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NOVEL SYNTHESIS OF NANOPARTICLES CATALYZED BY IMIDAZOLIUM IONIC LIQUIDS, THEIR CHARACTERIZATION AND ANTIBACTERIAL ACTIVITIES

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Abstract:
Nanotechnology is an escalating field that has made its contribution to all spheres of human life. Conventional synthesis of nanoparticles are complicated and suffer from serious problems like high temperature, poor yield, longer reaction time, and use of toxic and highly sensitive compounds. The green synthesis of nanoparticles has paved for better methodologies and approaches in the medicinal field. The present paper explores the synthesis of stable CdS and ZnO nanoparticles using imidazolium based ionic liquids as green solvents. Size controlled CdS and ZnO nanostructures with distinct morphologies have been successfully synthesized and this process was found to be simple, fast and feasible. Higher level of crystallinity with high intense peak and no contamination of CdS and $Zn(OH)_2$ or other components were proved from the XRD analysis of synthesized CdS and ZnO nanoparticles. The as synthesized nanoparticles were screened for their anti-microbial activities and found that they possess significant antimicrobial activity and have the potential to act as a new antimicrobial agent and their activity may be enhanced in combination with other antimicrobial agents.

Keywords: *ZnO nanoparticles, CdS nanoparticles, ionic liquids, antimicrobial activity, scanning electron microscopy.*

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INTRODUCTION:

Room-temperature ionic liquids (RTILs) are attractive environmentally benign solvents for organic chemical reactions, separations, and electrochemical applications. The advantages of ILs in inorganic nanomaterials synthetic processes have been gradually realized and have received more and more attention due to their unique physical and chemical properties, such as large electrochemical window, high polarity but low interface tension, low interface energies, high thermal stability, and extended hydrogen bond systems [1–5]. Room-temperature ionic liquids(RTILs) have attracted intensive interests only in recent years as a replacement for classical molecular solvents in fundamental researches and application including separation, catalysis, organic synthesis, and so on [6]. Nanoparticles have been extensively investigated due to the attraction of their unique physical properties, chemical reactivity, and potential applications with high academic and industrial impacts [7].Semiconductor nanoparticles have optical and electrical properties that vary as a function of the particle size. The variability of these properties allows the nanoparticles to be tailored for specific applications, such as nano-electronics, photoluminescence, biological markers and photocatalysis. By adjusting the particle size, the opto-electrical properties can be tuned to have a suitable band gap and electric potential to drive the water-splitting reaction and other photoelectrochemical reactions. CdS (with Eg = 2.42 eV at room temperature) has promising applications in multiple technical fields including mechanical, optoelectronic, solar cells, photodegradation of water pollutants and hydrogen generation by visible light [8,9]. Therefore, preparation of CdS nanoparticles has been a very popular research area in recent years [10,11]. Generally these reactions are complicated and require high temperature, long reaction time and use of toxic and highly sensitive compounds. Zinc oxide has been famous for a wide range of applications in the functional devices, photo-catalysts, optical materials, cosmetics, nanostructure varistors, UV absorbers, gas sensors, and industrial additives. Ionic liquid assisted and size controlled ZnO nanostructure with distinct morphologies has been successfully synthesized by many researchers. This process was found to be simple, feasible. Fast and facile process without any use of external template or surfactants for the well defined morphology with less nanosize. Higher level of crystallinity with high intense peak and no contamination of $Zn(OH)_2$ or other components were proved from the XRD analysis of synthesized ZnO nanoparticles [12].

EXPERIMENTAL:

Materials

AR grade 1-Methylimidazole, Bromoethane, Sodium hydride, Acetonitrile, Ether, Trichloroethane, Ethyl acetate, Sodium tetrafluoroborate, Dichloroethane, Potassium hexafluorophosphate, Magnesium sulfate, Ammonium tetrafluoroborate, Ethanol, Cadmium acetate dihydrate, Thioacetamide (TAA), Zinc acetate dihydrate, sodium hydroxide, Deionized water were purchased from Merk, SD Fine chemicals Limited, Sigma Aldrich and used without further purification. The homogeneity of the products was checked on TLC plates coated with silica gel-G and visualized by exposure to iodine vapors.

