and pigments [31]. It is one of the fascinating chemical compounds which is used as MRI (magnetic resonance imaging) contrast agent in medicine with the combination of other metals e.g. gold, graphite, iron and platinum [32]. Cobalt oxide with improved catalytic activity, has already been used as catalyst for the oxidation of many volatile organic compounds (VOCs). It shows better catalytic activity among other transition metal oxides [33].

In this research paper, co precipitation method has been used for synthesis of cobalt oxide nanoparticles by using cobalt chloride as metal precursor. The nanoparticles prepared by this method have been characterized by using different instrumental techniques. Synthesized nanoparticles have been used for the determination of variation and comparison in physiochemical properties of diesel fuel. In order to investigate catalytic properties, thermo gravimetric analysis has also been performed.

2 Experimental Section

2.1 Materials

Sodium carbonate, deionized water, absolute alcohol, and Cobalt chloride hexahydrate (CoCl₂·6H₂O) as the cobalt source were used. All the chemicals used during the process of synthesis were purchased from Sigma Aldrich, USA. The chemicals were of analytical grade and used as received without any more purification.

2.2 Synthesis

The following procedure was adopted to prepare the Co₃O₄ nanoparticles by co-precipitation method. 2.5 g of CoCl₂·6H₂O is used as the precursor for this process, dissolved in deionized water stirred magnetically for 20 mins. After stirring, 20 ml sodium carbonate solution (1M) was added to the above solution. The mixtures were stirred for 5 h at 60.0°C. After 5 h, light purple color precipitates are collected by centrifugation at 30,000 rpm. The precipitates are washed three times with deionized water and absolute alcohol, respectively. The collected precipitates are dried in an oven at 80.0°C for 12 h. The obtained product is calcined in an electric furnace for 3 h at 500.0°C. The product prepared by co-precipitation method is subjected to instrumentation for the investigation of morphological aspects.

2.3 Structure Characterization

X-ray powder diffraction (XRD) characterizations were performed on a Rigaku D/max Ultima III X-ray diffractometer with a Cu-Ka radiation source (λ = 0.15406 nm). The instrument was operated at 40 kV and 150 mA at a scanning step of 0.02° in the 2θ in the range of 10-80°. Scanning electron microscopy (SEM) observations were executed on a scanning electron microscope (JEOL JSM-6480A). Transmission electron microscopy (TEM) observation was performed on an FEI Tecnai G2 S-Twin transmission electron microscope (TEM) with an accelerating voltage of 200 kV. Commercial Diesel, PSO Limited was used as fuel with 0, 2, 4, 6, 8 and 10 ppm dosage of synthesized product Co₃O₄ particles. Flash and fire points were studied by APEXJ/309 Closed Cup Flash Point Tester (working standard ASTM D93). Cloud and pour points were tested manually in accordance of standard methods ASTM D2500 and D97 respectively. Digital viscometer was used to measure viscosity of fuel samples according to standard procedure ASTM D445.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 XRD analysis

The X-ray diffraction pattern (XRD) of synthesized products are given below as Figure 1a and 1b. The diffraction peaks of Figure 1a are associated with wurtzite structured hexagonal sphero cobaltite (CoCO₃). No extra peak is observed which confirms the purity of product. The XRD pattern gives the strong diffraction peaks at 25.18°, 32.81°, 35.73°, 42.8°, 46.4°, 51.36° 2-theta values which are associated with the planes (012), (104), (006), (110), (113), (202) and (024) respectively. Pattern of wurtzite structure of Co₃O₄ is given as Figure 1b. The peaks can be observed at 18.89°, 31.21°, 36.81°, 38.40°, 44.79°, 49.10° and 55.65° 2-theta values which are indexed to planes (111), (220), (311), (222), (400), (330) and (422) respectively. Diffraction pattern of as-prepared product confirms that each lattice possesses the face centered cubic structure. No surplus peaks can be seen which ensures that the there is no impurity present in the product.
3.2 SEM Characterization

