BAUSTJ
BAUST Journal

Study of the Effect of Sodium Dodecyl Sulphate & Polyvinylpyrrolidone on the Morphology and Size of Cobalt Nano Particles Synthesized by Wet Chemical Reduction Method

Dr. Kazi Mohammad Anamoul Haque[1*] and Mizanur Rahman [2]

[1] Department of Arts and Sciences, Bangladesh Army University of Science and Technology, Saidpur, Bangladesh
[2] Department of Chemistry, Hajee Mohammad Danesh Science and Technology University, Dinajpur, Bangladesh

emails: *[1]anamnano@gmail.com and [2]mizan.che72@tch.hstu.ac.bd ('*' - corresponding author)*

ARTICLE INFO

Article History:

Received: 14th January 2025
Revised: 12th March 2025
Accepted: 15th April 2025
Published online: 7th May 2025

Keywords:

Chemical Reduction
SDS
PVP
Spiky
Spherical

ABSTRACT

Applying bottom-up approach cobalt nano particles have been synthesized, using cobalt chloride as precursor and hydrazine as the reducing agent. The effects of cationic polymer polyvinylpyrrolidone (PVP) and anionic surfactant sodium dodecyl sulphate (SDS) have been studied. It was found that presence of SDS and PVP reduces the particle size. Using Transmission Electron Microscope (TEM) (JEOL-JEM 200F) and Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Analysis (EDX) facilities (FEI-NOVA 200 nanolab), these nano cobalt particles have been characterized. TEM analysis confirms the existence of cobalt nanoparticles as small as 10 nm in diameter when hydrazine has been used in this synthesis; however, while SDS and PVP were present in the synthesis, the particles' diameter reduced to 5 nm. The synthesized particles' shape was shown by the SEM images to be spherical, however on higher magnification, the nanoparticles were observed to be spiky spherical. When SDS and PVP were applied, the nanoparticles' spikiness appeared to increase. The cobalt nanoparticles synthesized with hydrazine only, exhibit the cobalt particle peak on the SEM-EDX plot. A very weak peak for the oxygen in SEM-EDX plot indicates some of the synthesized cobalt nano particles have been oxidized. SEM-EDX plot of cobalt nano particle synthesized in presence of SDS and PVP shows a strong peak of oxygen which indicates that the synthesized nano cobalt particles were oxidized more, there is a small peak of carbon which is because of PVP.

1. INTRODUCTION

Nanomaterials are constantly being explored and used because of their unique features that set them apart from single atoms or the bulk. Therefore, nano metals find use in a wide range of fields, including electronics (Cui *et al.*, 2001; Mhetre *et al.*, 2021) optics (Eychmüller, 2000), magnetism (Puntes *et al.*, 2001), material sciences (Rao *et al.*, 2000), both homogeneous and heterogeneous catalysis (El-Sayed, 2001; Thomas *et al.*, 2003), fuel cells catalysis (Sun *et al.*, 2000; Mashola *et al.*, 2022) and even the biological and health sciences (Malik *et al.*, 2022; Niemeyer, 2001). Although the design of nanomaterials with functionalities that depend on size is becoming increasingly important, synthetic methodologies have been corresponding with their application requirements, enabling a "made to order" relationship. Not only may any desired bi-metallic and multimetallic composition be created using these newly adjustable synthetic techniques, but the size and internal structure of the resulting nano-metals can also be controlled. There are two methods of producing nano-structured materials: the "top down method" and the "bottom up method". In the top-down approach, the bulk metals are broken down first, and the resultant nanosized metallic particles of colloidal protecting agents are subsequently stabilized (Hussain *et al.*, 2008; Carone *et al.*, 2023). On the other hand, the wet chemical nano-particle synthesis method, which is the bottom-up technique, depends on producing nanoparticles from the metal's atom level. A growing number of material systems, encompassing hair care products,

detergents, emulsions, foams, gene-therapy DNA-lipid complexes, and mineral oil extraction have employed mixed polymer-surfactant systems, which has led to a greater interest in the interaction of surfactants and polymers in aqueous solutions. This article describes a synthetic technique to produce nano-structured cobalt particles using a bottom-up, wet chemical approach. This process will enable the low-cost synthesis of nano-cobalt particles with a diameter of as little as 10 nm. Because of its special qualities and range of uses, the manufacture of nanocobalt particles have been thoroughly investigated in the last ten years. Scientists and engineers from almost every field have been very interested in research on nanoparticles and nanoscale materials in recent years.