Instruments

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Joel JNN ECX 400P spectrometer. The FT – IR spectra were obtained on a Varian 800 FT-IR as thin films or for solid samples. Nanoparticles were well characterized by powder X-ray diffraction (powder XRD) and Scanning Electron Microscope (SEM). The phase, purity and crystalline size of the CdS and ZnO nanoparticles were studied by XRD. In addition to identification of the crystalline phases, the XRD data were used to estimate the size of the constituent crystallites by Scherer's equation. The average particle size, D was determined by Eq. $D = K\lambda / (\beta.Cos\theta)$. Where λ is the wavelength of X-ray radiation (0.15406), K, the Scherer's constant (K= 0.9), θ, the characteristic X-ray radiation and β is full width at half maximum of the plane. The X-ray diffraction (XRD) patterns were recorded on a Philips Xpert X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm) employing a scan rate of 1º / min in the 2θ range from 20º to 80º. Surface morphology and the distribution of particles were characterized by a LEO 1430VP Scanning Electron Microscopy (SEM) using an accelerating voltage of 15 kV. The samples used for SEM and EDX observations were prepared by transferring the particles, which were first dispersed in ethanol, to a glass substrate attached to the SEM stage. After the evaporation of ethanol from the substrate, the particles on the stage were coated with a thin layer of gold and palladium.

Synthesis of Cadmium sulphide Nanoparticles

1-Ethyl-3-methylimidazolium tetrafluoroborate [EMIM] BF_4,1-Ethyl-3-methylimidazolium hexafluoro phosphate [EMIM] PF_6 were prepared as per the procedure given in the literature [13]. In a typical synthesis procedure, cadmium acetate dihydrate (5.06 g) was dissolved in 12.5 ml of distilled water, and 12.5 ml of the IL under stirring at room temperature. In addition, 1.50 g of

thioacetamide (TAA) was dissolved in 12.5 ml of distilled water, and 12.5 ml of the IL. Then, the TAA solution was slowly added into the solution of cadmium acetate under magnetic stirring. The solution was refluxed approximately at 95°C for 60 min [14]. The formed yellow colour suspension was centrifuged to get the precipitate which was then washed three times with double distilled water and ethanol, respectively to remove the unreacted reagents and dried in an oven at 50°C for 24 h.

Synthesis of Zinc oxide Nanoparticles

Zinc acetate dihydrate (5.5g, 0.025 mol) was dissolved in 50ml of distilled water, and then solid sodium hydroxide (16g) was slowly added into the solution under magnetic stirring at room temperature, and formed a transparent $[Zn(OH)_4]^{2-}$ solution. Then 2ml of L was added to 3ml of the above solution. The suspension was put into a domestic microwave oven in air, 30% of the output power of the microwave was used to irradiate the mixture for 2-9 min in a cycling mode (on: 10s, off: 5s) [15]. The white precipitate was separated by centrifugation, washed with deionized water and ethanol several times, and dried in vacuum oven at 40°C for 10h.

Antimicrobial Activity (Broth dilution assay)

Antimicrobial activity of the as synthesized CdS and ZnO nanoparticles was carried out using Broth dilution technique. In this method, a series of fifteen test tubes were filled with 0.5 ml sterilized nutrient broth. Sequentially, test tubes 2–14 received an additional 0.5 ml of the sample serially diluted to create a concentration sequence from 500 – 0.06 µg. The first test tube served as the control [16]. All the test tubes received 0.5 ml of inoculums. The test tubes were vortexed well and incubated for 24 h at 37°C. The resulting turbidity was observed, and after 24 h the minimum inhibition concentration (MIC) was determined where growth was no longer visible by assessment of turbidity by optical density readings at 600 nm.

