Journal of Chemical Reviews, 2020, Volume 2, Issue 3, Pages 201-210

Short Review Article

Facile Plant Extract Mediated Eco-Benevolent Synthesis and Recent Applications of CaO-NPs: A State-of-the-art Review

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Receive Date: 27 March 2020, **Revise Date:** 05 May 2020, **Accept Date:** 10 May 2020

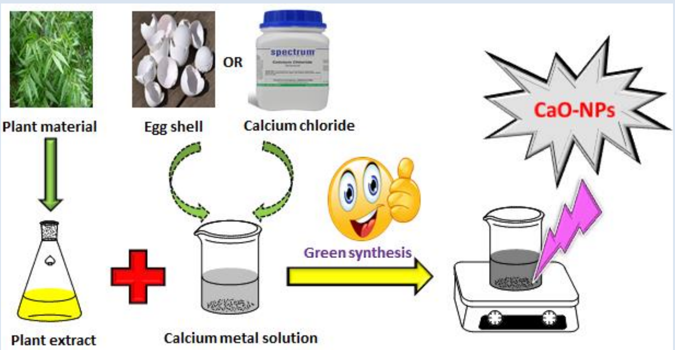
Abstract:

Ameliorating the sustainable and eco-accommodating routes for the procurable synthesis of nanoparticles (NPs) is a crucial aspect in the area of green nanotechnology. The known conventional routes for the production of NPs are complicated, noxious, expensive and not safer to human and environment. To overcome these threats, natural precursors such as biopolymers, plant, fungi, and bacteria have been used to fabricate the calcium oxide nanoparticles (CaO-NPs). The shape, size, and applications of the CaO-NPs are prominently affected by the reaction parameters under which they are synthesized. Moreover, the CaO-NPs synthesized by green approach have found potential applications in a wide spectrum of areas including, catalysis, bio-ceramics, additive in refractory, biodiesel production, adsorbent, antimicrobial agent, removal of Cr(VI) and trans esterification of oils. This research study discussed various plants and the different plant parts that have been used for the synthesis of CaO-NPs. The protocol, characterization techniques, mechanism, and eco-benign synthesis of the CaO-NPs along with various recent applications were also discussed.

DOI: 10.33945/SAMI/JCR.2020.3.7

Keywords: Green nanotechnology; Plant extracts; CaO-NPs; Mechanism; Applications

Graphical Abstract:



Biography:

Trupti Pagar was born in Surgana (Maharashtra), in **1997**. She completed her B.Sc. (**2019**) degree from Arts, Science and Commerce College, Surgana, Savitribai Phule Pune University, Maharashtra. At present she is pursuing her M. Sc. degree in organic chemistry from Department of Chemistry, G.M.D Arts, B.W Commerce and Science College, Sinnar (Savitribai Phule Pune University) Maharashtra, India. Her area of research interest is synthesis of nanomaterial and their applications in biological activity.

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Bishnu P. Marasini did MSc in Microbiology and PhD in Mulecular Medicine. He is working as Head, Department of Biotechnology, National College, Tribhuvan University, Kathmandu, Nepal. His area of research interest is drug discovery through the study of enzyme inhibition and kinetics, antibacterial activity, bioinformatics as well as medicinal plants. Moreover, he is an Editor-in-Chief of International Journal of Medicine and Biomedical Science.

1. Introduction

Nowadays, nanotechnology is a broad domain of science and technology which opens new horizons for renewable energy, medical therapy and human health. Nanoparticles (NPs) have unique and eclectic biological and physicochemical properties due to their size (1-100 nm). Subject to their size, morphology, stability and dispersity, NPs shows excellent properties compared with the bulk compound. Additionally, the higher surface area to volume ratio of NPs is significant, which plays a key role for more capability in catalytic and biological applications. In particular, NPs have an ample number of applications in the sector of agriculture, catalysis, medical, electronics, water purification, defense and energy. Moreover, nanomaterials contain several properties including tensile strength, durability, charge capacity, melting point, and so on. During the last few years "green nanotechnology" has grown excessively in industrial sectors whose qualitatively deploying the nanotechnology in their area are rapidly increasing [1-25].

