Green fabrication of zinc oxide nanospheres by *aspidopterys cordata* for effective antioxidant and antibacterial activity

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Abstract

The present work portray the *Aspidopterys Cordata (AC)* leaf extract-assisted fabrication of zinc oxide nanospheres (ZnO NSs) using an eco-friendly approach for antibacterial and antioxidant activity. As fabricated ZnO NSs were characterized by X-ray diffraction (XRD), fouriertransform infrared (FT-IR), energy dispersive X-ray diffraction (EDX), UV-Visible diffuse reflectance spectroscopy (UV-DRS), Raman, X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and transmission electron microscope (TEM) for authenticate the structure, shape, size, chemical state, and morphological facet. XRD pattern showed the strong and intense diffraction peaks indicating the formation of crystalline ZnO NSs with hexagonal phase. Further, EDX revealed the formation of highly pure ZnO with signals of Zn and O elements. UV–DRS reveals absorption band at 370 nm, assigned to the intrinsic band-gap absorption of ZnO, owing to the electron transitions from valence band to conduction band. TEM images inveterate the formations of ZnO NSs with mean particle size of 11.6 nm. The antibacterial activity of ZnO NSs was examined against gram-positive (*Staphylococcus aureus)* and gram-negative (*Proteus vulgaris, Escherichia coli,* and *Klebsiella pneumonia)* human pathogenic bacteria using ZnO NSs by *agar-well diffusion method*. Furthermore, ZnO NSs exhibited significant antioxidant activity against scavenging 1, 1-Diphenyl-2-picrylhydrazyl (DPPH) free radicals.

Keywords: ZnO nanospheres, aspidopterys cordata, electron spectroscopy, antioxidant activity, antibacterial assay.

Introduction

Nanotechnology is emerging as a fast-rising field with its applications in science and technology for the rationale of developed novel materials at the nanoscale level [**1**]. Nanomaterials (NMs) of diverse composition dimension and controlled morphology can be fabricated using green nanotechnology, which has huge applications in the area of medical science, biology and pharmacology [**2**]. NMs are main ingredient of a commercial rebellion that has resulted in an outburst of innovative products, due to their different physico-chemical properties, enabling their usage in a wide range of novel applications [**3-4**].

Majority of nanostructured synthesis has associated with the use of toxic organic solvents, hazardous chemicals as surfactants or reducing agents and severe reaction conditions such as high temperature, pressure, and long refluxing time. Owing to the ever-increasing environmental concerns, attempts have been routinely made to develop NMs fabrication using plant extracts, microorganism over chemical and physical methods. An eco-friendly NMs synthetic approach doesn't use any noxious solvents and chemicals in the synthesis protocols. In these facets, synthetic approach based on naturally occurring biomaterials offer a low cost substitute means for obtaining industrially required NMs.

The nanostructured zinc oxide nanoparticles (ZnO NPs) with features of high surface area to volume ratio, high ultraviolet absorption and long lifespan has been widely used in numerous applications such as catalyst, gas sensor, active filler for rubber and plastic, UV absorber in cosmetics and antiviral agent in coating applications [**5-12**]. Usually, ZnO NPs are synthesized by employing various methods [**13-17**]. However,

several reports are documented in the literature on plant assisted-synthesis of ZnO [**18-21**]. The plant-mediated ZnO synthesis is preferred because of its low-cost, eco-friendly and safe nature for human therapeutic uses.

Earlier, authors have reported the synthesis and antibacterial properties of histidine-capped ZnO NPs [**22**], α, γ-bismuth oxide (Bi_2O_3) for as photocatalyst for dye degradation [**23**] and copper aluminate ($CuAl_2O_4$) nanocomposites for electrochemical application [**24**]. In the present study reported a green approach for the fabrication of ZnO NSs using *Aspidopterys Cordata (AC)* leaf extract, which is an eco-friendly route due to their vital applications. As per authors' knowledge, it is the first report on the synthesis of ZnO NSs by *AC* leaf extract, and no attempts have been made earlier. The fabricated ZnO NSs have been consequently characterized by various electron spectroscopy techniques. Furthermore, the antibacterial assay against gram-positive and gram-negative human pathogenic microorganism. Moreover, the scavenger activity of synthesized ZnO NPs was examined in ethanol and methanol by 1, 1-Diphenyl-2-picrylhydrazyl (DPPH) free radicals.