RESULTS AND DISCUSSION:

FT- IR Spectra

FT-IR spectral frequencies of main peaks of pure [EMIM] BF_4, the CdS, ZnO nanoparticles in [EMIM] BF_4, pure [EMIM] PF_6 and the CdS, ZnO nanoparticles in [EMIM] PF_6 are listed in table1. Compared with the pure ionic liquids, several significant changes are observed in the FT-IR spectra of the CdS, ZnO nanoparticles in the same. The above changes of bands demonstrate that CdS, ZnO nanoparticles have an effect on the electron cloud density of imidazole ring. Based on the analysis of FT-IR spectra, it is concluded that there are strong interactions between RTILs and CdS, ZnO nanoparticles and the interactions focus on the imidazole ring of RTILs. Present findings are synonymous to the results previously reported [17].

Table 1: Frequencies of FT-IR absorption bands for the Pure ILs-1, 2 and the ILs in CdS and ZnO nanoparticles

[EMIM] BF_4(IL-1), cm^{-1}	IL-1 in CdS, cm^{-1}	IL-1 in ZnO, cm^{-1}	[EMIM]PF_6 (IL-2) cm^{-1}	IL-2 in CdS, cm^{-1}	IL-2 in ZnO, cm^{-1}	Assignment
3436,3160	3444, 3110	3857, 3743, 3568, 3438	3662,3432, 3172, 3127	3850, 3743	3849, 3743	C-H of imidazole ring stretching vibration
2879	2883	2948, 2888	2987	-	-	The stretching vibrations of the methyl and methylene groups
1634	1631	1648	1617	1648	1650	C=C stretching vibration
1574,1454	1573, 1448	1515, 1464	1575, 1520, 1463	1518, 1461	1543, 1433	C-H of imidazole ring inplane deformation vibration
1393,1165, 1071	1209,1075	1335,1130,1052	1395, 1344,1117, 1088	1391	_	Stretching vibration of anions
Below 1000	Below 1000	Below 1000	Below 1000	Below 1000	1170	m-substituted imidazole ring