The synthesis of nanoparticles has been accomplished using a variety of methods, such as the reduction of metal oxide salts (Kimijima *et al.*, 2005), the reduction of solutions by strong reducing agents and the breakdown of carbonyls (Petit *et al.*, 1993). Reducing agents that correspond to the synthesis of metal borides are potassium borohydrides, sodium hypophosphite, and hydrazine. It is already commonly recognized that in an aqueous solution, anionic surfactant like sodium dodecyl sulphate (SDS) interacts significantly with water-soluble non-ionic macromolecules like polyvinylpyrrolidone (PVP) or polyethylene oxide (PEO). Surfactant aggregates on macromolecule chains in micellar structures over the critical association concentration (CAC), a phenomenon referred to as bound micelle. Despite platinum having two drawbacks—it is expensive and corrodes over time, It works quite well in hydrogen fuel cells as a catalyst. The widespread use of large-scale hydrogen fuel-cell devices has been impeded by a severe cost issue that may be resolved by eliminating the valuable metal platinum. In recent years, a new catalytic material based on the metal cobalt has been suggested as a platinum substitute, potentially enabling the development of more affordable and durable hydrogen fuel cells. Because of its nearly comparable qualities to those of platinum, cobalt is regarded as the first catalyst produced from a nonprecious metal (Yu *et al.*, 2013). Cobalt serves as a model system for the macroscopic magnetic response because to its low to moderate crystal anisotropy, which allows the effects of shape, size, internal structure of the crystal, and surface anisotropy to be examined in a single system (Puntes *et al.*, 2001; Skumryev *et al.*, 2003). Research on the effects of size, shape, crystal structure, and surface anisotropy on the material's macroscopic magnetic response is made easier by cobalt's low crystal anisotropy.

There have been reports of several techniques to produce magnetic colloid dispersions. The epsilon phase, face-centered cubic (fcc) phase, and hexagonal closed packed (hcp) phase are three metastable phases of cobalt with distinctive crystalline structures, making it one of the most significant ferromagnetic metals. (Pandey *et al.*, 2012; Lu *et al.*, 2007). Wet-chemistry methods for the synthesis of metallic nanoparticles are an effective means of achieving a reproducible, macroscopic amount of homogenous sample (Puntes *et al.*, 2002; Lee *et al.*, 2024). Cobalt crystals with various morphologies can be created using a variety of wet-chemical techniques, such as template-based methods, pyrolysis, solvothermal and hydrothermal breakdown, microfluidic synthesis, and modified polyol processes. It has been stated that liquid-phase reduction techniques are not complicated and don't call for specialized tools. Furthermore, they are thought to be quicker and less expensive to install, which are advantageous characteristics for upcoming large-scale production endeavours. Utilizing organisms such as fungus, algae, bacteria, plants, and their metabolites—which function as reducing and capping agents—biogenic production of nanoparticles is possible. (Ahmed *et al.*, 2016; Gholami-Shabani *et al.*, 2014). The physical characteristics of the nanoparticles are influenced by their size and shape. Controlling shape and size will therefore make it more likely that these materials will be used commercially using the liquid-phase reduction approach, we tried to synthesis cobalt nanoparticles at room temperature in this work. Hydrazine (N_2H_4) was used as a reducing agent in a solution comprising a cobalt compound and Co^{2+} in order to precipitate the cobalt. Given that citric acid is a unique capping agent that keeps metal nanoparticles stable and safe, (Barnes *et al.*, 2000; Kim *et al.*, 2006; Niemeyer *et al.*, 2001), it was determined how citric acid additions affected the size and form of the nanoparticles that were created.