Experimental

Materials and methods

Zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) was purchased from Himedia Laboratories Ltd. 1-Diphenyl-2-picrylhydrazyl (DPPH) was procured from Merck (India). *Aspidopterys Cordata (AC)* leaf was collected from Gorewada National Park, Nagpur (India). *Staphylococcus aureus* (*sa*), *Pseudomonas aeruginosa (pa), Escherichia coli (ec), and Klebsiella pneumonia (kp)* were purchased from National Centre for Cell Collection (NCCS), Pune (India). Standard antibiotics (Ampicillin, Streptomycin and Chloramphenicol) and Muller-Hinton agar was obtained from Hi-Media Pvt. Ltd. Bombay (India). All chemicals were used without further purification.

Characterization techniques

The crystal structure of ZnO was analyzed by X-ray diffraction (XRD) using Advance X-ray diffractometer (Bruker AXSD8) with CuKα radiation. The qualitative elemental analysis of ZnO was performed on Energy Dispersive X-ray diffractometer (EDX; JEOL (Model JED-200). Fourier-transformed infrared (FT-IR) spectra were recorded on a Bruker (IFS 66v) FT-IR, at a resolution (2 cm^{-1}) from 4000 to 400 cm^{-1} using KBr pellets technique. UV-diffused reflectance spectrum (UV-DRS) was recorded on (Cary-100UV) spectrophotometer and band gap $(\alpha h\upsilon)^2$ vs photon energy) is calculated using Kubelka-Munk (K-M) remission function. Raman spectra were performed using a JY Horiba (HR-800) spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed with a Sigma Probe, Thermo-VG, and monochromatic Al Kα X-ray source for exciting photoelectrons. The morphology of ZnO was examined by a JEOL JSM-6380 LA SEM and a JEOL TEM 2100F TEM with an acceleration voltage of 200 kV.

Preparation of AC leaf extract

The leaf of *AC* was washed several times with de-ionized water to remove the dust particles from surface. The *AC* leaf extract was prepared by placing 20 g of finely cut dried leaves in 500 mL round bottom flask along with 100 mL of de-ionized water. The mixture was then boiled at for 20 min. until the color of solution changes from watery to light yellow. The extracts was cooled at room temperature and filtered through simple filter through Whatman filter paper (Grade-42). The filtrate was again centrifuged for 15 min at 1500 rpm and was stored in a refrigerator.

Synthesis of ZnO NSs

ZnO NSs was synthesized by precipitation method at room temperature. An aqueous solution of $ZnSO_4.7H_2O$ (0.1 M) was added in round bottom flask (RBF). Then, 10 mL freshly prepared *AC* leaf extract was added dropwise to the above solution. The reaction mixture was kept under continuous stirring at room temperature for 3 h. A pale-milky precipitate of ZnO was obtained. The obtained product was repeatedly centrifuge with de-ionized water and ethanol. The obtained white precipitated was kept 80 ºC in vacuum oven for 24 h. The dried ZnO powder was calcined at 800 ºC for 2 h to get nanosized dimension. The fabrication scheme of ZnO NSs is given in supplementary information.

Antibacterial activity

The antibacterial activity of ZnO NSs was performed against four bacterial strains namely: *sa*, *pa*, *ec*, *and kp* by *agar-well diffusion method* [**22**]. About 20 mL of sterile molten Muller-Hinton agar was poured into sterile petri plates. Triplicates plates were swabbed with the overnight culture (10^8cell/mL) of pathogenic bacteria. Wells of size 6 mm have been made on Muller-Hinton agar plates using gel puncture. Finally, ZnO samples were dissolved in de-ionized water (50 μg/mL) were added from the stock into each well and incubated for 24h at 37±2 °C. After 24 hour the zone of inhibition was measured and expressed as millimeter in diameter.

