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Review Article

Mechanistic approaches and current trends in the green synthesis of cobalt oxide nanoparticles and their applications

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ABSTRACT

Nowadays, nanotechnology is a buzzword in scientific area with diverse number of applications. The advancement in the eco-friendly and reliable systems for the development of nanoparticles are a crucial key in nanotechnology. Nanoparticles have been incessantly evaluated and utilized in numerous industrial applications. Specifically, the rule of cobalt oxide nanoparticles has received an incredible interest due to its UV filters properties and photochemical, antifungal, high catalyst, and antimicrobial activities. In chemical and physical techniques, high rate of harmful chemicals are used for the synthesis of nanomaterials. To overcome this issue various clean and green methods are adopted which use plants, organisms and microscopic organisms for the synthesis of nanoparticles. This paper reviews different green synthesis techniques used for synthesis of cobalt oxide NPs and their applications. It was found that, the green route of synthesis is safe and eco-friendly. Additionally it is expected that the biomedical applications in this area will expand in different procedures including bio imaging, drug delivery, biosensors, and gene delivery. Also, cobalt oxide NPs are capable of acting against numerous drug resistant microorganisms and as a gifted substitute for antibiotics.

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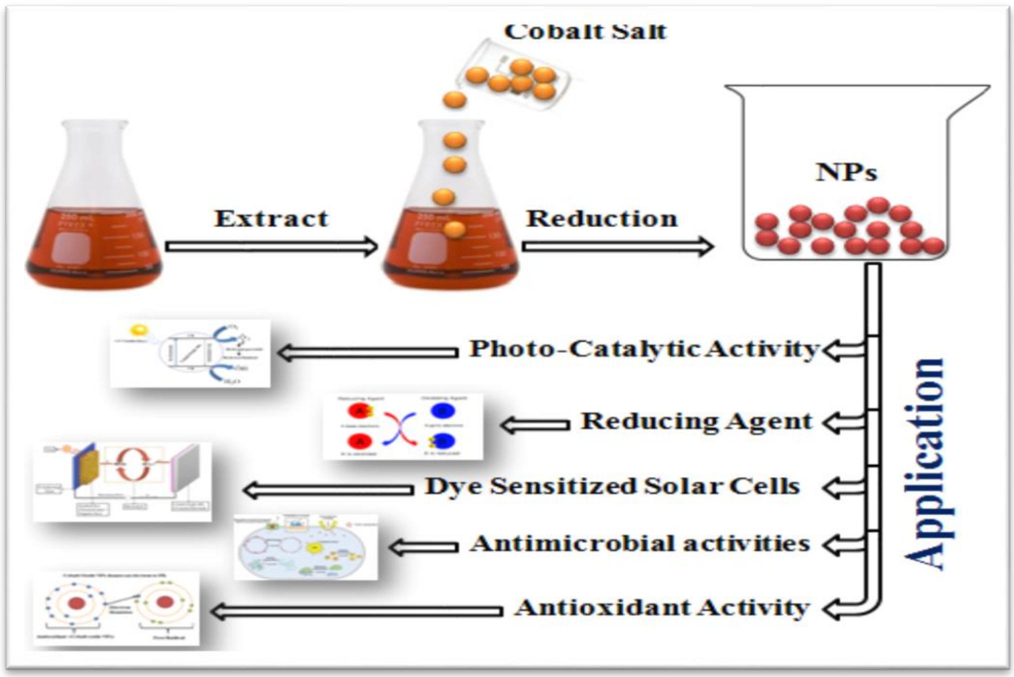
Graphical Abstract



Biographies

Mr. Naimat Ullah is a PhD scholar at Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan. His research interest lies in the synthesis of nanoparticle, respective core/shells by using various shell materials and adopting facile synthesis methods and their applications for energy devices.

Ms. Rotaba Ansir is a PhD scholar at Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan. Her research interest lies in the development and employment of novel semiconducting nanomaterials for solar to chemical energy conversion via using metal free organic dyes and natural dyes as sensitizers and computational studies of dyes and nanomaterials to explore their structural compatibility.