CaO is an alkaline earth metal oxide with a high dielectric constant of 11.8 and a wide band gap of 7.1 eV [26]. CaO-NPs are non-toxic, low cost, readily available raw material for heterogeneous catalysis for diverse reaction procedures [27–29]. There are several other applications (Figure 1) of CaO-NPs such as catalyst [30], bio-ceramics [31], additive in refractory [32], biodiesel production [33], adsorbent [34], removal of Cr(VI) [35], photocatalyst [36], trans esterification of palm [37] and sunflower oil [38], CO_2 capturing [39], pollutant emission control [40] and also removal of other toxic metal ions [41]. In addition, CaO-NPs plays an immense role in the domain of antibacterial agent [42], antifungal agent [43], potential drug delivery agent [44], tissue dissolution [45], photo-thermal therapy, photodynamic therapy and synaptic delivery of chemotherapeutic agents [46] due to their reliable curative biomedical applications.

Hitherto, CaO-NPs can be easily synthesized using several known methods such as microwave-assisted [47], co-precipitation [48], sonication [49], ball-mill [50], thermal decomposition [51], solution combustion [52], flame-assisted [53], sol-gel [54], solvothermal [55], and ultra-sonication method [56]. Nevertheless, aforementioned methods have a high yield; however, they have some drawbacks such as the high-cost and energy requirement, complicated, noxious, tedious and time-consuming protocols. Henceforth, urgent need to mitigate the limitations and develop a safer, cheap and eco-accommodating process through "green nanotechnology". Therefore, parts of plant extract mediated NPs syntheses have become predominant due to the cheap, safe, rapid synthesis and free of from noxious chemicals [4-7]. Also, plant extract mediated NPs creates a better protocol for CaO-NPs synthesis as they provide natural reducing/stabilizing and capping agents [4-7].

The present review focused on the biogenic synthesis, characterization techniques, mechanism, and recent applications of the CaO-NPs using the plants material sources.

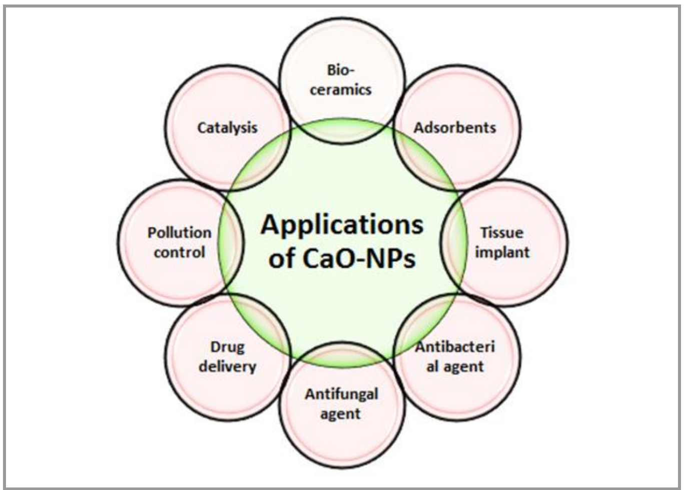


Figure 1. Various applications of CaO-NPs.

2. Scope of this Review

Despite sporadic reports, there is no any systematic overview covering the plant mediated synthesis of CaO-NPs and their uses. This review discusses the applications of CaO-NPs in the discipline of biomedical and catalysis. The synthetic routes of the CaO-NPs followed by a discussion on characterization of CaO-NPs by XRD, diverse spectroscopic as well as microscopic techniques were discussed. We believe that a respective survey of the established protocols for preparing CaO-NPs using plants extract and their notable applications would be encouraging to a broad community of researchers working in the sectors of nanotechnology, agriculture, biomedical and environmental remediation.

3. Plant Material Assisted Eco-benign Synthesis of CaO-NPs

Amongst the diverse biomaterials, plant extract from stems, roots, bulbs, leaves, petals or fruits, has been used as it is considered more reliable and an environmentally gracious route for synthesizing metal oxide NPs. Proteins, amino acids, vitamins, polysaccharides, enzymes and flavonoids present in the plant broth are biomolecules accountable to synthesize targeted NPs.

The benefits (Figure 2) of utilizing parts of plant extract mediated biosynthesis include the abundance of plant diversity, non-mephitic, cheap, straightforward, rapid rate of fabrication, eco-benevolent. Due to these benefits, a few investigations have been made to facilitate different plant species for their capability to synthesize CaO-NPs (Table 1).