Here, we describe the synthesis of cobalt nanoparticles using a wet chemical reduction approach, which transforms $CoCl_2$ into Co particles at the nanoscale through a chemical reduction process. In a basic media, hydrazine was used as a reducing agent in conjunction with the anionic surfactant sodium dodecyl sulphate and the cationic polymer polyvinylpyrrolidone. Water pools coated with surfactants provide a special microenvironment for nanoparticle production. In addition to serving as tiny reactors for processing processes, they also prevent excessive particle aggregation since surfactants may adsorb on the particle surfaces when the particle size becomes close to that of a water pool. The particles produced in such a medium are often monodispersed and very fine as a consequence.

2. MATERIALS AND METHODS

The substances utilized in this study effort comprised analytical grade cobalt chloride, hydrazine hydrate solution 80% LOBA Chemie India, sodium carbonate 99% Sigma, sodium dodecyl sulphate (SDS) 92% LOBA Chemie, India, and polyvinylpyrrolidone (PVP) Winlab, UK. All of the solutions were prepared using de-ionized distilled water. All solutions were produced utilizing deionized distilled water. In this study, a magnetic stirrer and thermostatically controlled hot plate (Yellowline) were used. 10g of $CoCl_2$ were dissolved in 100mL of deionized water in a glass beaker at 40°C to synthesize the cobalt nanoparticles. The cobalt chloride solution was mixed with a concentrated aqueous sodium carbonate solution to maintain a pH of 10.2. At 70°C, 150 mL of hydrazine was added gradually while swirling constantly.

The formation of cobalt particles was detected by the emergence of gray/blackish precipitate in the beaker at 70°C. The reduction of cobalt ions into cobalt nanoparticles can take several hours to complete because this reaction is not instantaneous. Cobalt nanoparticles settled at the bottom of reaction vessel. Before being characterized, the cobalt

nanoparticles were collected, centrifuged at 4000 rpm (using Centrifuge machine Faithful, FTD4C), triple-washed in deionized water and ethanol, and then allowed to dry at ambient temperature. The identical experiment was carried out to examine the effects of 20g/l PVP and 20g/l SDS on the size and morphology of the cobalt nano particles that were formed. Before the addition of hydrazine, these substances were added to the cobalt chloride aqueous solution.

3. RESULTS AND DISCUSSIONS

Synthesized cobalt nano particles were characterized using Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Analysis (EDX) facilities (FEI-NOVA 200 nanolab) and Transmission Electron Microscope (TEM) (JEOL-JEM 200F).

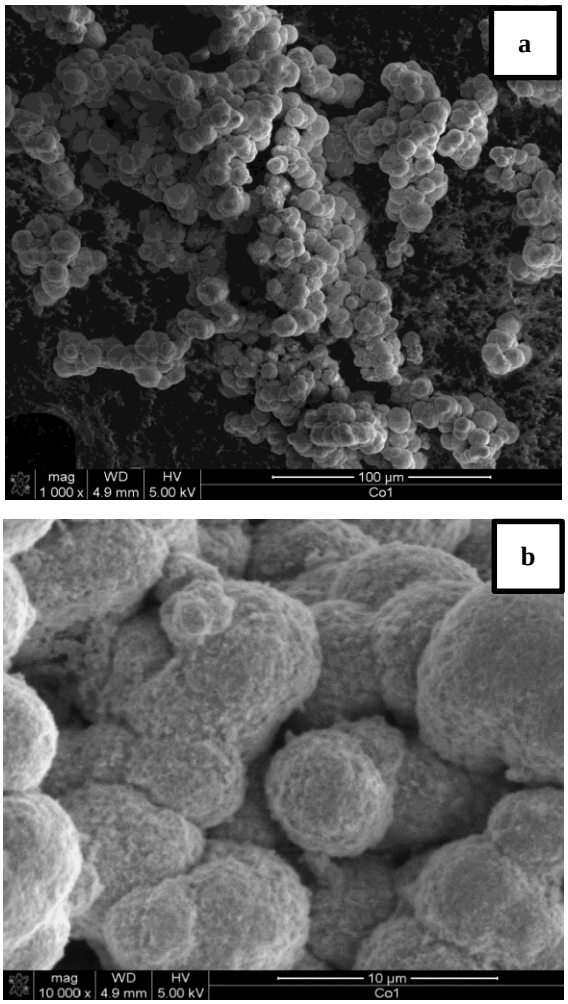

Figure 1: (a) SEM image of cobalt nanoparticle at mag × 1,000. (b) SEM image of Co nanoparticles Mag. ×10000. Synthesized using hydrazine only

The SEM images of nano cobalt particles synthesized using cobalt chloride as precursor hydrazine as a reducing agent without any SDS and PVP at 60°C, at Mag. × 1,000 and mag. × 10,000 have been shown in figure 1(a) and 1(b). Images show that the synthesized particles are spherical in shape at lower magnification. But at higher magnification the spherical object possesses small spiky particles.