The activity was studied with *AC*-assisted ZnO and at the same time the standard antibiotics (as positive control) were tested against the pathogens by using Streptomycin and Chloramphenicol as positive control. Then, the plates were incubated at 37 °C for 36 h. After the incubation period, the zone of inhibition of each well was measured and the values were recorded, average values were calculated for the eventual antibacterial activity.

Antioxidant activity

The antioxidant activity of ZnO NSs was carried out by free radical scavenging activity of DPPH assay at concentrations of 50–200 μg/mL, at an equal volume of

ethanol and methanol solution of DPPH. The mixture was allowed to react at room temperature in the dark for 30 min. Ascorbic acid was used as a standard control. The optical density of DPPH radical is monitored. After 30 min, the absorbance (A) was measured at 518 nm using visible spectrophotometer and converted into the percentage antioxidant activity using the equation:

$$\text{Activity (\%)} = [(A_0 - A_1)/A_0] \times 100$$

where, A_o was the absorbance of the control and A_1 was the absorbance in the presence of composite.

Results and discussion

Structural and morphological aspect

XRD pattern of *AC*-assisted ZnO NSs is presented in **Fig. 1a**. The distinct diffraction peaks at 2θ = 31.50°, 34.14°, 35.97°, 47.29°, 56.38°, 62.67°, 66.19°, 67.76°, 68.88°, 72.42° and 76.80° were allocate to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes respectively. The obtained diffraction peaks well matches with the hexagonal wurtzite structure (JCPDS File No-36-1451). The existence of (100), (002) and (101) planes in the XRD pattern confirmed the formation of high purity ZnO NSs using *AC* leaf extract. The sharp and strong diffraction peaks intensity of ZnO NSs indicated that the resulting product was highly crystalline in nature. Average crystallite size of ZnO NSs was estimated by *Debye–Scherer* formula and it was found in the range of 16-17 nm. The particle size of AC-assisted ZnO is presented in **Table 1** and compare with the previous reports [**25**].

Table 1. Morphology and particle size comparison of present study with documented literature.

Source	Part	Morphology	Size (nm)
Aloe vera	Leaf	Spherical & hexagonal	8-18
Azadirachta indica	Leaf	Spherical	40
Solanum nigrum	Leaf	Spherical	20-30
Moringa oleifera	Leaf	Spherical	6-20
Citrus aurantifolia	Fruits	Spherical	50-200
Mimosa pudica	Leaf	Wurtzite	3
Hibiscus rosa-sinensis	Leaf	Spherical	23-48
Carica papaya	Leaf	Hexagonal	10
Pongamia pinnata	Leaf	Spherical	100
Calotropis procera	Latex	Spherical & Granular	5-40
*Aspidopterys chordata**	Leaf	Hexagonal	16-17

*Present study

A Raman spectrum of *AC*-assisted ZnO NSs is depicted in **Fig. 1b**. The acoustic phonon overtone and optical overtone with A_1 (LO) symmetry located at 205 cm^{-1} and 335 cm^{-1} respectively. The E_2 (high) mode is at 446 cm^{-1}, which indicating the crystal quality of ZnO NSs. The bands at 589 cm^{-1} are the contributions of the E_1 (LO) mode of ZnO associated with oxygen (O) atoms. The additional peak at 689 cm^{-1}, contributes the $2E_1$ (*LO*) mode. The bands appeared at 1150 cm^{-1} is overtones and/or combination bands in ZnO [**26, 27**].