Mr. Wali Muhammad is a PhD scholar at Department of Biotechnology, Quaid-i-Azam University, Islamabad, Pakistan. His research interest lies in the biological synthesis of metallic nanoparticles and the exploitation of nanoparticles as novel bactericidal, antifungal, antileishamnial and anticancer agents.

Ms. Sadaf Jabeen is an M phil scholar at Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan. Her research interest lies in the electrochemical application and clean energy generation by nanomaterials synthesized via green routes.

Table of Contents

Introduction

Metallic oxide, bioinspired and multifunctional metal nanoparticles are considered as a brilliant zone of research due to their energizing optoelectronics and physio-chemical properties [1]. Metal oxide nanoparticles has been consistently synthesized and tested in a wide scope of uses. Fast advancements on the nano biotechnological interface have brought about a wide exhibit of biomedical applications including vaccine administration and drug delivery. Nanoparticulate matter is not quite the same as their micro-scale counter parts in their electro-optical, mechanical, synthetic magneto-optical and surface area, indicating its use as a powerful tool for biomedical applications. Cobalt oxide has fascinating properties and consequently attracted various researchers for considering their conceivable biomedical applications [2]. Beside their physiological rule as a cofactor of vitamin B_{12}, cobalt can be utilized in a wide range of applications, including, anti-ferromagnetic, multifunctional *p*-type semiconductor [3]. Pigments, electrochromic sensors, energy storage, heterogeneous catalysis, dyes and in lithium ions rechargeable batteries as an anode material. Cobalt based nanostructures have been effectively utilized in amino acids, methanol, nitrites and glucose. On account of their fascinating physical properties, cobalt oxides possess spintronic applications as well [4–8]. Numerous chemical and physical techniques such as hydrothermal method, solution combustion, sono-chemical, microemulsion strategy, chemical spry pyrolysis, microwave assisted, co-precipitation, vapor deposition technique have used for the synthesis of cobalt oxide nanoparticles [8–14].

Despite being viable all of these synthesis methods are accompanied by some disadvantages such as high cost, great energy and time consumption, and being unfriendly to environment. To overcome the issue of toxic wastes and energy imbalance, greener and eco-friendly strategies has been proposed. For that purpose, biological recourses for example, plants and microorganisms can be utilized in a fast, simple, effective and economical approach for production of desired metal or metallic oxide nanoparticles. Plant intervened biosynthesis of cobalt oxide nanoparticles has been effectively demonstrated. Here we review synthesizing cobalt oxide nanoparticles; mechanistic approach, total green approaches. This method involves neither the utilization of organic/inorganic solvents, nor the consumption of any surfactants, hence, making the procedure eco-friendly and green. The interface of medicinal plants and biosynthesis of nanoparticles gives emerging opportunities for a number of applications [15, 16].

Green synthesis of cobalt oxide NPs by using different sources

In an attempt to build up an eco-friendly and energy effective methodology, researchers have made full use of the biological resources for the synthesis of cobalt oxide NPs [16]. The biosynthesis process and its application to synthesize cobalt oxide involves the mixing of precursor salt with biological extract. The metabolites present in the extract would then reduce and stabilize the bulk metal into elemental structure following different mechanical steps. This biosynthetic methodology offers numerous preferences and has emerged as a safe, simple and viable substitute to chemical and physical techniques of synthesis [17–21]. In addition, biological methodology can sufficiently catalyze the synthesis process at any scale and condition. Additionally NPs with controlled size and shape can likewise be produced [22]. Amongst the various organic species, plants are considered as the most appropriate candidate for the synthesis of nanoparticles as they are environment friendly, safe and effectively accessible [23]. Many plants species have been reported for synthesis of cobalt oxide NPs (Table 1).