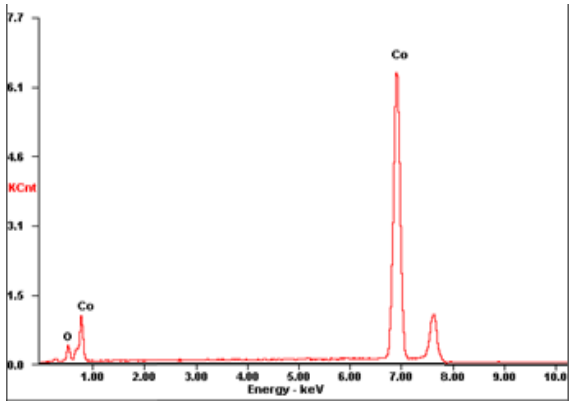

Figure 2: SEM-EDX image of cobalt nanoparticle synthesized using hydrazine only

The SEM-EDX plot of the cobalt nano-particles synthesized using hydrazine is shown in figure- 2. Plot exhibit the peak for the cobalt particles. There is a very weak peak for the oxygen indicates some of the synthesized cobalt particles are oxidized.

Figure 3(a) and 3(b) are the SEM images of cobalt nanoparticles were synthesized in the presence of SDS and PVP using cobalt chloride as a precursor and hydrazine as a reducing agent. Images show that at lower magnification i.e. in figure 3(a) particles are spherical in shape but at an increased magnification, such as in figure 3(b) the spherical shaped object possess many spiky particles.

In presence of SDS and PVP the produced particles' shape shifts from spherical to spiky. Figure 4 is the SEM-EDX plot of cobalt nano particle synthesized along with PVP and SDS. Plot exhibits a peak of oxygen and carbon which indicates that the synthesized nano cobalt particles were oxidized and there are some carbons because of presence of some SDS and PVP. The oxygen peak for these particles is higher than that of the cobalt nano particles which indicate that these particles are easily oxidized. The reason for easier/higher oxidation of these particles is the presence of SDS and PVP. Figure 4 shows a very weak peak for carbon which may because of the presence of polymer PVP.

The TEM image of cobalt nanoparticles formed solely with hydrazine is shown in figure 5(a). Image exhibits that the size of the particles is approximately 10 nm calculated using the scalebar at bottom-left of the image. Figure 5(b) is the TEM image of cobalt nano particles produced using cobalt chloride as precursor, hydrazine as a reducing agent when SDS and PVP are present. According to the image, the particles have a diameter of about 5 nm calculated using the scalebar at the bottom-left of the image.

It can be stated from the above results that the diameter of the cobalt particles reduces in presence of SDS and PVP. When cobalt nano particles are reduced using only hydrazine, they can aggregate from a small number of atoms generating large clusters. Nonetheless, a comparatively tiny number of cobalt agglomerates in the absence of SDS/PVP, and oxide layers may form around them.

