Review Paper:

A review on green synthesis of coinage metal sulphide nanoparticles and their applications

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Abstract

Being a sustainable, eco-friendly and cost effective technique, the green methodology for the synthesis of various nanomaterials including metal sulphide nanoparticles has drawn great attention in recent years. In the conventional chemical and physical methods, high rate of hazardous chemicals and extreme reaction conditions are used. To overcome these problems nowadays, green synthesis pathway has been adopted. Among other metal sulphide nanoparticles, coinage metal sulphides such as silver sulphide and copper sulphide nanoparticles are very much important due to their remarkable optical, electrical, catalytic and biological properties.

This review briefly summarizes the recently reported biogenic synthesis of silver and copper sulphide nanoparticles using various bio-based sources and also focuses on some of the important properties of the said green synthesized nanoparticles like optical properties, photocatalytic abilities and different biomedical activities.

Keywords: Green synthesis, Ag_2S nanoparticles, Copper sulphide nanoparticles, Optical property, Photocatalytic property, Biomedical activity.

Introduction

Coinage metal chalcogenide nanoparticles (NPs) have been studied intensively over the past two decades due to their various applications in several fields. Among these compounds, silver sulphide (Ag_2S) and copper sulphide attract considerable attention[9,11-13,16,23,25-27,39,41,43,46,49,51,53,55]. Ag_2S, a direct, narrow band gap semiconductor (~1.1 eV) has good chemical stability[12,23]. It can be used in photoconductors[46], near-infrared photo-detectors[13], light-emitting diodes (LED)[41,43] and in biological applications[11,53]. On the other side, copper sulphides have several stable and metastable phases of varying stoichiometry such as Cu_2S, CuS, $Cu_{1.8}S$, Cu_7S_4, $Cu_{31}S_{16}$, $Cu_{39}S_{28}$ etc.

These variable stoichiometric phases result in some unique properties which make them suitable for applications in various fields. These can be used in solar cells, solar radiation absorbers[26,49], photocatalysts[27,39], chemical sensors[51], supercapacitors[55], high-capacity cathode materials in lithium secondary batteries[9,25] and thermoelectric cooling materials[16].

Silver and copper sulfide NPs have been synthesized by a variety of techniques[4,8,10,14,17-19,28,29,32,45,47]; however, the "green" route for synthesis of nanomaterials using bio-based materials has been of great interest mainly due to several advantages such as: (i) it is eco-friendly technique (ii) biomaterials are easily available in nature, so it is a cost-effective process, (iii) organic moiety present in the biomaterials serves as reducing as well as capping agent in the reaction[5,37,56].

The present study briefly summarizes the biosynthesis of silver and copper sulphide nanoparticles (NPs) using various bio-based sources and also highlighted various properties of these green synthesized NPs like optical properties, photocatalytic abilities and different biomedical activities.

Biosynthesis of Ag_2S NPs: Due to the increasing popularity of bio-based green methods, different works have been done to prepare Ag_2S NPs and copper sulphide NPs (Cu_2S, CuS) using different sources like plant parts, protein and amino acid molecules, bacteria, fungus, and others. These are summarized in table 1.

Using plant materials: Sibiya et al[38] prepared Ag_2S NPs at room temperature by using various bio-based sources such as green tea, leaves of velvet bushwillow *(Combretum molle)* and black wattle plant as capping agents. They varied the pH of the reaction mixtures from 3 to 11 by adding NH_4OH solution and noticed the effect of pH on the size, shape and properties of the NPs. FTIR study revealed that the nature of the peak of phenolic O-H group (present in the biomolecules) was longer and broader in basic medium rather than acidic medium and this was explained by considering that in acid medium, there might be more prominent H-bonding between the functional groups of the capping agent which stabilized the structures leading to the ineffective utilization of the capping agent in the reduction process.[24]

It was observed from TEM study that all the capping agents used in the procedure produced more agglomerated NPs in acid medium and the formation of smaller size NPs were found under basic conditions rather than acidic medium.