Green synthesis of cobalt oxide NPs by using aspalathus *Linearis*

Linearis of the family Fabaceaeae called Rooibos is a plant initially found in the Southern Africa, as shown in Figure 1 [24]. Alinearis's extract had been utilized to reduce many cobalt-based salts, including cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), cobalt chloride hexahydrate ($CoCl_2.6H_2O$, and cobalt hydroxide ($Co(OH)_2$ just as ammonium-cobalt(II)-sulfate-hexahydrate (($(NH_4)_2$ $Co(SO_4)_2{\cdot}6H_2O$)) based precursors. This correspondence focus on the green reduction of Co $(NO_3)_2{\cdot}6H_2O$ precursor as a proof of idea of bio-synthesis of single-phase Co_3O_4 nanoparticles the techniques employed to investigate surface/interface and optical properties are shown in Table 1. Additionally the X-rays diffraction technique, the infrared, and Raman along with, the X-ray photoelectron spectroscopy were also used to conform the single period of the Co_3O_4 nanoparticles. The calculated average size was~3.6 nm [16].

Green synthesis of cobalt oxide NPs by using *Punica granatum* peel

Cobalt-oxide nanoparticles (NPs) were synthesized by *Punica granatum peel* (Figure 2) [26] extract using cobalt nitrate hexahydrate precursor at low temperature. For the synthesis of cobalt

Table 1. Green synthesized Cobalt oxide nanoparticles Co_3O_4 NPs using different bio sources

S.No	Source of synthesis	Characterization technique used	Size	Morphology	References
1	*Aspalathus linearis's*	XRD, Raman, TEM, XPS	~3.6 nm	quasi-spherical	[16]
2	*Punica granatum* peel	XRD, SEM, EDX, AFM, FTIR and UV-Vis spectroscopy	40–80 nm	spherical	[25]
3	*Calotropis gigantea*	XRD, SEM, TEM, EDX and UV-Vis spectroscopy	60 nm	spherical	[27]
4	*Listeria innocua*	TEM, SEC, DLS and UV-Vis spectroscopy	4.34 ±0.5 nm	-	[29]
5	Gelatin	XRD, SEM, EDX, TEM and TGA	28 nm	agglomerates	[30]
6	*Apoferritin (protein)*	XRD, XPS, EELS and TEM	6 nm.	-	[31]
7	*Conocarpus erectus; Neriumindicum*	XRD and SEM	20-60 nm	spherical	[28]
8	*Ocimum sanctum*	XRD, SEM, EDX, and FTIR	-	irregular spherical	[25]
9	*Sageretia thea*	XRD, HR SEM, HR TEM, EDS, and Raman	20.03 nm	Cubic	[15]

Figure 1. *Aspalathus linearis* plant

Figure 2. Peel of *Punica granatum*

oxide NPs, 90 mL freshly prepared peel extract was added to 1 M solution of cobalt nitrate hexahydrate, heated at 70 °C till precipitates showed up and afterward, temperature decreased to 60 °C and kept the solution at 60 °C for 90 min. Then the mixture was kept at room temperature and ultimately centrifuged at 14,000 rpm for 10 min. Later on, the acquired precipitates were dried at 60 °C [25]. Characterization techniques and properties of cobalt oxide nanoparticles obtained from *Punica granatum* peel are shown in Table 1.

Green synthesis of cobalt oxide NPs by using *Calotropis gigantean* leaves

Calotropis gigantean leaves (Figure 3) extract used for the cobalt oxide nanoparticles (Co_3O_4NPs). 100 g leaves were washed thoroughly along with cutting and boiled in 200 mL of deionized water to extract the phyto-constituents present in the leaves. Than filtered in hot condition to expel fibrous impurities. 100 mL of leaves extract was taken and boiled again to 60–80 °C utilizing a stirrer-hot plate. Later on, 10 g [Co $(NO_3)_2 \cdot 6H_2O$] was dissolved in leaves extract under stirring. The glue was collected and heated in a furnace at 400 °C for 2 h to obtain theCo_3O_4 NPs [27]. Some properties of these synthesized cobalt oxide nanoparticles using *Calotropis gigantean* leaves extract are shown in Table 1.