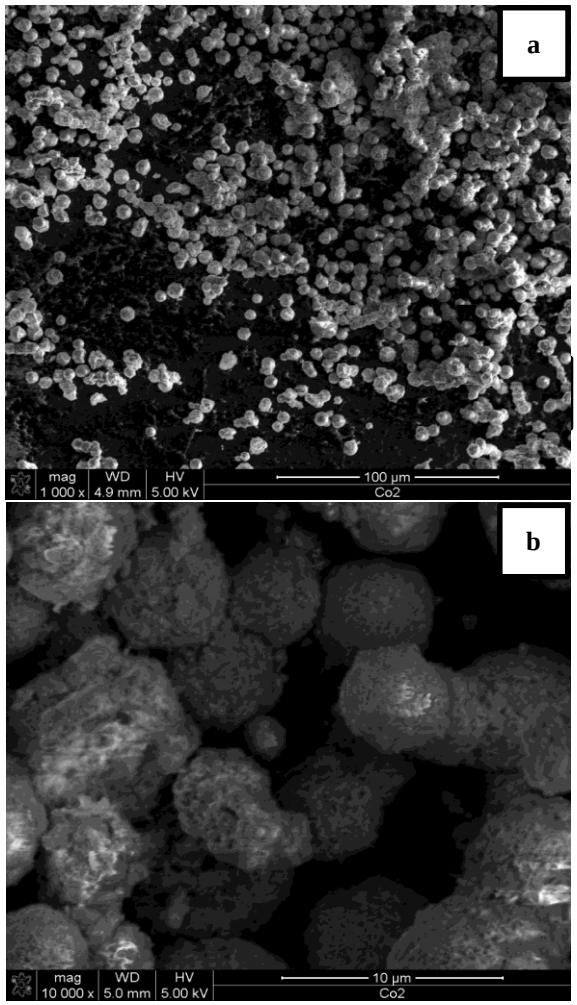

Figure 3: (a) SEM image of cobalt nanoparticle at Mag. × 1,000. (b) SEM image of Co nanoparticles Mag. ×10000 synthesized using hydrazine in presence of SDS and PVP

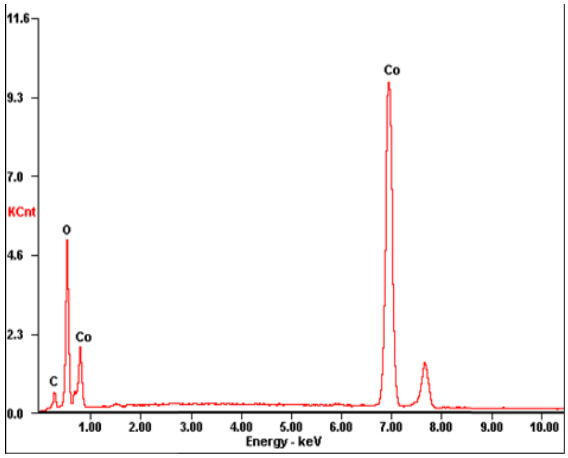

Figure 4: SEM-EDX image of cobalt nanoparticle synthesized using hydrazine in presence of SDS and PVP

Because the oxide layers around the cobalt particle clusters are so thin, they attract to other clusters that are identical to them and keep getting bigger. As linear PVP molecules have a template effect (Chen *et al.*, 2023), fresh cobalt nanoparticles will be drawn to the PVP template and ultimately grow along the PVP chain. PVP hindered the agglomeration process in the reduction of cobalt ions into cobalt nanoparticles in the presence of SDS and PVP. The polymer layer around the cobalt nanoparticles is significantly thicker than the natural oxide polymers, portrayed by the HRTEM/HRSEM images. These significantly stouter polymer (C) films were able to cushion the agglomerated cobalt clusters and prevent further agglomeration of the cobalt clusters early in the chemical reduction process. Therefore, in the process when SDS and PVP are present, finer cobalt nanoparticles can be formed with spiky morphology.