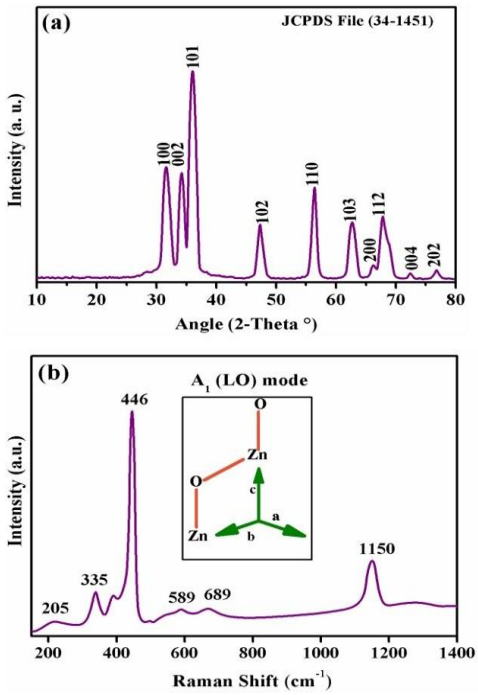

Fig. 1. (a) XRD and (b) Raman spectra of *AC*-assisted ZnO NSs.

Furthermore, the chemical composition of *AC*-assisted ZnO was analysed by EDX and spectra displayed in (**Fig. 2a)**. An existence of strong signals of zinc (Zn) and oxygen (O) and carbon (C) atom at very low intensity (**Fig. 2a**), which confirms the compositional purity. It is also well-supported by XRD and Raman study. The atomic and weight percentage of Zn, O and C is presented in **Fig. 2a**. Following, FT-IR spectra of *AC*-assisted ZnO NSs show the absorption band at 3739 cm^{-1}, 3429 cm^{-1}, 2931 cm^{-1}, 1637 cm^{-1}, 1452 cm^{-1}, 1056 cm^{-1}, 875 cm^{-1}, 457 cm^{-1} respectively. The peaks in the region between 600-400 cm^{-1} are allotted to Zn-O linkage [**28**]. The band at 457 cm^{-1} confirms stretching vibrations of ZnO NSs [**29**].

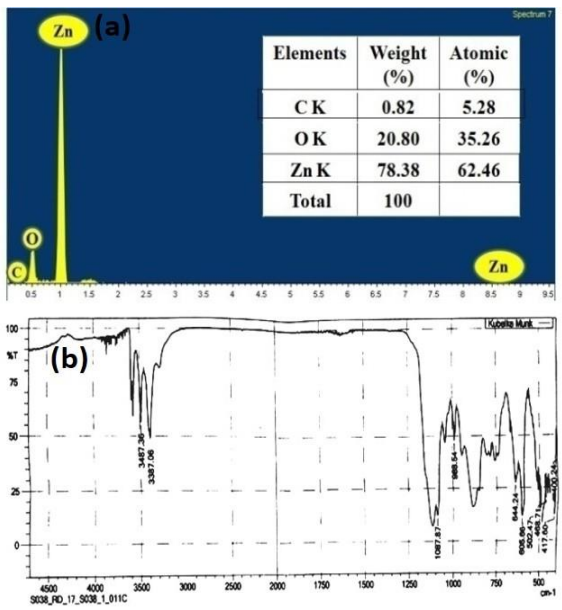

Fig. 2. (a) EDX and (b) FT-IR spectra of ZnO NSs.

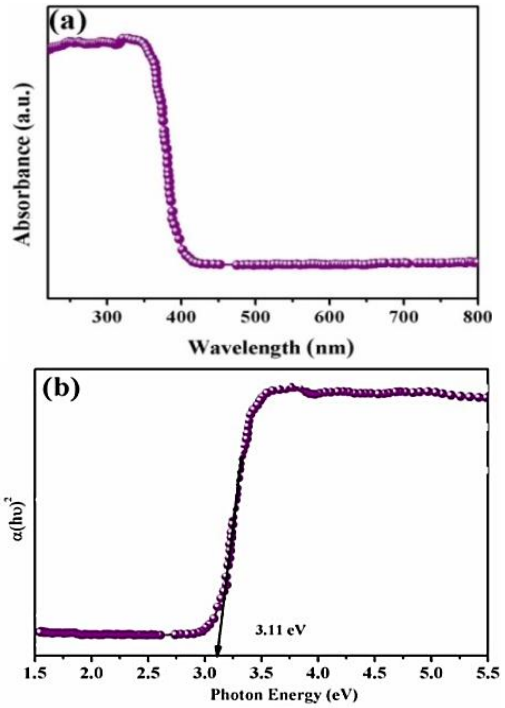

Fig. 3. (a) UV-DRS spectra and (b) K-M plot of ZnO NSs.