A few parts of plant such as stem, leaves and fruits can be utilized for procurable synthesis of CaO-NPs. The aqua soluble phytochemical constituents are mainly accountable for production and stabilization of CaO-NPs. Thereafter, the fabricated CaO-NPs need to be characterized using numerous updated techniques.

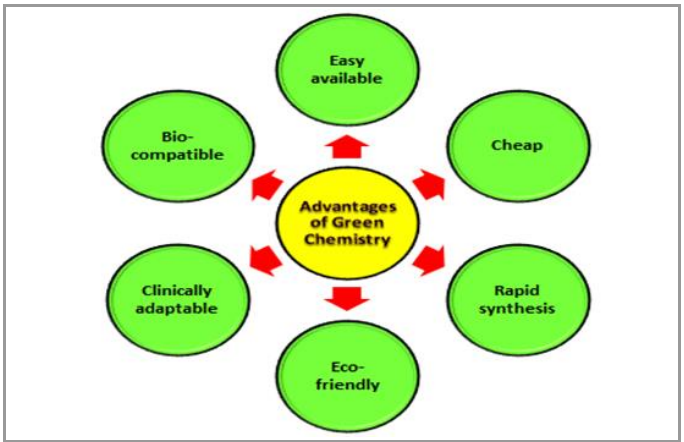


Figure 2. Importance of biosynthesis of metal oxide NPs.

4. Methodology for Plant Mediated Green Synthesis of CaO-NPs

In plant extract based route of CaO-NPs production using different plant parts such as stem, fruits and leaves are washed with distilled water, chopped into small pieces using domestic blender and boiled in double distilled water to obtained aqueous broth.

Table 1. Biosynthesis of CaO-NPs using different plant source with morphology and size.

Entry	Name of Plants	Part	Precursors	Shape	Size (nm)	Reference
1	*Azadirechta indica*	Leaves	$Ca(NO_3)_2$	Star shaped	50-200	[42]
2	*Broccoli*	Leaves	$CaCl_2$	Cube, Spherical, Hexagonal	32-45	[36]
3	*Cissus quadrangularis*	Stem	$CaCl_2$	Hexagonal	58	[57]
4	*Cissus quadrangularis*	Leaves	Egg shell	-	-	[58]
5	*Acalypha indica*	Leaves	Egg shell	-	-	[58]
6	*Solanum nigrum*	Leaves	Egg shell	-	-	[58]
7	*Phyllanthus niruri*	Leaves	Egg shell	-	-	[58]
8	*Hylocereus polyrhizus*	Fruits	$CaCl_2.2H_2O$	Rod	18.98	[43]
9	*Mentha piperata*	Leaves	$CaCl_2$	Disc	-	[59]
10	*Oscimum Sanctum*	Leaves	Egg shell	-	40-70	[60]
11	*Rhododendron arboreun*	Leaves	$Ca(NO_3)_2$	Broad needle like shape	-	[61]
12	*Papaya*	Leaves	$Ca(NO_3)_2.4H_2O$	Agglomerated	86-117	[62]
13	*Tea*	Leaves	$Ca(NO_3)_2.4H_2O$	Agglomerated	89-180	[62]

The plant broth may further be purified using the centrifugation and filtration methods. Variant ratio of calcium metal salt or egg shell powder and plant broth at various pH, time interval and temperature can be used for creation of CaO-NPs. The plant broth is easily blended with the variant concentrations of calcium metal salt or egg shell powder solution at room temperature and their conversion into CaO-NPs take place within minutes in efficient, one pot, sustainable and eco-accommodating approach. Due to the abundant phytochemicals that present in the plant broth and acts as natural/herbal reducing and/or stabilizing agents, there is no need to add external noxious stabilizing/capping additives. The brief protocol of biogenic synthesis of CaO-NPs by broccoli leaves extract is described by authors demonstrated in [36]. Finally, the NPs can be separated by centrifuging at high speed, wash thoroughly in appropriate solvent/water. Thereafter, CaO-NPs paced in a muffle furnace using ceramic crucible and calcined at high temperature. A fine powder of CaO-NPs is obtained and collected for further characterization and application purposes.