The result was explained as under basic conditions that there might be the enhancement of the distribution of the hydroxyl groups of the capping agents leading to effective capping, thereby formation of smaller sized nanoparticle and the observation led them to choose basic condition as optimum for the synthesis of Ag_2S NPs.

Table 1
Various sources and morphological studies of Ag_2S and Copper Sulphide NPs

Biological entities	Types of NPs Synthesized	Precursor(s)	Morphology and Size
Green tea[38]	Ag_2S	$AgNO_3$, NH_2CSNH_2	Spherical
Combretum molle leaves[38]	Ag_2S	$AgNO_3$, NH_2CSNH_2	Spherical
Black wattle plant leaves[38]	Ag_2S	$AgNO_3$, NH_2CSNH_2	Spherical
Rosemary leaves[2]	Ag_2S	$AgNO_3$, Na_2S	Spherical, 14 nm
Pistacia atlantica leaves[50]	Ag_2S	$AgNO_3$, NaSH	Spherical, 12–15 nm
Pistacia atlantica seed[50]	Ag_2S	$AgNO_3$, NaSH	Spherical, 8–12 nm
Rice husk ash-MCM-41[22]	Ag_2S	$AgNO_3$, Na_2S	Spherical, 14 nm
Cochlospermum gossypium gum[3]	Ag_2S	$AgNO_3$, Na_2S	Spherical, 25 nm
Pepsin (enzyme)[33]	Ag_2S	$AgNO_3$, CH_3CSNH_2	worm-like nanochains, 25 nm
BSA (protein)[31]	Ag_2S	$AgNO_3$, Na_2S	Spherical, 6.3 nm
BSA (protein)[48]	Ag_2S	$AgNO_3$, CH_3CSNH_2	spherical, 65 nm rod shaped, dia and length: 40 nm; 200 nm wire shaped: dia 50 nm and length >1000 nm
BSA (protein)[42]	Ag_2S	$AgNO_3$, CH_3CSNH_2	spherical, 65 nm rod shaped, dia and length: 40 nm; 200 nm wire shaped: dia 50 nm and length > 1000 nm
L-cysteine (amino acid)[44]	Ag_2S	$AgNO_3$, L-cysteine	Spherical, 20 nm
Cysteine- and Glutathione (amino acid)[6]	Ag_2S	$AgNO_3$, Na_2S	Spherical, 9 nm
Ribonuclease-A (enzyme)[7]	Ag_2S	$AgNO_3$, Na_2S	Irregular, 5.6 nm
Chitosan (amino polysaccharide)[20]	Ag_2S	$AgNO_3$, NH_2CSNH_2	Fork shaped, 8 nm
Shewanella oneidensis MR-1 Bacterial cell[40]	Ag_2S	$AgNO_3$, $Na_2S_2O_3$	Spherical, 9 ± 3.5 nm
Shewanella oneidensis MR-1 Bacterial cell[54]	CuS	$CuCl_2$, $Na_2S_2O_3$	Spherical,~5 nm
Fungus *Fusarium oxysporum*[21]	Cu_2S	$CuSO_4$	Round shaped, 20 nm
Fungus *Fusarium oxysporum*[36]	CuS	Waste water (acid mine drainage)	10–40 nm

XRD patterns revealed the formation of acanthite phase of Ag_2S. Awwad et al[2] described a green route for the synthesis of Ag_2S NPs in presence of rosemary leaves extract at ambient temperature (27°C). Formation of crystalline Ag_2S NPs was confirmed by XRD analysis. TEM image revealed the formation of spherical shaped Ag_2S NPs with an effective diameter of 14 nm.