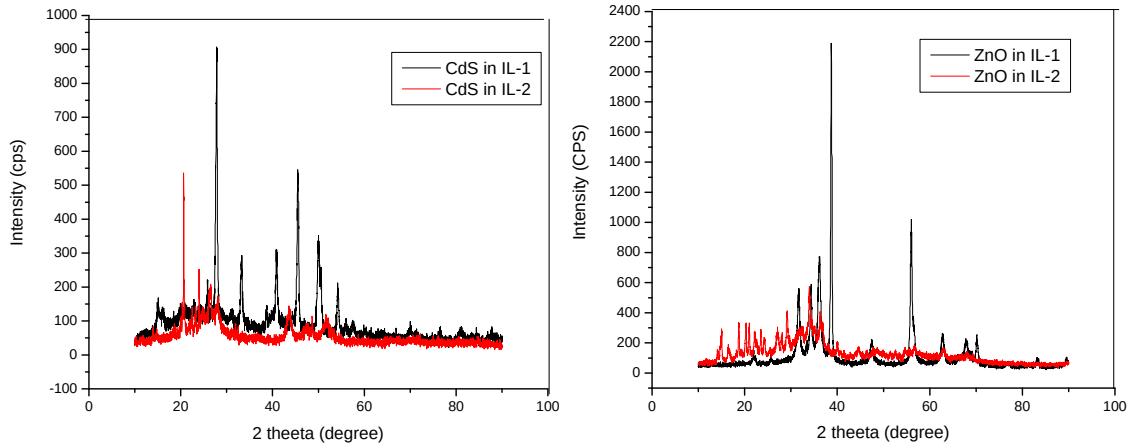


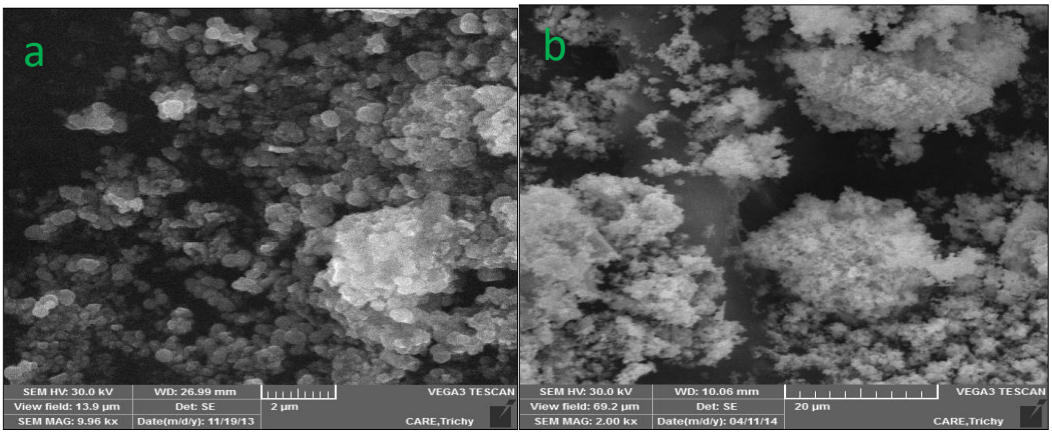
Fig. 1 Powder XRD Pattern of as - prepared CdS and ZnO nanoparticles in two different ILs (a) CdS in [EMIM] BF_4 and [EMIM] PF_6; (b) ZnO in [EMIM] BF_4 and [EMIM] PF_6

ZnO nanoparticles synthesized in [EMIM] BF_4, all the reflections were indexed as pure hexagonal ZnO phase which are in good agreement with the data reported for Zincite [JCPDS 89-0510]. XRD pattern indicates that the products are pure powders with no observable peaks relevant to such impurities as $Zn(OH)_2$. It is obvious from the results that suitable mole ratio of the IL / Zn^{2+} plays an important role in the morphology and purity of zinc oxide. Applying the Debye Scherrer formula [$D = 0.94\ \lambda / (\beta\ Cos\theta)$] equation, the average crystallite size was estimated to be 11.81nm.

Figure 1b is the powder X-ray diffraction patterns of the ZnO nano products prepared in IL [EMIM] PF_6. The diffraction patterns and interplane spacing's can be well matched to the standard diffraction pattern of wurziteZnO, demonstrating the formation of wurziteZnO nanocrystals. The mean particle size obtained for as prepared ZnO nanoparticle in IL-2 is 8.96 nm.

SEM analysis

Morphology of the as synthesized CdS nanoparticles in two different ILs was investigated by scanning electron microscope (SEM) recorded at different magnifications are shown in figure 2. Figure 2a and 2b show the SEM image of CdS nanoparticle assisted by [EMIM] BF_4 and [EMIM] PF_6respectively. It is inferred that the structure of the nanoparticles is nanospheres. It is quite apparent that aggregation of the nanoparticles has been controlled by ionic liquids.