5. Characterization Techniques for CaO-NPs

After biogenic synthesis of the CaO-NPs, their characterization is also an imperative and important aspect. CaO-NPs are generally characterized by their size, stability, shape, surface area, dispersity, and elemental composition [1-2]. Collectively of all these properties of the CaO-NPs are very important in many applications. The general techniques for the characterization of the CaO-NPs are as follows: UV–visible spectrophotometry, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR).

The UV-visible spectroscopy is a normally used technique in which the light wavelength in the range of 200-800 nm is generally used. For characterizing the CaO-NPs, spectrophotometric absorption measurements in the size range of 400–450 nm and 260-410 nm, respectively, used. UV-visible spectrum of the CaO-NPs synthesized from Cissus quadrangularis evince absorption peak ranging from 400-450 nm and this is due to their surface plasmon resonance [57]. The crystal planes, structure and average particle size of the CaO-NPs were examined using the XRD pattern (Figure 3) [57]. Generally, the strong and narrow diffraction peaks indicated the well crystalline nature of fabricated CaO-NPs. The average size of the CaO-NPs was measured from the broadening of the diffraction peaks corresponding to the most prominent reflections according to the standard JCPDS (Joint Committee on Powder Diffraction Standards) cards. Scherrer's equation (Equation 1) [63] was used to analyze the crystallite size from the XRD diffraction pattern measured for the CaO-NPs.

$$d = K\lambda / \beta COS\theta \quad (1)$$

Where,

d– the average dimension of crystallites in nm,

λ – the wavelength of the X-ray radiation

K– the Scherrer constant (usually taken as 0.94)

β– the line width at half-maximum height (FWHM) in radians

θ– the Bragg angle.

The SEM images provided the information about the exact topography (Figure 3) and mean size of the biosynthesized CaO-NPs [43]. EDX spectroscopy is generally used for identifying the chemical composition (Figure 4) of the biosynthesized CaO-NPs [43]. TEM is the most common characterization technique to analyze the exact shape and size distribution of the CaO-NPs [42]. FTIR spectroscopy, used to evaluate chemical bonding between plant extract and metal atom on the surface of NPs, can be used to analyze the physical properties of NPs and their functions. In the biogenic synthesis of the CaO-NPs using the plant aqueous extracts, FTIR spectroscopic techniques were carried out to identify the possible biomolecules in extracts accountable for capping leading to capable stabilization of CaO-NPs [57]. Apart from aforementioned characterization techniques, researchers also have utilized different imperative techniques for characterization of other metal oxide NPs (Figure 5).

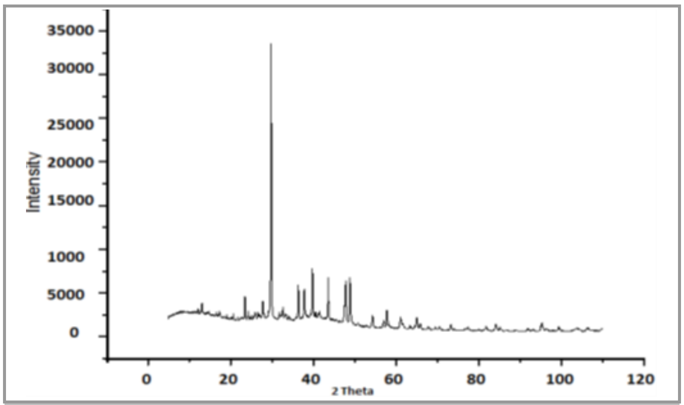


Figure 3. XRD pattern of biosynthesized CaO-NPs (Reproduced from ref. 61).