To characterize and analyze the morphology, the prepared products are analyzed by SEM as shown in Figure 2. The scanning electron microscopy is used to determine the shape or morphology of the prepared powders. The particles are irregular in shape and aggregated together. In the aggregates, the size of the particles is not uniform so determination of morphology by SEM is done but not the size of the particles. The primary particles can aggregate upon standing in air. The particles obtained by carbonate precipitatin without any surfactants are poly disperse and form plate-like aggregates. The product before calcination is shown in Figure 2a b and c. It can be clearly observed from the Figure 2c that the small particles are fused together and create an irregular, flower like structures and these irregular structures are of different sizes and shapes. Some of these structures are very big with lots of small particles aggregated together compactly while o some of these particles are small aggregates too. A close overview of the morphology obtained by SEM shows some single small particles are also present among the product. This arrangement of particles is although compact, but many intrinsic spaces and small holes/ pores can also be seen within any aggregate of the product. Figure 2d, e and f shows the SEM observation of the product after calcination. Figure 2a shows the product comprises of nano and microparticles that are interlinked to form an irregular arrangement. It is evident from the Figure 2, the morphology before calcination is different from the morphology after calcination. After calcination, the product contains particles that are nearly spheroids, and these are not very compactly packed with each other. There are visible spaces in the arrangement of particles and morphology is somehow an irregular array of nano and lots of microparticles that did not acquire the shape of flowers as in case of the Co$_3$O$_4$ before calcination. Many particles are broken apart from the big aggregates so very small nanosized and microsized particles can also be seen in the product obtained after calcination. It is important to note that these particles have an anisotropic morphology extending from exterior to inter – particle open space forming loosely packed microstructures a few micrometers thick and with sufficient space between the adjacent particles.

3.3 TEM Observations

Figure 3 shows the TEM images of the production prepared by the co-precipitation method before calcination Figure 3a, b, c and after calcination Figure 3c, d, f. TEM images of the product before calcination shows that most of the particles are clustered together forming different shapes that are not differentiable to describe. Mainly, these big micro particles are composed of small nanoparticles in various size ranges, in the rough approximation, from 50 nm to several micrometers.

TEM images in Figure 3 shows that these micro architectures exhibit a varied range of dimensionalities that undermine the exact size valuation from the micrographs. These particles are tightly fused with each other leaving behind some pores or spaces in the arrangement. These are not very thick walled particles that are the main constituents of big architectures. TEM image in Figure 3a-c shows that these micro architectures exhibit a varied range of dimensionalities that undermine the size valuation from the micrographs. Figures 3d-f shows the product obtained after calcination. The TEM micrograph shows a certain change in morphology. The randomness of the product that was very obvious in the TEM micrograph before calcination is relatively reduced and nano and microparticles show trends towards some sequence. The nano and microparticles join mostly head to tail arrangement, but at some points, these particles show multi-dimensional arrangements of particles around them as shown in Figure 3d and e. The exact morphology of these constituent nano and microparticles can be cylindrical, nearly spherical, cuboid flakes or rods that is not clearly differentiable as many different shapes
which can be seen within one microarchitecture (formed by interlinking of these particles processing different shapes and sizes). These particles are loosely packed in some sequence with more inter-particles spaces.

### 3.4 Preparation Scheme

Synthesis scheme of $\text{Co}_3\text{O}_4$ via co-precipitation method is shown as Figure 4. $\text{CoCl}_2\cdot6\text{H}_2\text{O}$ and sodium carbonate react and give rise to CoCO$_3$ that is further annealed in oxidative atmosphere resulting in the formation of Co$_3$O$_4$ precipitates that is final product for this reaction. The product is not of uniform morphology. After annealing, the morphology shows a trend towards the uniformity but still it is aggregated together leaving some inter-particles spaces.

### 3.5 Catalytic Activity

As an important material for the use in solid propellant formulations for application in airspace and defense materials industries, the oxidizer salt, AP, thermal decomposition is very important to study. To study the catalytic activity of the Co$_3$O$_4$ particles by the co-precipitation method, the thermal decomposition of AP is investigated by thermogravimetry-differential scanning calorimetry (TG-DSC). The result shows that the thermal decomposition curve peaks of AP containing Co$_3$O$_4$ prepared microstructures do not not emerge more ahead than that of pure AP. Figure 5 demonstrates the TG curves for pure AP and the mixtures of AP and Co$_3$O$_4$ microstructures obtained by co precipitation method. It can be seen the decomposition temperature of AP reduces to some extent as a result of adding the Co$_3$O$_4$ particles. The initial thermal decompositions of AP is 300.0°C and for samples containing 2% Co$_3$O$_4$ microstructures process flake like micro particles and 98% AP is 280.0°C. The final temperatures are about 418.0°C and 450.6°C, respectively. This data shows a decrease of 32.0°C in thermal decomposition of AP that validates the fact that these prepared micro particles lower the thermal decomposition temperature significantly.