Zahedifar et al[50] employed cellulose/Fe_3O_4 nanocomposite template for the preparation of Ag_2S NPs. Although the seed (sample A) and leaf (sample B) extracts of *Pistacia atlantica* plants were used as reducing and stabilizing agent, use of leaf extract was found more fruitful for the synthesis of Ag_2S NPs on the nanocomposite surface. After the preparation of Fe_3O_4/Cell-SH nanocomposite by *in situ* reaction of iron (II) and iron (III) chlorides with an aqueous solution of Cell-SH, the adsorption of Ag^+ ions onto the surface of Fe_3O_4/Cell-SH took place on addition of $AgNO_3$ solution through electrostatic attraction with negatively charged SH groups. Finally, the addition of the seed and leaf extract of the *P. Atlantica* plant helped to grow Ag_2S NPs on the surface of the cellulose/Fe_3O_4.

The EDS analysis of Ag_2S NPs confirmed the 2:1 elemental composition. Morphological pattern and size of the particles were observed from SEM and TEM images. The size distribution of spherical shaped Ag_2S NPs in sample B was found 12–15 nm while the size in sample A was 8–12 nm.

Jafari et al[22] used rice husk ash (RHA) as raw material and successfully prepared mesoporous MCM-41 nanoparticles loaded with Ag_2S NPs by a green chemical method. They produced amorphous rice husk ash under controlled burning conditions and it was utilized as a cheap source of SiO_2 for the preparation of MCM-41 NPs at room temperature.

Finally, through an ion exchange process, Ag_2S NPs were synthesized in matrix nanoparticles (MCM-41). XRD pattern of Ag_2S/RHA-MCM-41 nanocomposites revealed the similarity with the monoclinic form of Ag_2S crystals. FTIR study also confirmed the formation of Ag_2S NPs. Formation of spherical shaped Ag_2S NPs with an effective diameter of 14 nm was observed. It was also seen that no free Ag_2S NPs were present; all the NPs were stucked into the surface of RHA-MCM-41 nanoparticles.

Using gum of *Cochlospermum gossypium* (kondagogu) Ayodhya et al[3] synthesized Ag_2S NPs by a hydrothermal method maintaining 15 lbs pressure and 120°C temperature for 1h. FTIR result showed an indication of coordinated interactions between Ag_2S and *Cochlospermum gossypium (CG)*. Formation of monoclinic phase of Ag_2S with acanthite structure was confirmed by XRD analysis. TEM image revealed the formation of spherical particles with an average diameter of 25 nm. Measurement of zeta potential over the incubation period of 30 days under static condition showed the stability of the Ag_2S NPs.

Using proteins, amino acids, enzymes and amino polysaccharide: Qin et al[33] reported the synthesis of Ag_2S NPs conjugated with pepsin. XRD pattern revealed that the crystallinity of Ag_2S NPs was not good due to the coating of pepsin molecules. The SAED pattern and XRD analysis revealed that monoclinic ∞-Ag_2S phase was formed. EDX analysis showed the formation of slightly Ag rich product. They also investigated the influence of pepsin molecules on the formation of products through FTIR study. The experimental result revealed the coordination interaction between Ag_2S and functional groups of pepsin. Thermo-analysis (TGA) also confirmed the existence of pepsin in the products. Parallel aligned worm-like nanochain morphology having average diameters of about 15–25 nm and length of hundreds of nanometres could be seen from TEM images.

It was found that with the increase of concentration of pepsin from 5 to 8 g l^{-1}, the nanochains diameter increased accordingly and the morphological pattern of the products started to change from worm-like structure to cross-linked networks with fractal geometry. At the pepsin concentration of 2 g l^{-1}, only disordered aggregation of nanorods and nanoparticles was observed. It was thought that in high pepsin concentration, the amounts of free Ag ions in solution become reduced. Therefore, with the fewer seed crystals, larger nanocrystals were formed. It was also found that the slow release of S^{2-} ions from thioacetamide controlled the nucleation and growth rate of Ag_2S nanocrystals and this was the basis for the morphological changes of Ag_2S nanocrystals.