Green synthesis of cobalt oxide NPs by using *Conocarpus erectus* and *Neriumindicum* plants leaves

In the present work phenolic compounds in leaf extract of *Conocarpus erectus* (Figure 4**a**) and *Neriumindicum* (Figure 4**b**) were used and after that cobalt oxide nanoparticles (Co_3O_4NPs) were synthesized by utilizing just methanol extract of *Conocarpus erectus* leaves as reducing agent in light of its higher values (296±9 μg/g) the phenolic compounds in contrast with *Neriumindicum* having

185 ± 6 μg/g the phenolic compounds [28] and further characterized with different techniques as listed in Table 1.

Figure 3. Leaves of *Calotropis gigantean* plant

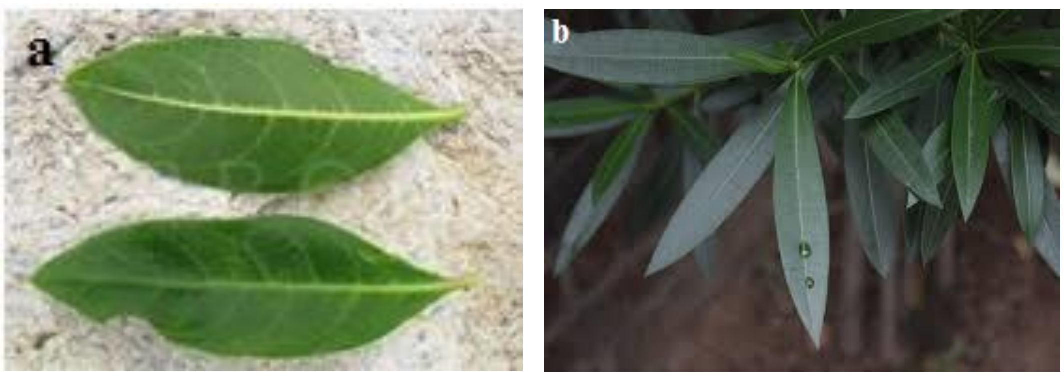


Figure 4. Leaves of plants a) *Conocarpus erectus* and b) *Neriumindicum*

Green synthesis of cobalt oxide NPs by using *Ocimum sanctum*

In this study, cobalt nanoparticles were synthesized by a recyclable and cost viable strategy utilizing *Ocimum sanctum* leaves (Figure 5) extract. Where 20 mL of 50 mg/mL cobalt solution were added to 1-2 mL of osmium sanctum leaf extract under constant stirring. After that, of 60 mL of leaf extract were added as well, and the dark bluish color was observed which indicates the formation of cobalt oxide nanoparticles [25]. Various characterization techniques were employed as depicted in Table 1.

Green synthesis of cobalt oxide NPs by using *Sageretia thea*

Cobalt oxide nanoparticles were effectively biosynthesized by the complete green procedure utilizing fluid leaf concentrates of *Sageretia thea* (Figure 6) as chelating agent. Leaf extracts were acquired by adding deionized water (200 mL) to 30 g of powdered plant material, heating at of 80 °C for 1 h. The resultant solution of extract was filtered. To 100 mL of filtered solution 6.0 g of cobalt acetate was added while maintaining pH from 5.7 to 4.5. The solution was then allowed to cool to room temperature and centrifuged (10,000 rpm/10 min) and washed multiple times with deionized water. Acquired pellet was dried at 100 °C for 2 h, annealed at 500 °C for the obtaining crystalline unadulterated cobalt oxide nanoparticles [15]. The as prepared NPs were subjected for different characterization techniques mentioned in Table 1.