UV-DRS spectrum is presented in **Fig. 3a**, which reveals a typical absorption peak of ZnO NSs at wavelength (λ = 370 nm). This is assigned to the intrinsic band-gap absorption of ZnO NSs, owing to the electronic transitions from valence band to conduction band. Band gap energy was calculated by using K-M plot function (**Fig. 3b**). The band gap (3.11 eV) was obtained by the extrapolation of a linear regression on X-axis in the plot.

To further ascertain the chemical state characteristic of *AC*-assisted ZnO NSs. The sample was analysed by XPS. The XPS (**Fig. 4**) of *AC*-assisted ZnO NSs comprise of Zn, O and a trace amount of C was mainly accredited to the adventitious hydrocarbon from XPS itself [**30**]. The deconvolved XPS spectrum of O 1s region can be fit by the two peaks at 534.2 eV and 537.6 eV. The less intense low energy component at 534.2 eV was attributed to O^{2-} ions in ZnO NSs and an intense high energy component at 537.6 eV, was credited to hydroxyl species present on the surface of NPs [**30**]. The peaks located at 1024.1 eV and 1046.7 eV were associated to Zn $2P_{3/2}$ and $Zn2P_{1/2}$ respectively, which confirms the presence of Zn^{2+} as Zn^{2+} as well as oxygen vacancies [**31**].

Furthermore, morphological aspect like shape and size of as-synthesized ZnO NSs were analyzed by SEM and TEM (**Fig. 5**). AC-assisted ZnO material exhibited well distributed spherical shaped morphology with aggregation. However, aggregation is seen probably due to high surface energy of ZnO particles that usually occurs when synthesis is carried out in aqueous medium and also possibly due to densification resulting in narrow space between particles [**32, 33**]. Further, a TEM image of *AC*-assisted ZnO fully supported for nanospheres like structures with sizes in the range 20-30 nm. The interplanar *d*-spacing calculated from the image matches closely with (002) plane *d*-spacing of hexagonal ZnO, well-supported by XRD [**34**]. The morphology of earlier leaf assisted ZnO reports is presented in **Table 1** along with *AC*-assisted ZnO NSs [**25**].