Meziani et al[31] synthesized bovine serum albumin protein-conjugated Ag_2S NPs by applying rapid expansion of a supercritical solution into a liquid solvent (RESOLV) method and found that the obtained yellowish product remained suspended into the aqueous solution without precipitating for minimum time period of 4 months. Well dispersed particles with average diameter of 6.3 nm could be found from TEM images. AFM study revealed a uniform distribution of core-shell like arrangement of BSA capped Ag_2S NP. In BSA protein, 60 amino moieties in lysine residues, 26 arginine moieties in guanidino side chains and 17 disulfide bonds with one free thiol in cysteine residues are present[1,15,35]. It was reported that thiolate and alkylamine linkage with the colloidal surfaces of Ag_2S NPs might be responsible for the direct BSA-Ag_2S nanoparticle conjugation. They found that with the change of reaction pH, protein-nanoparticle conjugates could be assembled or deassembled in a reversible fashion driven by the isomeric conversion of the protein corresponding to different pH values[1,15,35].

Using BSA, a simple and controllable synthesis of protein–conjugated Ag_2S NPs, nanorods (NRs) and nanowires (NWs) was done by Yang et al.[48] NPs were prepared by one step process where into the BSA solution the aqueous solution of $AgNO_3$ and thioacetamide was added and the mixture was stirred for 72 h under nitrogen environment. For the preparation of NRs, the same reagents were used, but the reaction procedure was completed by two step process. For the 1st case, no chelation time was given between Ag^+ and BSA, but for the latter, the first step was the generation of the Ag(I)–BSA complex by mixing of the $AgNO_3$ and BSA solutions for 6 h. Then addition of thioacetamide was done at ambient condition. Ag_2S NWs were synthesized by using the AAO template-based method[30].

TEM images showed the formation of different morphological patterns like NPs, NRs and NWs. It was observed that the smaller sized (10 nm) particles were present inside the relatively larger NPs (65 nm) and the average diameter of nanorods and nanowires was found 40 and 50 nm with the length of 200 nm and 1000 nm respectively. A strong hint about the coordination between Ag_2S surfaces and –OH and –NH groups in BSA was revealed from FTIR spectra. The protein content in NPs, NRs and NWs was evaluated from Thermogravimetry-differential thermal analysis (TG/DTA) and found to be 6%, 11% and 12%, respectively. SAED patterns revealed the formation of crystalline NRs and polycrystalline nature of NPs, NWs.

Wang et al[42] also utilized BSA to prepare protein-conjugated Ag_2S nano-crystals. Different morphological patterns of Ag_2S nanocrystals like nano-particles, nano-rods, and nanowires were observed from TEM analysis. Indication of a strong coordination between silver sulphide surfaces and –OH and –NH groups in bovine serum albumin was revealed from FTIR spectra of protein conjugated Ag_2S nanocrystals. Using L-cysteine, Xiang et al[44] synthesized Ag_2S NPs by hydrothermal method. In this process, L-cysteine, a chelating reagent, acts as the sulphur source. They performed the reaction at different concentrations and temperatures. The formation of monoclinic form of ∞-Ag_2S was confirmed by XRD patterns and X-ray photoelectron spectra (XPS).

TEM images revealed the formation of cross-linked spherical particles with average diameter of ~20 nm. It was also seen from TEM images that with the increase of cysteine concentration with respect to Ag^+ ions, diameter of Ag_2S NPs was also increased. The chelation between cysteine and Ag^+ could decrease the Ag_2S crystal growth leading to controlled growth of Ag_2S nanocrystals. Brelle et

al[6] developed a synthetic method for the preparation of cysteine or glutathione capped Ag_2S NPs. They chose cysteine and glutathione as these thiol-containing biomolecules have ability to dictate the formation of metal-sulfide nanoparticles.

HRTEM images showed the formation of aggregated spherical particles with average diameter of 9 nm and the electron diffraction pattern revealed the crystallinity of the particles. Particles aggregation might occur due to the interaction of the capping biomolecules. Due to outstanding thermal stability of Ribonuclease-A (RNase A), Chen et al[7] successfully synthesized water-soluble Ag_2S quantum dots (QDs) in aqueous phase by using RNase A. RNase A-Ag_2S QDs clusters with irregular morphologies found from TEM images.