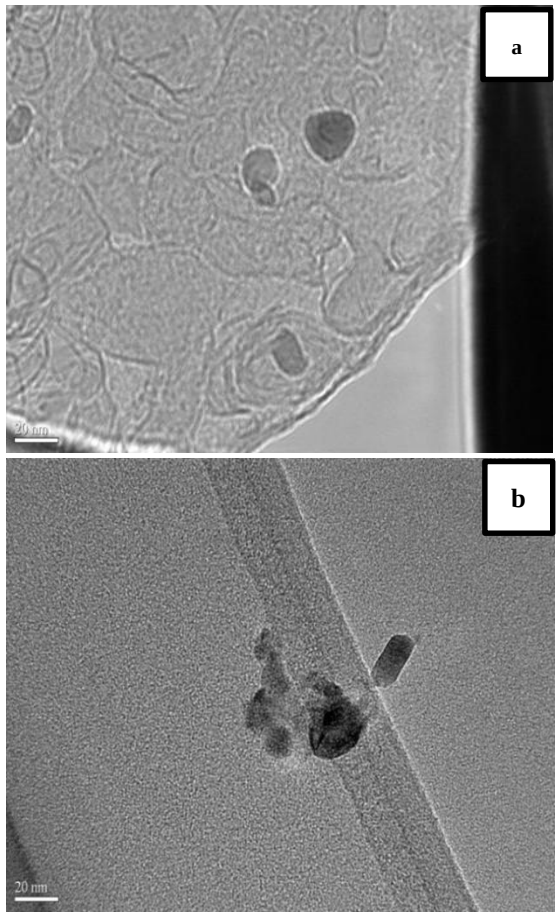

Figure 5: (a) TEM image of cobalt nanoparticle synthesized using hydrazine only (b) TEM image of cobalt nanoparticle synthesized using hydrazine in presence of SDS and PVP

4. CONCLUSION

Cobalt chloride was used as a precursor and hydrazine as a reducing agent in a wet chemical method to synthesize cobalt nanoparticles. Shape of the synthesized cobalt nano particles are spherical with diameter less than 10 nm when cobalt ions reduced to cobalt nano particles with hydrazine only. Size of the synthesized particles dramatically reduced when reduction take places in presence of combination of SDS and

PVP along with hydrazine, In the presence of PVP and SDS, hydrazine has been used to create cobalt nanoparticles as small as 5 nm in diameter. According to SEM/EDX analysis, the surface oxidized cobalt nano particles was surrounded by an exterior carbon (polymer) film after an oxide layer coated them. This polymer layer stopped further agglomeration of the cobalt nano particles. Morphology of the synthesized cobalt nanoparticles were spiky when SDS and PVP were used. Presence of SDS and PVP transform the nanoparticles' spherical shape into spiky because of the surfactant-polymer interaction. So, the presence of SDS and PVP reduces the size of cobalt nanoparticles as well as change the morphology from spherical to spiky.

REFERENCES

Ahmed, S., Ahmad, M., Swami, B. L., & Ikram, S. (2016). A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: a green expertise. *Journal of advanced research*, *7*(1), 17-28.

Barnes, K. A., Karim, A., Douglas, J. F., Nakatani, A. I., Gruell, H., & Amis, E. J. (2000). Suppression of dewetting in nanoparticle-filled polymer films. *Macromolecules*, *33*(11), 4177-4185.

Carone, A., Emilsson, S., Mariani, P., Désert, A., & Parola, S. (2023). Gold nanoparticle shape dependence of colloidal stability domains. *Nanoscale Advances*, *5*(7), 2017-2026.

Chen, Y., Chen, J., Hao, Z., Selim, M. S., Yu, J., & Chen, X. (2023). Polyvinylpyrrolidone-bridged MXene skeleton constructed by photothermal assisted sacrificial template method for phase change materials with form stability and photothermal conversion. *Chemical Engineering Journal*, *463*, 142375.

Cui, Y., & Lieber, C. M. (2001). Functional nanoscale electronic devices assembled using silicon nanowire building blocks. *science*, *291*(5505), 851-853.

El-Sayed, M. A. (2001). Some interesting properties of metals confined in time and nanometer space of different shapes. *Accounts of chemical research*, *34*(4), 257-264.

Eychmüller, A. (2000). Structure and photophysics of semiconductor nanocrystals. *The Journal of Physical Chemistry B*, *104*(28), 6514-6528.

Gholami-Shabani, M., Akbarzadeh, A., Norouzian, D., Amini, A., Gholami-Shabani, Z., Imani, A., & Razzaghi-Abyaneh, M. (2014). Antimicrobial activity and physical characterization of silver nanoparticles green synthesized using nitrate reductase from Fusarium oxysporum. *Applied biochemistry and biotechnology*, *172*, 4084-4098.

Hussain, M. S., & Haque, K. M. A. (2008). Aggregated Nano-Nickel Crystals Obtained by Hydrazine Reduction in the Presence of Sodium DodecylSulfate-Polyvinylpyrrolidone Clusters J. *Bangladesh Chem. Soc*, *21*(1), 1-10.

Kim, B. J., Bang, J., Hawker, C. J., & Kramer, E. J. (2006). Effect of areal chain density on the location of polymer-modified gold nanoparticles in a block copolymer template. *Macromolecules*, *39*(12), 4108-4114.