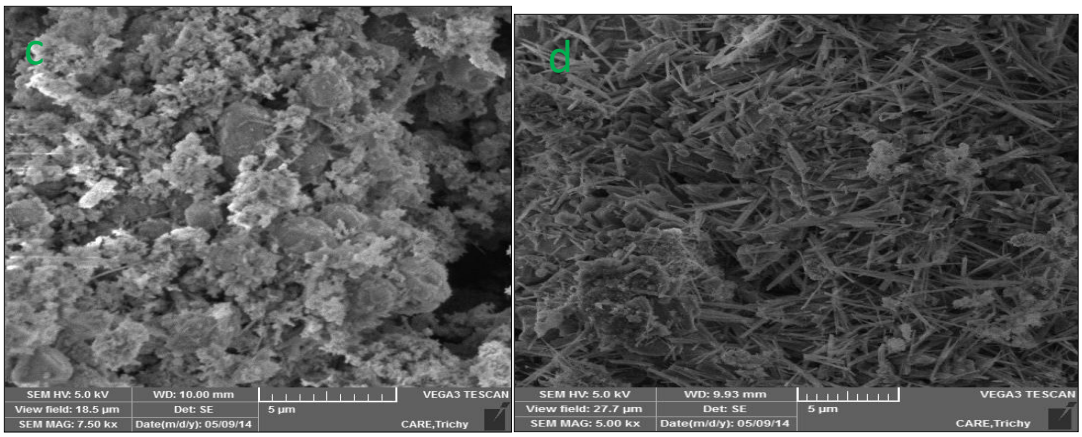
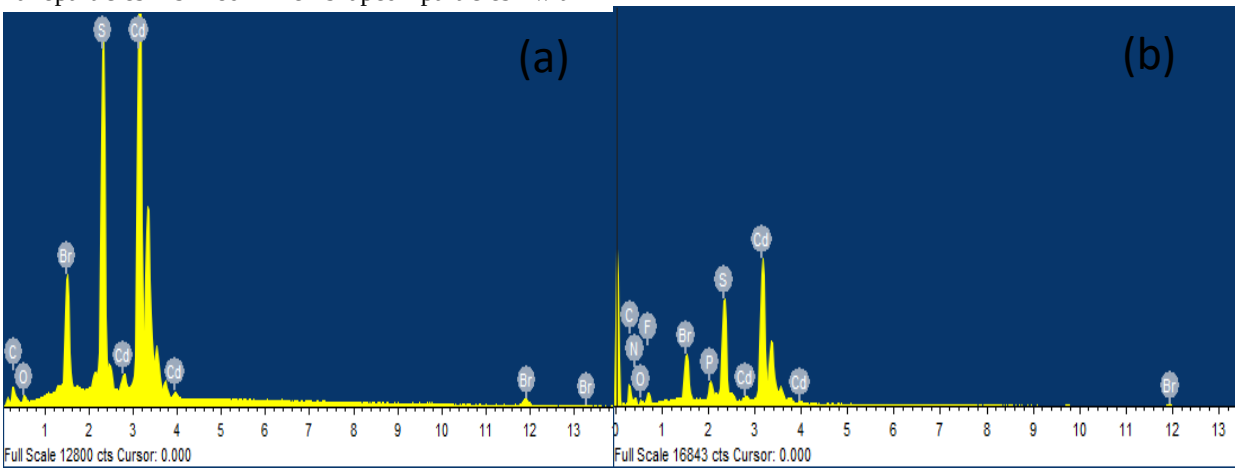


Fig .2 SEM image of as prepared CdS nanoparticles and ZnO nanoparticles in various ILs (a) CdS in [EMIM] BF_4 (b) CdS in [EMIM] PF_6 (c) ZnO in [EMIM] BF_4 (d) ZnO in [EMIM] PF_6

Figure 2c shows the SEM micrograph of the synthesized ZnO nanoparticle in [EMIM] BF_4. The SEM image illustrates that the polycrystalline flower-like zinc oxide has nanoparticles on the surface with average size of about 28 nm. In this investigation, the formation of ZnO flower-like is due to the initial formation of nuclei by the microwave radiations, and then the IL molecules may serve as a growth controller [19]. As it is known, ZnO is a polar crystal; O^{2-} is in hexagonal closest packing, and each Zn^{2+} lies within a tetrahedral group of four oxygen ions [20]. The IL is ionic compound, which completely ionizes in water. The cations of ionic liquid can be easily absorbed on the surface of the O^{2-} terminated by electrostatic force, and the hydrogen bond, formed between the hydrogen atom at position - 2 of the imidazole ring and the oxygen atoms of O–Zn, may act as an effective bridge to connect the O^{2-} terminated plane of the produced nuclei of metal oxide and cations of ionic liquids. Figure 2d shows the SEM image of ZnO nanoparticle in [EMIM] PF_6. It is evident from the figure that the structure of the nanoparticles is rod like shaped particles with different sizes. Morphologies of nanoparticles can also be explained by the assistance of IL. When the PF_6- anion is introduced, the synthesized ZnO particles size is constricted due to the high coordination, dimension of the particle decreases from flower to rod like. It is obvious from the results that anionic part of the IL played an important role in the morphology and size of zinc oxide.