HRTEM image also revealed that the average size of nanocrystals was about 5.6 nm. EDS spectrum confirmed that the elemental composition of Ag_2S and XRD patterns revealed the formation of crystalline monoclinic α-Ag_2S.

Hashmi et al[20] performed the synthesis by using chitosan (aminopolysaccharide) and maintaining a basic reaction environment (pH=10). To get Ag_2S Nps they refluxed the obtained Ag_2S precursor solution in an open-air condition at 80 °C and 100 °C for 30 minutes. SAED, XRD and Raman study confirmed the formation of crystalline monoclinic α-Ag_2S. FTIR study indicated that through an electrostatic interaction, the Ag^+ ion was attached with the C=O bond of the chitosan molecules. Chelation of Ag^+ ions by $–NH_2$ groups present in chitosan molecule was also found to be highly effective at their reaction condition (pH=10) and this was confirmed from FTIR and Raman Spectroscopic analysis.

SEM images revealed the changes of morphological patterns with the change of reflux temperature. It was seen that at 60°C, non uniform tape like Ag_2S assemblies were formed and with the increase of reaction temperature (100˚C), length of the tail portion of the fork shaped particle increased significantly. Well separated spherical particle was seen from TEM image and the average particle size was found to be 8 nm.

Using Bacterial cell: Suresh et al[40] performed a study for the preparation of extracellular Ag_2S NPs by the metal-reducing bacterium *Shewanella oneidensis* MR-1 under ambient temperatures and pressures and found these nanoparticles were very stable in aqueous suspension for several months. The presence of a protein/peptide bound surface of the biogenic Ag_2S NPs was confirmed by FTIR spectroscopy.

XRD analysis revealed the formation of monoclinic form of ∞-Ag_2S. The homogeneous distribution of nearly monodispersed spherical particles having average diameter of 9 ± 3.5 nm was found. One of the reasons for the long term stability of nano particles was that these particles were negatively charged and had a zeta potential of -1 mV.

Bio synthesis of Copper Sulphide (Cu_2S, CuS) Nps

Using Bacterial cell: Zhou et al[54] employed dissimilatory metal reducing bacterium *Shewanella oneidensis* MR-1 to prepare CuS NPs and found that highly stable, water soluble, uniformly distributed ~5 nm sized particles were formed.

Using Fungus: Hosseini et al[21] synthesized spherical Cu_2S NPs by treating cells or secretion of *Fusarium oxysporum* fungus with copper sulphate solution under mild reaction condition. It was observed that the size of the nanoparticles was about 20 nm and the agglomeration of particles was prevented by the presence of proteins on the surface of the NPs. For the preparation of copper sulphide NPs, Schaffie et al[36] added a fungus, *Fusarium oxysporum* to the acid mine drainage (copper concentration of about 60 mg/l) of Sarcheshmeh Copper Complex (Kerman, Iran).

The presence of a large amount of oxygen, carbon and nitrogen along with copper and sulphur was revealed from EDS analysis which indicated that the cell bodies and proteins were accompanied with the produced nanoparticles. TEM image revealed the formation of particles having size range of 10–40 nm. They found that the properties of the biosynthesized NPs were the same as the NPs prepared from the pure $CuSO_4$ solution.

Optical Properties

Ag_2S: Ag_2S is a direct, narrow band gap (0.9–1.05 eV) semiconductor and has a large absorption coefficient which makes it an effective material for photovoltaic application. Sibiya et al[38] studied the effect of pH and capping agent on the optical properties of the Ag_2S NPs by using UV-Vis spectroscopy. It was found that in acidic medium, Ag_2S NPs synthesized using all the selected capping agents showed broader absorption maxima at higher wavelength than in basic medium.

This indicated that at lower pH, either particles size increases or agglomerated particles were present. It was also observed from the UV-Vis spectra that the chitosan capped Ag_2S NPs were smaller in size compared to the other capping agents.