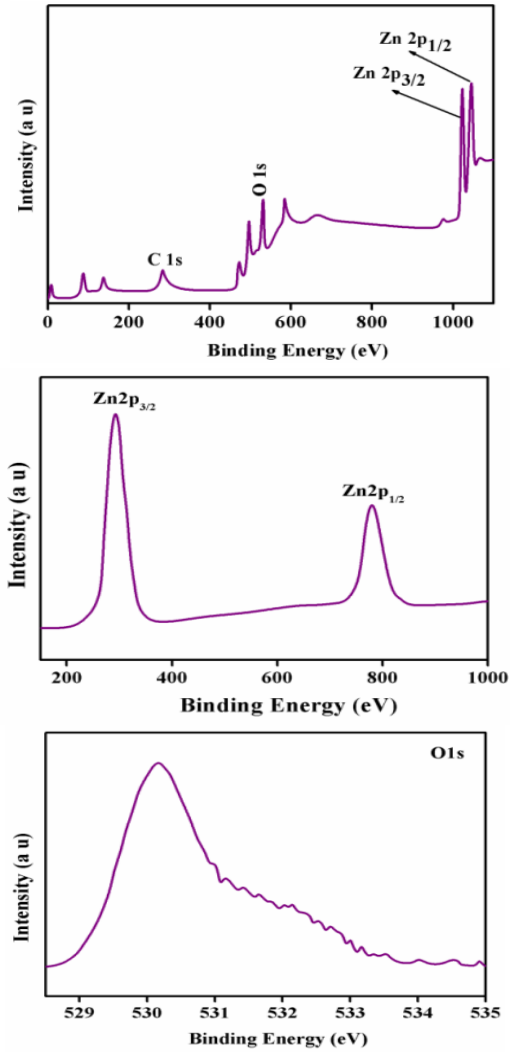

Fig. 4. XPS spectra of ZnO NSs

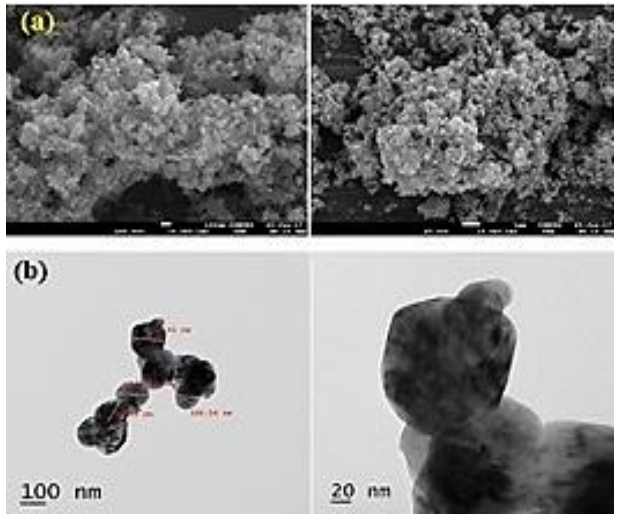

Fig. 5. (a) SEM and (b) TEM images of ZnO NSs.

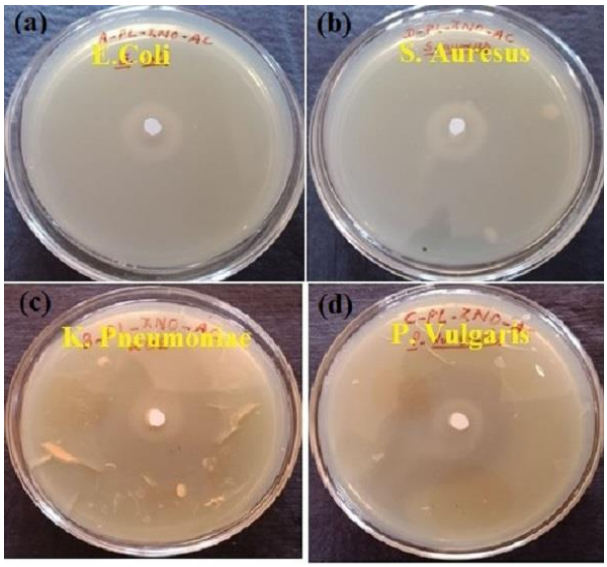

Fig. 6. Antibacterial activity against human pathogens (a) *ec* (b) *sa* (c) *kp* (d) *pv*.

Antibacterial assay

The antimicrobial activity of ZnO NSs was examined against gram-positive and gram-negative human pathogens on the basis of a zone of inhibition and compared with standard antibiotics. An antibacterial activity of ZnO NSs against human pathogens viz *ec*, *sa*, *kp* and *pv* are presented in **Fig. 6**. An enhanced antibacterial activity observed for gram-negative than gram-positive bacteria (**Fig. 7a**). This may be due to difference in cell wall structure and chemical composition of bacteria. The cell wall of gram-positive bacteria made up of thick peptidoglycan and teichoic acid on the outside of plasma membrane. While, cell wall of gram-negative contains thin peptidoglycan surround by lipopolysaccharides owned negative electricity leading to whole membrane to be negatively charged, thus ZnO ions able to bind the sulfhydryl group (SH) of bacterial enzyme, leads to cell death quickly. Among the standard antibiotics, chloramphenicol showed maximum zone of inhibition than ampicillin, and streptomycin. The opposite charges of bacteria and ZnO NSs are attributed to their adhesion and bioactivity due to an electrostatic force. The antimicrobial activity of ZnO NSs depends on the availability of the surface area for interaction.