Green synthesis of cobalt oxide NPs by using *Listeria innocua*

Protein like cage of the 12-subunit ferritin-like protein from *Listeria innocua* (Figure 7) has been used as a size and shape constrained reaction environment for the synthesis of cobalt oxide Co_3O_4NPs. Reaction of Co(II) between H_2O_2 at pH 8.5 at elevated temperature (65 °C) results in the formation of cobalt oxide nanoparticles encapsulated inside the protein cage. Their properties and characterization techniques for the green synthesized cobalt oxide nanoparticles are shown in Table 1 [29].

Green synthesis of cobalt oxide NPs by using gelatin

Green synthesis of cobalt oxide nanoparticles had been carried out utilizing gelatin from bovine skin. The fundamental advantages of utilizing gelatin as a stabilizing agent is that it gives long term stability for nanoparticles by inhibiting particles agglomeration. In this typical synthesis 3 g cobalt nitrate was dissolved in deionized water (50 mL) and then stirred for 30 min. 5 g gelatin was dissolved in 100 mL of deionized water and mixed for 30 min at 60 °C to obtain gelatin solution. At that point the cobalt nitrate solution was added to the gelatin solution. The temperature of the water shower was fixed at 80 °C. The final prepared product was put in furnace at temperature 500 °C for 8 h to acquire cobalt oxide nanoparticles and then characterized with different technique [30] as enlisted in Table 1.

Green synthesis of cobalt oxide NPs by using apoferritin (protein)

The one-pot synthesis of the cobalt oxide nanoparticles in the apoferritin cavities was considered. A point by point study revealed that the optimum conditions are the mixing of 3 mM Co(II) ions with apoferritin (0.5 mg/mL) in HEPES (100 mM) at pH 8.3. The oxidation of Co(II) ions by the addition of hydrogen peroxide at 50 °C. Under these optimized conditions, cobalt oxide NPs were formed in practically all the apoferritin cavities and then the characterization of synthesized Co oxide NPs was carried out using various characterization techniques in (Table 1) [31].

Figure 5. Leaves *Ocimum sanctum* plant

Figure 6. Leaf of *Sageretia thea* (Osbeck) plant

Figure 7. Ribbon diagram of *L. innocua*

Applications of green synthesized cobalt oxide NPs

Photo-catalytic activity

Photo-catalytic activity (PCA) of synthesized NPs by using *Punica granatum* peel was evaluated by degrading remazol brilliant orange 3R dye and achieved 78.45% efficiency for degradation (dye conc. 150 mg/L) utilizing 0.5 g cobalt-oxide NPs for 50 min irradiation. In perspective of cost effective nature, the present investigation revealed that *Punica granatum* could be utilized for the synthesis of cobalt-oxide NPs for effective photo-catalytic applications [25]. The proposed mechanism to carry out the dye degradation is depicted in Figure 8.

Reducing agent

Cobalt oxide nanoparticles (Co_3O_4NPs) synthesized by using just methanol extract of *Conocarpus erectus* leaves acts as strong reducing agent on account of its higher values of 296 ± 9 μg/g total phenolic compounds [28].

Thermal decomposition and Dye sensitized solar cell

The green synthesized cobalt oxide NPs by using *Calotropis gigantean* and gelatin showed great catalytic effect on the thermal decomposition of ammonium per chlorate (AP) and burning rate of CSPs (composite solid pollutants). Kinetics of the slow and fast thermal decomposition has been explored by is conversional and ignition delay strategies, individually. In addition, the electro-catalytic performance of green synthesized cobalt oxide NPs in DSSC (dye sensitized solar cell) has likewise been investigated (Figure 9). The cyclic voltammeter measurement were used to investigate electro-catalytic action of cobalt oxide NPs toward the reduction of $I^{3-}$to I^{-}ions and promising results were observed [27–30].

Antimicrobial activities

The use of plant extract for synthesis of cobalt oxide NPs makes the procedure cost effective, non-hazardous and a clean strategy. Antibacterial activity of green cobalt oxide nanoparticles by using *Ocimum sanctum, Sageretia* thea was estimated by zone inhibition technique. The cobalt oxide nanoparticles possessed viable antibacterial activity against human pathogenic microbes, for example, *Pseudomonas aeruginosa* and *Escherichia coli*. The mechanistic antimicrobial actions of green synthesized NPs [15, 25] are exhibited in Figure 10.