The surface plasmon resonance of biosynthesized Ag_2S NPs (rosemary mediated) was noticed around 355 nm by Awwad et al.[2] Jafari et al[22] observed the UV-Vis absorption spectra of Ag_2S/RHA-MCM-41 nanocomposites and found the presence of absorption tail between 400 and 550 nm. Ayodhya et al[3] also noticed a wide visible absorption from 400 to 800 nm for synthesized Ag_2S NPs. They also compared the UV-vis spectra of Ag_2S NPs and CG-Ag_2S NPs and found that the effect of adsorption of *Cochlospermum gossypium* (CG) capped Ag_2S NPs was better than that of uncapped Ag_2S NPs.

Qin et al[33] observed the absorption edges of Ag_2S NPs at 500–550 nm which are blue-shifted relative to the bulk value of Ag_2S. Xiang et al[44] observed a broad absorption peak centred at about 515 nm, broadened spectrum occurred due to aggregation of nanoparticles. The large blue-shift indicated the quantum confinement effect. Brelle et al[6] studied the ground-state electronic absorption spectra of different Ag_2S NPs samples capped with cysteine and GSH and noticed that all the samples showed virtually identical spectra possessing absorption peak toward shorter wavelengths. The large blue shift of absorption indicated that the NPs were in the quantum confinement regime.

Ultrafast dynamics of photoinduced electrons of Ag_2S NPs was also studied by Brelle et al[6] using femtosecond transient absorption/bleach spectroscopy. They experimented on four samples prepared with the initial sulfide: Ag (I) ratios of 0.5:1.0 (using cyseine and GSH, named as sample-1 and sample-2 respectively) and 1:1 (using cyseine and GSH, named as sample-3 and sample-4 respectively) and found that for most of the cases, the early time transient profiles showed a pulse-width limited rise followed by a fast decay (750 fs) and a slower rise (4.5 ps). A slow decay for sample-1, sample-3 and sample-4, or a slow rise in the case of Sample-2, with time constant of >1 ns could be seen on longer time scales.

It was observed that the signal contained both transient absorption and transient bleach. UV-Vis absorption spectrum of the Ag_2S NPs was recorded by Hashmi et al.[20] The study revealed the existence of both direct and indirect band gap of nearly 5.3 eV which indicated that the nanospheres behaved within the quantum confined regime.

CuS: Zhou et al[54] observed that the bacterium mediated CuS nanoparticles exhibited a broad absorbance maxima at 1100 nm in the NIR region which might be originated from d-d intra-band transitions of Cu^{2+}. They estimated the photothermal conversion efficiency of the prepared CuS NPs and found a high value of 27.2%. Schaffie et al[36] found the absorbance maxima at 300 nm which indicated the formation of the copper sulfide nanoparticles.

Photoluminescence (PL) and Fluorescence study of Ag_2S NPs: Ayodhya et al[3] recorded the PL emission spectrum of Ag_2S NPs which showed an emission peak centred at ~470 nm under excitation of 350 nm. The effect of Ag_2S NPs on the fluorescence emission spectrum of bovine serum albumin (BSA) was also investigated and it was found that the quenching of fluorescence emission occurs due to the interaction between BSA and Ag_2S. Experimental results revealed that the quenching effect of BSA on the fluorescence emission of Ag_2S NPs was concentration dependent.

Qin et al[33] observed that the fluorescence intensity of pepsin reduced drastically which indicated that the interaction of Ag_2S with pepsin molecule quenched its intrinsic fluorescence. A red shift from 348 to 360 nm (with respect to pepsin from 300–400 nm) was also found for the maximum emission wavelength which showed the formation of nanoparticles had influenced on environment of pepsin.