The DSC curves are obtained for pure AP and a mixture of 2% prepared sample of Co$_3$O$_4$ and 98% AP, and the results obtained at high temperature as well as low temperature by the DSC are presented in Figure 6. The crystallographic transition of AP from orthorhombic form to cubic form corresponds to the endothermic peaks at temperature of 250.0°C as shown in Figure 8. The change of phase for the mixture of Co$_3$O$_4$ prepared sample and pure AP is 250.0°C which is in complete agreement with the transition of phase for pure AP. DSC graph showing that this process is complete at 450.0°C for pure AP. While the mixture of AP and sample, it completes at almost 418.0°C. The decomposition
mechanism of AP powder of fine particle size differs that of AP of larger particle size.

### 3.6 Fuel Additive Activity

Application of Co$_3$O$_4$ particles as a fuel additive is determined by analyzing the values of fuel quality parameters: fire point, flash point, cloud point, pour point and kinematic viscosity. The energy demand is increasing very quickly due to rapid increase of the world’s population. This has diverted the attention of researchers to increase the energy output from the available commercial fuels by using different means like modifying the construction and working of available engines to use fuel additives [4, 34-37].

![TEM images of the Co$_3$O$_4$ prepared by co-precipitation method: (a-c) Co$_3$O$_4$ prepared sample before calcinations, (d-f) Co$_3$O$_4$ after calcination.](image)

![Preparation scheme of product Co$_3$O$_4$ via co-precipitation method followed by calcination.](image)
For this purpose, synthesized $\text{Co}_3\text{O}_4$ particles are used as an additive to increase the efficiency of fuel. The properties of fuel are found to be enhanced by the addition of $\text{Co}_3\text{O}_4$ particles. In order to investigate the influence of this additive on fuel characteristics, the properties of modified fuel are also compared with the properties in the absence of the additive.

A plot of flash and fire points as a function of dosage of additives is given as Figure 7. The flash and fire points (the fuel spark point is fire point and fuel burning point is flash point) are observed to decrease with an increase in additive dosage. It means the volatility of fuel is increased with addition of additive. As particles are very small in size, they provide sites for vapor formation, and volatility is increased. Additive particles come in between the layers of fuel (liquid) and overcome the inter-layer interactions. Both of these factors play role in decreasing the flash and fire points. The flash and fire points are found to be function of additive dosage up to 2 ppm. After 2 ppm, the values of these parameters are observed to be independent of additive dosage. These results indicate that saturation level has been achieved up to 2 ppm additive dosage. The value of flash point is greater than that of fire point at every dosage of additive which is in accordance to the general rule of ASTM.

The dependence of cloud and pour points on the dosage of additive is shown in Figure 8. The cloudy appearance of fuel is indicated by cloud point. The trend in both of these properties is observed to be opposite of each other. The cloud point is found to increase with addition of additive and pour point is found to decrease with addition of additive. The depression in freezing of modified fuel is due to colligative properties phenomenon. The decrease in pour point of modified fuel increase the use of fuel in engines in countries located near poles.

Plot of kinematic viscosity of fuel versus dosage of additive is given as Figure 9. The kinematic viscosity of fuel is found to decrease with increase in additive dosage. Kinematic viscosity of fuel is linearly decreased with addition of dosage up to 6 ppm and its value is
remained same with increase in additive dosage from 6 to 10 ppm. The additive particles decrease the attractive forces among layers of fuel, so its viscosity increases. It means the fluidity of fuel is increased with the addition of additive. The modified fuel increases the flow speed in engine pipes and rapidly reaches the ignition chamber. Small size droplets are formed if viscosity is low. Thus, chances of combustion are also increased by using an additive. The results of studied applications suggest that the synthesized Co$_3$O$_4$ particles are a good candidate to be used as fuel additive as it increases the efficiency of the engine and scope of usage of fuel.