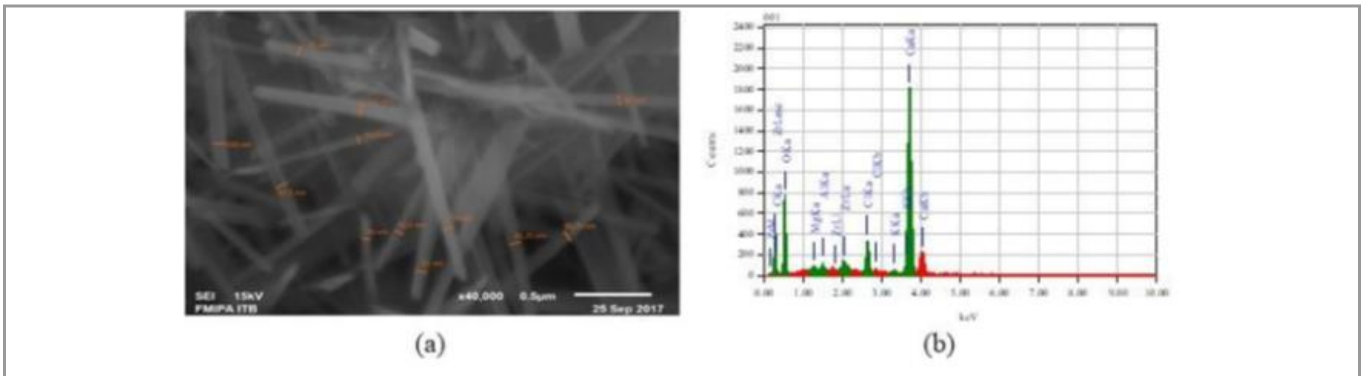


Figure 4. SEM imagage and EDX profile of biosynthesized CaO-NPs (Reproduced from ref. 43).

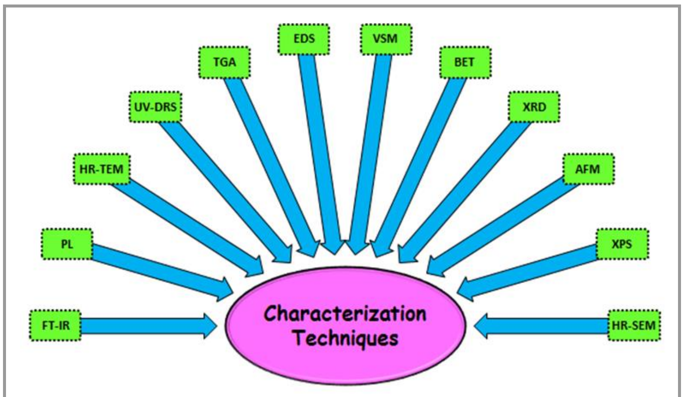
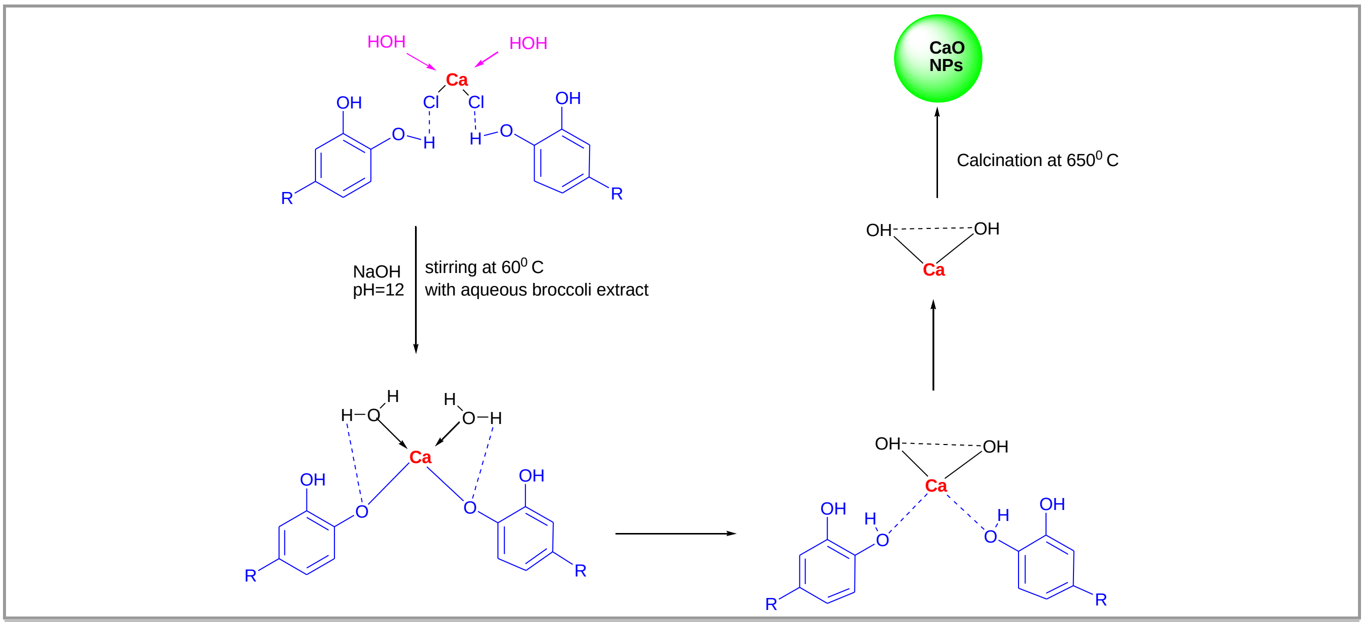