The antioxidant activity of *AC*-leaf extract and AC-assisted ZnO NSs in methanol, ethanol, and standard ascorbic acid at a concentration (100 ug/mL) is given in **Fig. 7b**. The main intention of this study is to authenticate the antioxidant property of as-fabricated materials. Among the solvents, sample in ethanol shows more scavenging activity than in methanol. The higher antioxidant activity was seen for *AC*-leaf extract than *AC*-assisted ZnO NSs. This may be due to the presence phenols, hydroxyl groups, which are known to be good natural antioxidants [**35, 36**]. Antioxidant activity of ZnO NPs ascribed due to smaller particle grain size and may be a phenomenon of transfer of electron density from oxygen atom to odd electron located at nitrogen atom in DPPH, which results in decreasing transition intensity at 517 nm [**37**].

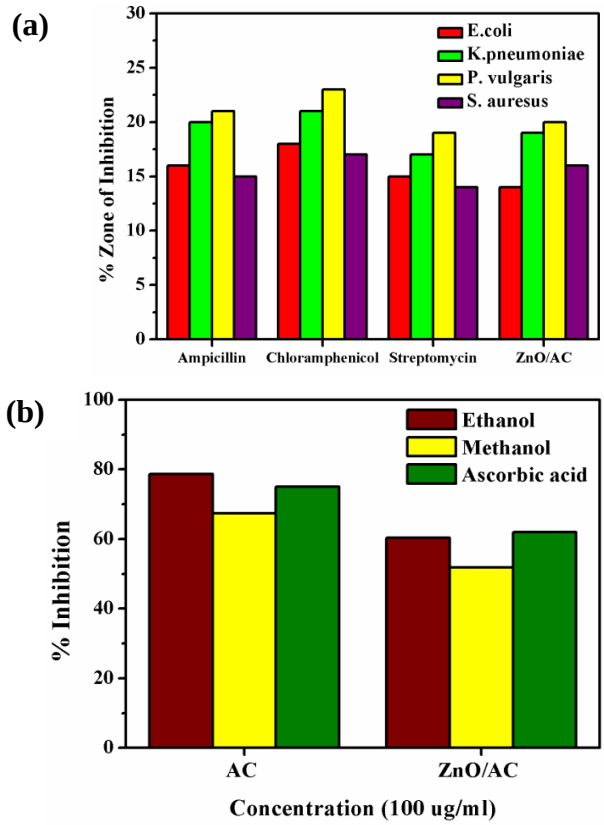

Fig. 7. (a) Antibacterial activity of ZnO NSs against standard antibiotics and (b) Antioxidant activity of *AC* leaf extract and *AC*-assisted ZnO by DPPH scavenging.

Conclusion

AC-assisted ZnO NSs was fabricated *via* eco-friendly approach. The XRD patterns of ZnO NSs were indexed to hexagonal-wurtzite structure. EDX gives the compositional purity of ZnO NSs, while XPS results confirmed the existence of Zn^{2+} ions. The band gap energy calculated from K-M plot and was found 3.11eV. The *AC*-assisted ZnO NSs exhibited good antimicrobial activity against *kp* and *sa*. Also, displayed enhanced antioxidant activity. In brief, the present study established a simple, eco-friendly technique for the synthesis of ZnO NSs with effective antibacterial and potential antioxidant agents. Hence, it may be targeted drug delivery application.

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Author's contributions

Conceived the plan: R.G. Chaudhary, S. Somkuwar, R.K. Mishra; Performed the experiments: P.B. Chouke, A.K. Potbhare; Data analysis: R.G. Chaudhary, G.S. Bhusari, D. PWD. Shaik; Wrote the paper: P.B. Chouke, G.S. Bhusari, R.K. Mishra (PBC, AKP, RGC are the initials of authors). Authors have no competing financial interests.

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