Summary of different nano aggregates is mentioned in Table 1. Table 1 shows that synthesized Co$_3$O$_4$ nano aggregate is more efficient as compared to other metal aggregates reported previously. Synthesized aggregate decreased the thermal degradation temperature of AP by 32 °C which is comparable to other particles reported previously. Similarly, fuel additive properties are comparable to other additives reported previously [4, 34-40].

### 4 Conclusion

Cobalt oxide nano aggregates are successfully prepared by a wet chemical synthesis method followed by annealing at 500.0°C. The electron microscopies (SEM & TEM) showed considerable changes in morphology, size and sequence of arrangement of individual particles before and after calcination. The morphology obtained before calcination is random and densely packed; whereas, considerably loose but sequential arrangement of constituent particles is observed after calcination. The synthesized product was used as a catalyst in the thermal decomposition of ammonium perchlorate. Prepared Co$_3$O$_4$ nano aggregates proved to be a good catalyst, and it reduced the thermal
decomposition temperature by 32.0°C. The prepared product has also been found to be an efficient additive as it decreased the pour point and viscosity of fuel. It has also decreased the flash and fire points to make burning easier. Thus, synthesized product possesses a good combination of properties as it shows good catalytic and fuel additive applications.

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References

[1] Al Nafiey A., Addad A., Sieber B., et al., Reduced graphene oxide decorated with Co₃O₄ nanoparticles (rGO-Co₃O₄) nanocomposite: A reusable catalyst for highly efficient reduction of 4-nitrophenol, and Cr(VI) and dye removal from aqueous solutions, Chem Eng J., 2017, 322, 375-384. https://doi.org/10.1016/j.cej.2017.04.039

[2] Elazab H.A., Moussa S., Gupton B.F. et al., Microwave-assisted synthesis of Pt nanoparticles supported on Fe₃O₄, Co₃O₄, and Ni(OH)₂ nanopolymers and catalysis application for CO oxidation, J Nanopart Res., 2014, 16, 2477-2488.

[3] Jamil S., Janjua M.R.S.A., Khan S.R., Synthesis of self-assembled Co₃O₄ nanoparticles with porous sea urchin-like morphology and their catalytic and electrochemical applications, Aust J Chem., 2017, 70, 908-916.

[4] Jamil S., Janjua M.R.S.A., Khan S.R., Synthesis and structural investigation of polyhedron Co₃O₄ nanoparticles: Catalytic application and as fuel additive, Mater Chem Phys., 2018, 216, 82-92.

[5] Li L., Seng K.H., Chen Z., et al., Self-assembly of hierarchical star-like Co₃O₄ micro/nanostructures and their application in lithium ion batteries, Nanoscale., 2019, 11, 2106-2112.

[6] Nie M., Sun K., Meng D.D., Formation of metal nanoparticles by short-distance sputter deposition in a reactive ion etching chamber, J. Appl. Phys., 2009, 106, 054314-054318.

[7] Gubin S.P., Koksharov Y.A., Khomutov G., et al., Magnetic nanoparticles: Preparation, structure and properties, Russ. Chem. Rev., 2005, 74, 489-520.

[8] Cao M., Wang P., Ao Y., et al., Photocatalytic degradation of tetrabromobisphenol A by a magnetically separable graphene–TiO₂ composite photocatalyst: Mechanism and intermediates analysis, Chem. Eng. J., 2015, 264, 113-124. https://doi.org/10.1016/j.cej.2014.10.011

[9] D'Silva R., Binu K.G., Bhat T., Performance and emission characteristics of a C.I. engine fuelled with diesel and TiO₂ nanoparticles as fuel additive, Materials Today: Proceedings, 2015, 2, 3728-3735. https://doi.org/10.1016/j.matpr.2015.07.162

[10] Leong K.H., Monash P., Ibrahim S., et al., Solar photocatalytic activity of anatase TiO₂ nanocrystals synthesized by non-hydrolitic sol–gel method, Solar Energy., 2014, 101, 321-332. https://doi.org/10.1016/j.solener.2014.01.006

[11] Zhu K., Luo Y., Zhao F., et al., Free-standing, binder-free titania/super-aligned carbon nanotube anodes for flexible and fast-charging Li-ion batteries, ACS Sust.Chem. Eng., 2018, 6, 3426-3433.