Figure 5. Characterization techniques for NPs.

6. Proposed Mechanism for CaO-NPs Formation using Plant Extract

Currently, several plant parts extract were utilized in biosynthesis synthesis of metal oxide NPs. The biogenic synthesis of NPs and its mechanism is dependent on the phytoconstituents such as tannins, flavonoids, coumarins, saponins, phenols, amino acids, steroids, carbohydrates, and anthocyanins. These phytochemicals play an immense role in their biosynthesis using plant extracts [4, 16].

Onwudiwe and co-workers synthesized [36] CaO-NPs by using the broccoli leaves extract. He demonstrated from his studies that the flavonoid constituent like quertcetin present in the leaves extract behaves as reducing/stabilizing agent and the aromatic hydroxyl groups of quertcetin adhered to calcium metal ions which lead to the formation of a stable complex of calcium and quertcetin. He beautifully described the mechanism of formation of CaO-NPs (Scheme 1).



Scheme 1. Possible mechanism of biosynthesis of CaO-NPs by using broccoli leaves extract [36].

7. Applications of Biogenically Synthesized CaO-NPs

Owing to their eclectic features and/or properties, CaO-NPs are especially used in several fields such as anticancer, photocatalytic, antioxidant and antimicrobial activities. In particular, biogenically synthesized CaO-NPs are much precedenced especially for medical-based applications like antimicrobial applications as well as photocatalytic applications (Table 2).

Prashantha *et al*. [42] synthesized the CaO-NPs using the Azadirechta indica leaves extract and reported for the antimicrobial activity against the bacillus bacteria [42]. Onwudiwe and co-workers synthesized the CaO-NPs using the Broccoli leaves extract and studied the photocatalytic activity of synthesized NPs. The synthesized CaO-NPs are cubic, spherical and hexagonal in shape with the size ranges from 32-45 nm. They evaluated the photocatalytic degradation of bromocrescol green dye up to 57.63 % under the photo irradiation with ultraviolet light using the CaO-NPs as a photocatalyst [36].

Ayyasami and co-workers reported the green synthesis of the CaO-NPs using Cissus quadrangularis stem extract and also described their antibacterial activity. The average size of the CaO-NPs is 58 nm. They revealed that, the CaO-NPs possess considerable antibacterial activity against the Staphylococcus aureus, Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa, Salmonella typhi, Shigella dysenteriae, and Vibrio cholera [57].

Pasupathi and co-workers reported the biogenic synthesis of the CaO-NPs using Cissus quadrangularis, Acalypha indica, Solanum nigrum and Phyllanthus niruri leaves extract and evaluate their antimicrobial activity against Bacillus subtilis, Staphylococcus aureus and Escherichia coli by using agar well diffusion method [58]. Ramli and co-workers synthesized the rod shaped CaO-NPs using Hylocereus polyrhizus fruit extract and studied their antifungal activity against Candida albicans using turbidimetry method under various concentrations [43].

Mirza and co-workers [59] found that, the antibacterial activity of disc shaped the CaO-NPs which are mediated from aqueous leaves extract of Mentha piperata. Gurav and co-workers [60] described the biosynthesis of CaO-NPs using leaf extract of Oscimum sanctum were in the size of 40-70 nm and reported their antimicrobial activity.