EDX analysis

The purity and composition of the products (CdS and ZnO nanoparticles in [EMIM] BF_4 and [EMIM] PF_6) were studied by energy dispersive X-ray spectroscopy (EDX). The results are displayed in figure 3a-d. The other peaks in the figure corresponded to gold, palladium, and silicate which were due to sputter coating of the glass substrate on the EDX stage, and these were not considered in the elemental analysis of CdS nanoparticles and ZnO nanoparticles. It is clear that the CdS nanoparticles and ZnO nanoparticles prepared were sufficiently pure.



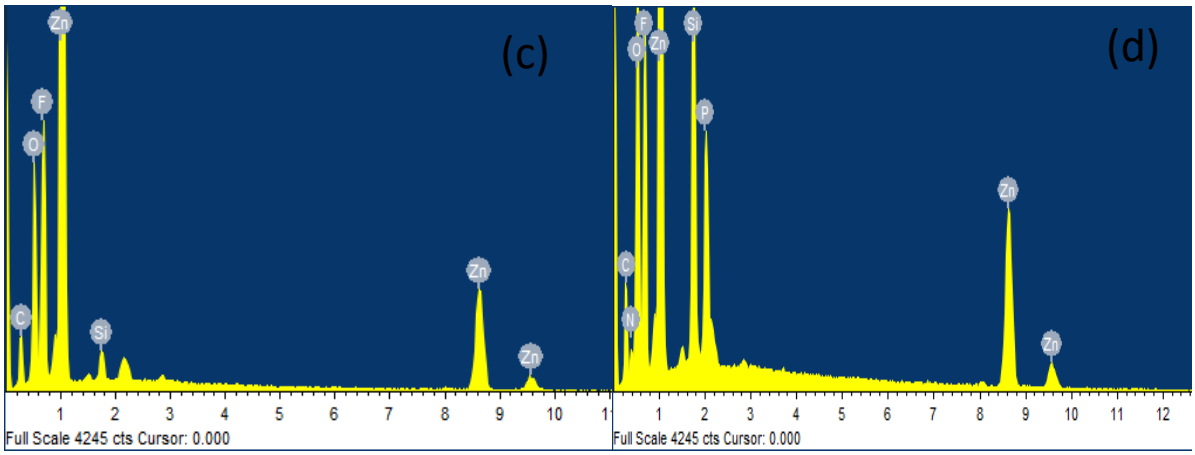


Fig. 3 EDX pattern of as prepared CdS nanoparticles and ZnO nanoparticles in various ILs (a) CdS in [EMIM] BF_4 (b) CdS in [EMIM] PF_6 (c) ZnO in [EMIM] BF_4 (d) ZnO in [EMIM] PF_6

Antimicrobial Activities

A preliminary investigation on the antibacterial activities CdS and ZnO nanoparticles stabilized by ILs were evaluated against bacterial strains through measurements of minimal inhibitory concentrations (MIC) expressed in µg / mL. The values after one day of exposure are shown in Figure 4. Six microorganisms were chosen as test strains: For three gram negative bacteria (*Escherichia coli MTCC739*, *Pseudomonas aeruginosa MTCC424* and *AeromonashydrophilaMTCC 1739*) and three gram positive bacteria (*Staphylococcus aureus MTCC3381*, *Micrococcus luteusMTCC2470* and *Bacillus cereus MTCC430*).

In view of the results, it appeared that ZnO nanoparticles are the most effective products against (all the three gram positive and three gram negative bacteria) the tested bacterial stains compared with CdS nanoparticles. These ZnO nanoparticles synthesized by us showed significant antimicrobial activity when tested against pathogenic bacterial strains. It was found to be less active against *Pseudomonas aeruginosa*. It may be pointed out here that ZnO nanoparticles were found to be bacteriostatic in vitro against both Gram positive and Gram negative bacteria.