Antioxidant activity

Bioinspired cobalt oxide NPs showed DPPH free radical scavenging potential, while moderate antioxidant capacity (Figure 11). Biogenic cobalt oxide was found as progressively cytotoxic to macrophages (IC50=58.55 mg/mL) than that of RBC's (IC50>200 mg/mL). The results demonstrated

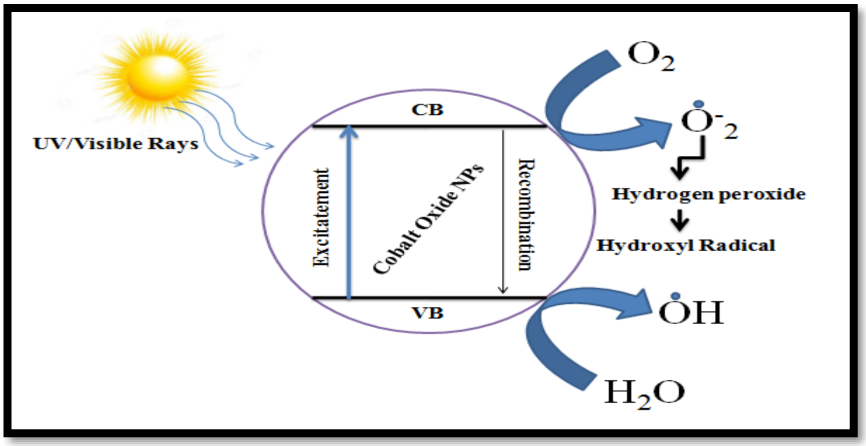


Figure 8. Suggested degradation pathway of dye by using Cobalt oxide NPs as photo catalyst

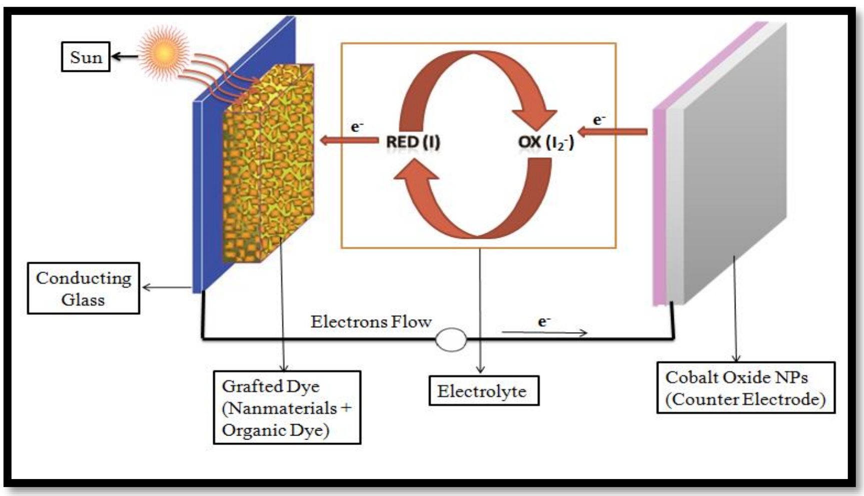


Figure 9. Schematic diagram of DSSC by using cobalt oxide NPs as a counter electrode