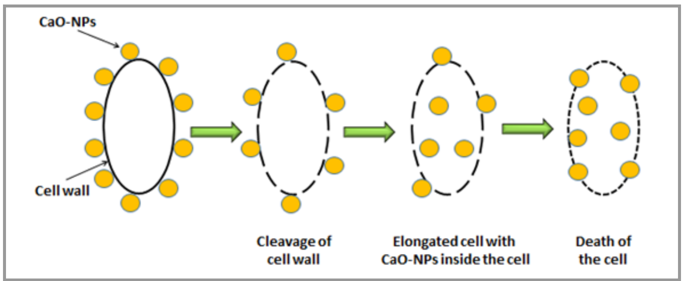


Figure 5. Plausible mechanism of antibacterial activity of CaO-NPs.

Joshi *et al*. [61] reported the biogenic synthesis of the CaO-NPs using the Rhododendron arboreum leaves extract and also studied the antimicrobial activity of CaO-NPs. They showed that CaO-NPs possess considerable antimicrobial activity against Escherichia coli, Streptococcus mutans and Proteus vulgaris. George and co-workers described green of CaO-NPs using leaves extract of Papaya and tea. They also examined the antibacterial and photocatalytic activities of synthesized CaO-NPs. The biosynthesized CaO-NPs were found size in the range of 86-148 nm. The photocatalytic study suggests the efficiency of these biosynthesized CaO-NPs in degrading Congo red dye

[62]. From the antibacterial studies, CaO-NPs will be useful in the food packaging industries because CaO-NPs react efficiently with the cell membrane and inactivate the bacteria as demonstrated in Figure 5.

Table 2. Recent applications of CaO-NPs synthesized using different plant extracts.

Entry	Name of Plants	Applications	References
1	*Azadirechta indica*	Antimicrobial activity	[42]
2	*Broccoli*	Photocatalytic activity	[36]
3	*Cissus quadrangularis*	Antibacterial activity	[57]
4	*Cissus quadrangularis*	Antibacterial activity	[58]
5	*Acalypha indica*	Antibacterial activity	[58]
6	*Solanum nigrum*	Antibacterial activity	[58]
7	*Phyllanthus niruri*	Antibacterial activity	[58]
8	*Hylocereus polyrhizus*	Antifungal activity	[43]
9	*Mentha piperata*	Antibacterial activity	[59]
10	*Oscimum Sanctum*	Antimicrobial activity	[60]
11	*Rhododendron arboreun*	Antimicrobial activity	[61]
12	*Papaya*	Antibacterial and photocatalytic activity	[62]
13	*Tea*	Antibacterial and photocatalytic activity	[62]

8. Future Prospects

Plant-extract assisted fabrication is considered as a proper green route for producing various types and size of CaO-NPs and recognized with fetching applications. Indeed, ample numbers of different kinds of plant species have been used to produce the CaO-NPs. Nevertheless, there is few research gaps that require to be filled in are as follows:

- The stoichiometric ratios between the plant extracts and precursors have not been clearly reported to understand the fabrication and morphological control.
- The lucid mechanism by which the plant extract used for the synthesis of CaO-NPs is not completely understood yet.
- The selection of plants or plant materials needs to be studied critically in order to obtain an understanding of the precise mechanisms involved.
- Only few plants have been reported for biogenic synthesis of CaO-NPs. Therefore, maximum numbers of medicinal plants are needed to use for the CaO-NPs synthesis.
- The green synthesized CaO-NPs should be deployed to various applications such as hydrogen production, biosensors, agriculture, and drug delivery.

9. Conclusion

This review discussed the current growing interest of several plant parts used in the facile biosynthesis of the CaO-NPs for various eclectic applications such as catalyst, bio-ceramics adsorbent, pollutant emission control, potential drug delivery agent and tissue dissolution. Different cost effective and environmentally gracious routes have been developed using the biological specimens and taking over from the known chemical and physical routes of NPs fabrication which are considered noxious and complicated. With the continual deployment of CaO-NPs for environmental reliability, there is a need to use newly updated characterization techniques and search for suitable plants to persist the goal without jeopardizing the existing plant diversity.

Acknowledgement

The authors are grateful to Dr. R. S. Oza and Dr. S. S. Pansambal for their constant valuable guidance.

Conflict of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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How to cite this manuscript: Trupti Pagar, Suresh Ghotekar, Shreyas Pansambal, Rajeshwari Oza, Bishnu Marasini, Facile Plant Extract Mediated Eco-Benevolent Synthesis and Recent Applications of CaO-NPs: A State-of-the-art Review, *Journal of Chemical Reviews*, 2020, 2(3), 201-210.