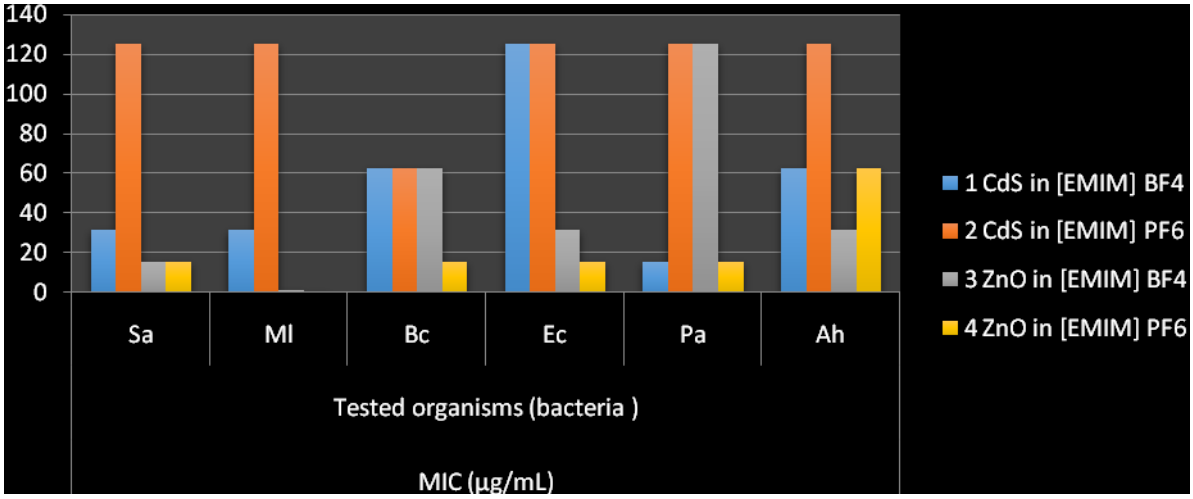


Fig 4: Comparison of MIC values of synthesized nanoparticles

Compared with the antimicrobial activities of CdS nanoparticles, CdS in [EMIM] BF_4 is the most effective products against the tested bacterial stains compared with CdS in [EMIM] PF_6 nanoparticle. There are several mechanisms that have been proposed to explain the antibacterial activity of nanoparticles like deactivation of cellular enzymes and DNA by coordinating with the electron donating groups, pits formation in bacterial cell walls, leading to increased permeability and eventually the cell death etc. It is believed that the high affinity of Ag towards sulphur and phosphorus is the key element of the antimicrobial effect [21, 22]. ZnO inactivation of bacteria involves the direct interaction between ZnO nanoparticles and cell surfaces, which affects the permeability of membranes where nanoparticles enter and induce stress in bacterial cells, subsequently resulting in the inhibition of cell growth and eventually in cell death. Besides that, the more positive charge on the cell surface of gram positive bacteria interacts stronger with the ZnO nanoparticles than the gram negative bacteria according to the previous reports [12].

The antibacterial activity also depends on the surface area and concentration of nanoparticles, while the crystalline structure and particle shape have little effect. Although the exact mechanism of action of CdS nanoparticles is not known but it may be any of the above mentioned mechanisms, through which CdS nanoparticles shows antimicrobial action. These results reveal that CdS and ZnO nanoparticles possess significant antimicrobial activity and have the potential to act as a new antimicrobial agent and their activity may be enhanced in combination with other antimicrobial agents.

CONCLUSION:

Stable CdS and ZnO nanoparticles were synthesized using [EMIM] BF_4 and [EMIM] PF_6. The FT-IR spectra of the chosen ILs after their utilization as green media for the synthesis of CdS and ZnO nanoparticles prove that there was an effective interaction between these ILs and the as prepared nanoparticles. Results clearly demonstrate that CdS, ZnO nanoparticles have remarkable effect on the electron cloud density of imidazole ring of the ILs.CdS and ZnO nanostructures with distinct morphologies have been successfully synthesized using ionic liquids as solvents for controlling the size and shape of nanomaterials. Crystalline nature (XRD), size and shapes (SEM) of nanoparticles (CdS and ZnO) are modulated by structural modifications in the counter ion associated with the cationic part of the ionic liquids. The as synthesized nanoparticles were screened for their ant-microbial activities against three gram (+) and three gram (-) bacteria. The minimum inhibitory concentration (MIC) revealed that the activity of these compounds is also modulated by structural modifications in the counter ion associated with the cationic part of the ionic liquids.

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