[12] Zhuang W., Lu L., Li W., et al., In-situ synthesized mesoporous TiO₂-B/ananate microparticles: Improved anodes for lithium ion batteries. Chin. J. Chem. Engin., 2015, 23, 583-589.

[13] Bhardwaj P., Goswami N., Narula P., et al., Zinc oxide nanoparticles (ZnO NP) mediated regulation of bacosides biosynthesis and transcriptional correlation of HMG-CoA reductase gene in suspension culture of Bacopa monnieri, Plant Physiology and Biochemistry., 2018, 130, 148-156. https://doi.org/10.1016/j.plaphy.2018.07.001

[14] Dong X., Jing Q., Shi Y., et al., Pb2Ba3 (BO3) 3Cl: A material with large SHG enhancement activated by Pb-chelated BO3 groups, J. Am. Chem. Soc., 2015, 137, 9417-9422.

[15] Shi G., Wang Y., Zhang F., et al., Finding the next deep-ultraviolet nonlinear optical material: NH2BO3F, J. Am. Chem. Soc. 2017, 139, 10645-10648.

[16] Wang X., Wang Y., Zhang B., et al., Cs2B4O7F: A congruent-melting deep-ultraviolet nonlinear optical material by combining superior functional units, Angew. Chem. 2017, 129, 14307-14311.

[17] Wang Y., Zhang B., Yang Z., et al., Cation-Tuned Synthesis of Fluorooxoborates: Towards Optimal Deep-Ultraviolet Nonlinear Optical Materials, Angew. Chem. 2018, 130, 2172-2176.

[18] Wu H., Pan S., Poepplmeier K.R., et al., K3B6O10Cl: A new structure analogous to perovskite with a large second harmonic generation response and deep UV absorption edge, J. Am. Chem. Soc. 2011, 133, 7786-7790.

[19] Wu H., Hu H., Yang Z., et al., Designing a deep-ultraviolet nonlinear optical material with a large second harmonic generation response, J. Am. Chem. Soc., 2013, 135, 4215-4218.

[20] Yu H., Wu H., Pan S., et al., A novel deep UV nonlinear optical crystal Ba₃B₂O₇F₂ with a new fundamental building block, B₂O₅ group, J. Mater. Chem., 2012, 22, 9665-9670.

[21] Zhang B., Shi G., Yang Z., et al., Fluorooxoborates: beryllium-free deep-ultraviolet nonlinear optical materials without layer growth, Angew. Chem. Int. Ed., 2017, 56, 3916-3919.

[22] Chen Q., Shen X., Gao H., Formation of nanoparticles in water-in-oil microemulsions controlled by the yield of hydrated electron: The controlled reduction of Cu¹⁺, J. Colloid. Interf. Sci., 2007, 308, 491-499. https://doi.org/10.1016/j.jcis.2006.12.021

[23] Ni Y., Ge X., Zhang Z., et al., A simple reduction-oxidation route to prepare Co₃O₄ nanocrystals, Mater. Res. Bull., 2001, 36, 2383-2387.

[24] Nam K.M., Shim J.H., Ki H., et al, Single-crystalline hollow face-centered-cubic cobalt nanoparticles from solid face-centered-cubic cobalt oxide nanoparticles, Angew. Chem. Int. Ed., 2008, 47, 9504-9508.

[25] Eranna G, Metal oxide nanostructures as gas sensing devices, CRC Press, 2011, ISBN 9780367381868

[26] a) Salavati-Niasari M., Mir N., Davar F., Synthesis and characterization of Co 3 O 4 nanorods by thermal decomposition of cobalt oxalate, J. Phys. Chem. Solid., 2009, 70, 847-852. b) Gupta R., Sinha A., Sekhar B.R., et al,
Synthesis and characterization of various phases of cobalt oxide nanoparticles using inorganic precursor, Appl. Phys. A., 2011, 103, 13-19.