Yang et al[48] recorded the PL spectra of pure BSA and all the protein conjugated nanocrystals with an excitation wavelength of 280 nm and noticed that the emission peaks appeared for BSA at 346 nm whereas at 425 nm it appeared for all the nanocrystals. This shifting (79 nm) to higher wave length was explained as might be due to the presence of conjugate bonds between the Ag_2S nanocrystals and BSA. The PL spectrum of the synthesized Ag_2S NPs recorded by Xiang et al[44] showed an emission peak 637 nm and a weaker shoulder band at 590 nm when the sample was excited at 490 nm.

It was thought that the PL spectrum might occur from the recombination of electrons and holes in the surface state of Ag_2S. Chen et al[7] found that Ag_2S NPs exhibited NIR luminescence with an emission peak around 980 nm. It was also noticed that the intensity of RNase A-Ag_2S quantum dots decreased after the period of incubation.

Photocatalytic activity of Ag_2S NPs: Photocatalytic degradation of organic contaminants by using semiconductor nanomaterials is an important step towards environmental protection. Zahedifar et al[50] monitored the catalytic activity of the methylene blue (MB), methyl orange (MO) and methyl red (MR) dyes through UV–Vis spectrophotometer and it was found that the values of rate constants for MB, MO, and MR dye degradation by Ag_2S nanocomposites (synthesized from leaf extract) were 0.3802 min^{-1}, 0.4554 min^{-1} and 0.3177 min^{-1} respectively and by the other synthesized nanocomposite (synthesized from seed extract) 0.1908 min^{-1}, 0.1450 min^{-1} and 0.1233 min^{-1} respectively.

Excellent recyclability of the as prepared catalyst was found by them and it was reported that the catalyst could be reused for 8 runs in the catalytic cycle. They presented a schematic representation for describing the possible mechanism of dye degradation and suggested that the structure of cellulose played an important role in dye degradation process. The structure of cellulose helped to distribute Ag_2S NPs properly on the catalyst surface which can adsorbed the dye molecules effectively. First, on the catalyst surface the adsorption of these dyes and BH^{4-} ions took place, then from BH^{4-} donor centre electron transfer occurred to the acceptor dye through Ag_2S NPs. This electron transfer process encourages hydrogenation of dye.

The activity of *Cochlospermum gossypium* (CG) incorporated Ag_2S NPs for the degradation of fluorescein (FL) dye was studied by Ayodhya et al[3] in presence of solar light. They evaluated the influence of other parameters such as H_2O_2 and temperature on dye degradation also.

Experiment showed no significant effect of Ag_2S NPs on the removal of FL even at low concentrations, but in presence of H_2O_2, within 30 min under solar irradiation degradation of about 48% of the FL dye was noticed. Therefore, it was suggested that Ag_2S NPs with H_2O_2 are more efficient to remove FL than Ag_2S NPs alone. For the degradation of FL, the optimum concentration of H_2O_2 was found to be 0.176 M and at temperature 343 K, in presence of a catalyst with H_2O_2, the degradation of FL dye showed more than 93% of degradation. Their study revealed that the photodegradation reaction approximately follows the pseudo-first order kinetics.

Antibacterial activity of Ag_2S NPs

Sibiya et al[38] investigated the antibacterial activity of chitosan, green tea, *Combretum molle (CM)* and black wattle (BW) capped Ag_2S NPs towards *Staphylococcus aureus* and *Escherichia coli* bacterial species by using the disc diffusion method. It was found that the Ag_2S NPs synthesized by using all the above mentioned capping agent were susceptible towards both the bacterial species, but with respect to the other, grater succeptibility of Ag_2S- *Combretum molle towards Escherichia coli* and Ag_2S- black wattle towards *Staphylococcus aureus* was found. For the 1st case, maximum zone of inhibition was found 12 ± 0.14 mm diameter and 11 ± 0.16 mm diameter was observed for the later. They reported that the antibacterial activity of the *Combretum molle* and black wattle leaves extract against gram negative *Escherichia coli* and gram positive *Staphylococcus aureus* was increased in case of CM and BW-capped Ag_2S nanoparticles (MIC values found 0.15-0.31 mg/mL).