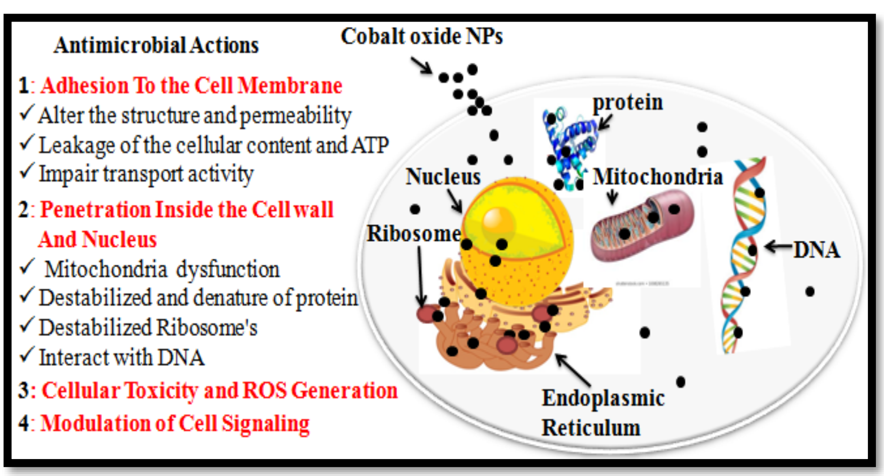


Figure 10. Mechanistic antimicrobial actions of cobalt oxide NPs

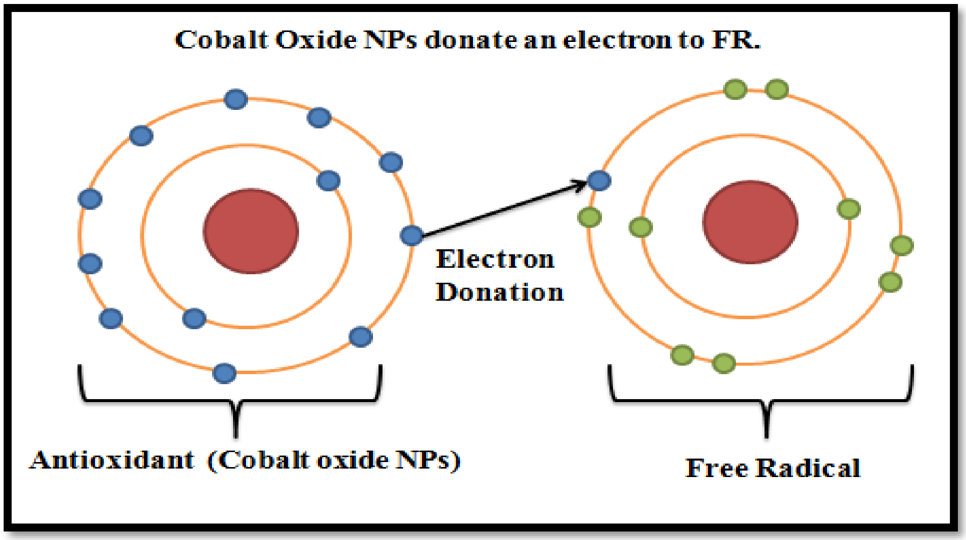


Figure 11. Proposed mechanism of the antioxidant activity of cobalt oxide NPs

green synthesis as an elective, viable and eco-friendly technique for the biosynthesis of cobalt oxide nanoparticles with various natural applications [15].

Conclusions

Cobalt oxide NPs synthesis is a safer and naturally well disposed than the physical and chemical techniques. Cobalt oxide NPs are a standout amongst the most significant and flexible materials, due to their diverse properties, functionalities, different benefits and applications. The green sources can act as a stabilizing and reducing agent for synthesis of nanoparticles with controlled size and shape. Comprehensively, the cobalt oxide NPs application to crops increases the development and yield in agriculture. As demand for food is increasing day by day, the yield of staple crops is low. Thus, it is important to commercialize metal oxide nanoparticles for economical agriculture. Then again, its biomedical applications in this area are expected to increase in different procedures including bioimaging, drug delivery, biosensors, and gene delivery. Cobalt oxide NPs are best substitutes of antibiotics and act as strong candidate against numerous drug resistant pathogens. It is expected that this review could additionally streamline the exploration on inventive methodological and clinical associations in this area. Meanwhile, solution for medical issues need to be proposed by referring to this complex through scientific and investigate reports.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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