Kimijima, K. I., & Sugimoto, T. (2005). Effects of the water content on the growth rate of AgCl nanoparticles in a reversed micelle system. *Journal of colloid and interface science*, *286*(2), 520-525.

Lee, H., Jeong, H., Jeong, W., Hwang, Y. J., An, B., Lee, Y., & Ha, D. H. (2024). Wet Chemistry Methods for Synthesizing High-Entropy Nanoparticles: A Review of the Synthesis Strategies and Various Applications. *Korean Journal of Chemical Engineering*, 1-23.

Lu, A. H., Salabas, E. E., & Schüth, F. (2007). Magnetic nanoparticles: synthesis, protection, functionalization, and application. *Angewandte chemie international edition*, *46*(8), 1222-1244.

Malik, A., Khan, J. M., Alhomida, A. S., Ola, M. S., Alshehri, M. A., & Ahmad, A. (2022). Metal nanoparticles: biomedical applications and their molecular mechanisms of toxicity. *Chemical Papers*, *76*(10), 6073-6095.

Mashola, T. A., Matthews, T., Msomi, P. F., & Maxakato, N. W. (2022). Novel nanostructured electrocatalysts for fuel cell technology: Design, solution chemistry-based preparation approaches and application. *Nano-Structures & Nano-Objects*, *29*, 100831.

Mhetre, H. V., Kanse, Y. K., & Patil, S. S. (2021). Nanomaterials: Applications in Electronics. *International Journal of Advanced Engineering and Nano Technology*, *4*(6).

Niemeyer, C. M. (2001). Nanoparticles, proteins, and nucleic acids: biotechnology meets materials science. *Angewandte Chemie International Edition*, *40*(22), 4128-4158.

Pandey, B. K., Shahi, A. K., Swarnkar, R. K., & Gopal, R. (2012). Magnetic property of novel cobalt sulfate nanoparticles synthesized by pulsed laser ablation. *Science of Advanced Materials*, *4*(3-4), 537-543.

Petit, C., Lixon, P., & Pileni, M. P. (1993). In situ synthesis of silver nanocluster in AOT reverse micelles. *The Journal of Physical Chemistry*, *97*(49), 12974-12983.

Puntes, V. F., Krishnan, K. M., & Alivisatos, A. P. (2001). Colloidal nanocrystal shape and size control: the case of cobalt. *Science*, *291*(5511), 2115-2117.

Puntes, V. F., Krishnan, K. M., & Alivisatos, A. P. (2001). Colloidal nanocrystal shape and size control: the case of cobalt. *Science*, *291*(5511), 2115-2117.

Puntes, V. F., Krishnan, K., & Alivisatos, A. P. (2002). Synthesis of colloidal cobalt nanoparticles with controlled size and shapes. *Topics in Catalysis*, *19*, 145-148.

Rao, C. R., Kulkarni, G. U., Thomas, P. J., & Edwards, P. P. (2000). Metal nanoparticles and their assemblies. *Chemical Society Reviews*, *29*(1), 27-35.

Restrepo, C. V., & Villa, C. C. (2021). Synthesis of silver nanoparticles, influence of capping agents, and dependence on size and shape: A review. *Environmental Nanotechnology, Monitoring & Management*, *15*, 100428.

Skumryev, V., Stoyanov, S., Zhang, Y., Hadjipanayis, G., Givord, D., & Nogués, J. (2003). Beating the superparamagnetic limit with exchange bias. *nature*, *423*(6942), 850-853.

Sun, S., Murray, C. B., Weller, D., Folks, L., & Moser, A.

(2000). Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices. *science*, *287*(5460), 1989-1992.

Thomas, J. M., Johnson, B. F., Raja, R., Sankar, G., & Midgley, P. A. (2003). High-performance nanocatalysts for single-step hydrogenations. *Accounts of chemical research*, *36*(1), 20-30.

Yu, Y., Mendoza-Garcia, A., Ning, B., & Sun, S. (2013). Cobalt-substituted magnetite nanoparticles and their assembly into ferrimagnetic nanoparticle arrays. *Advanced Materials*, *25*(22), 3090-3094.