[27] Lang D., Cheng F., Xiang Q., Enhancement of photocatalytic H₂ production activity of CdS nanorods by cobalt-based cocatalyst modification, Catal. Sc. & Tech., 2016, 6, 6207-6216.

[28] Guo S., Zhang S., Wu L., et al., Co/CoO nanoparticles assembled on graphene for electrochemical reduction of oxygen, Angew. Chem. Int. Ed., 2012, 124, 11940-11943.

[29] Zhang Y., Liu Y., Fu S., et al., Morphology-controlled synthesis of Co 3 O 4 crystals by soft chemical method, Mater. Chem. and Phys., 2007, 104, 166-171.

[30] Xiaohu L., Guanzhou Q., Xingguo L., Shape-controlled synthesis and properties of uniform spinel cobalt oxide nanocubes, Nanotechnology 2005, 16, 3035-3040.

[31] Papiz E., Rossi F., Raspanti M., et al., Engineered cobalt oxide nanoparticles readily enter cells, Toxic. Lett., 2009, 189, 253-259.

[32] Shaikh S.M., Desai P.V., Effect of CoO nanoparticles on the carbohydrate metabolism of the brain of mice "Mus musculus", J. Basic & Appl. Zool., 2016, 77, 1-7.

[33] Kim M.Y., Kamata T., Masui T., et al., Complete oxidation of toluene on Co3O4/CeO2–ZrO2–SnO2 catalysts, J. Asian Ceramic Societies., 2013, 1, 243-247.

[34] Jamil S., Ahmad H., Khan S.R., et. al., First synthetic study of cube-like cobalt hydroxystannate nanoparticles as photocatalyst for Drimarene red K-4BL degradation and fuel additive, J. Clust. Sci., 2018, 29, 685-696.

[35] Khalid M.U., Khan S.R., Jamil S., Morphologically controlled synthesis of cubes like tin oxide nanoparticles and study of its application as photocatalyst for congo red degradation and as fuel additive, J. Inorg. Organomet. Polym. Mater., 2018, 28, 168-176.

[36] Khan S.R., Khalid M.U., Jamil S., et al., Photocatalytic degradation of reactive black 5 on the surface of tin oxide microrods, J. Water Health, 2018, 16, 773-781.

[37] Kumar R., Kumar G., Akhtar M.S. et al., Sonophotocatalytic degradation of methyl orange using ZnO nano-aggregates, J. Alloy. Comp., 2015, 629, 167-172. https://doi.org/10.1016/j.jallcom.2014.12.232

[38] Ng C.T., Yong L.Q., Hande M.P., et al., Zinc oxide nanoparticles exhibit cytotoxicity and genotoxicity through oxidative stress responses in human lung fibroblasts and Drosophila melanogaster, Int. J. Nanomed., 2017, 12, 1621-1637.

[39] Jamil S., Khan S.R., Janjua M.R.S.A., Synthesis and structural analysis of mesoporous magnesium hydroxide nanoparticles as efficient catalyst, J. Chin. Chem. Soc., 2018, 1-6.

[40] Khan S.R., Jamil S., Janjua M.R.S.A., et al., Synthesis of ferric oxyhydroxide nanoparticles and ferric oxide nanorods by reflux assisted coprecipitation method and comparative study of their thermal properties, Mater. Res. Exp., 2017, 4, 115019-115025.

[41] Jia X., Yang X., Li J., et al., DNA-Hosted Copper Nanoclusters for Fluorescent Identification of Single Nucleotide Polymorphisms, ACS Nano., 2012, 64, 3311-3317.

[42] Okuda-Shimazaki J., Takaku S., Kanehira K., et al., Effects of tin oxide nanoparticle aggregate size on gene expression, Int. J. Mol. Sci., 2010, 11, 2383-2392.

[43] Pal A., Pal T., Silver nanoparticle aggregate formation by a photochemical method and its application to SERS analysis, J. Ram. Spect., 1999, 30, 199-204.

[44] Caro C., López-Cartes C., Zaderenko P., et al., Thiol-immobilized silver nanoparticle aggregate films for surface enhanced Raman scattering, J. Ram. Spect., 2008, 39, 1162-1169.