The reason behind the antimicrobial activity of Ag_2S NPs is that the positively charged silver ions can bind the bacterial cell membrane which contains negatively charged phospholipid molecules, changes the structures of bacteria and gets denatured. Ag^+ ions also bind with the thiol group (SH) of bacterial enzyme which results the inactivation and even death of enzymes[52]. Antibacterial activity of Ag_2S/RHA-MCM-41 nanocomposite against *Staphylococcus aureus* and *Escherichia coli* bacteria was examined by Jafari et al.[22]

It was found that the minimum inhibitory concentration (MIC) of Ag_2S/RHA-MCM-41 nanocomposite against *E. coli* and *S. aureus* was 15µg/ml for Ag_2S/RHA-MCM-41. It is thought that in relaxed state, replication of DNA molecule can be effectively conducted whereas in condensed form, it loses its replication ability[34]. In the present case, DNA molecules turned into a condensed form due to the penetration of Ag_2S NPs into bacterial cell membrane, which inhabited its replication ability, leading to distraction of bacterial cells.

Awwad et al[2] evaluated the antibacterial activity of biosynthesized Ag_2S NPs against gram negative *Escerichia coli*, and gram positive *Staphyococcus aureus*, *Shigell*, *Listeria bacteria*. They noticed that with the increase of Ag_2S NPS concentration the maximum zone of inhibition (MZI) of *Escherichia coli*, *S. aureus*, *Shigella* and *Listeria* bacteria were increased.

It was reported that their findings about MZI for bacteria were higher than the previously reported data[22,38] and the reason behind the difference was the particles size of NPs and capping agents used in the preparation process. The antimicrobial activity of biosynthesized Ag_2S NPs was carried out by Ayodhya et al[3] against different pathogenic bacteria like *E.coli*, *P. aeruginosa*, *S. aureus* and *B. thuringiensis*. Experimental results revealed that Ag_2S NPs had significant antibacterial action on all the said bacterial species but the antibacterial activity of Ag_2S NPs on *S. aureus* bacteria was greater than with others.

Other biomedical activities

Ag_2S: Yang et al[48] studied the inhibition effect of Ag_2S bulk crystals and nanocrystals (at the same content of 0.05 mg ml^{-1}) on the C6 glioma cell line through cell viability analysis method and found that the synthesized Ag_2S nanocrystals (especially NPs) showed good inhibition of C6 glioma cell viability but the bulk Ag_2S crystal had no significant effect on C6 glioma cell.

The results showed that the inhibition rate of NPs, NRs and NWs arrived to 35.9 – 5.6%, 20.1 – 4.3%, and 16.5 – 4.2% compared with the control group (without nanocrystals, $n = 6$, $p < 0.01$) respectively. Their experimental results suggested that the biosynthesized Ag_2S nanocrystals may be used in curing glioma disease or other tumors.

Wang et al[42] investigated the antineoplastic activities of protein-conjugated Ag_2S nano-crystals by cell viability analysis, optical and electron microscopy methods. It was noticed that nano-particles, nano-rods and nano-wires could inhibit the proliferation of human hepatocellular carcinoma Bel-7402 cells and C6 glioma cells. The inhibition rate of NPs was found higher than NRs and NWs under the same content treatment. The maximum values of the inhibition of NPs group, NRs group and NWs on the viabilities of Bel-7402 were found 59.1 ± 1.3%, 46.8 ± 7.8% and 37.0 ± 4.5%, whereas for proliferation of C6 glioma cells group the maximum value arrived 61.7 ± 3.5%, 55.5 ± 6.0% and 51.1 ± 7.7% respectively for a certain amount of sample content.

It was suggested that by the interaction between mitochondrial proteins (and membrane) and Ag^+ released from nano-crystals the function of mitochondria could be disrupted leading to cell death. Human hepatocellular carcinoma Bel-7402 cells were treated with NPs, NRS and NWs. Optical microscopy images showed almost similar cell morphologies between the NRs and the NWs treated group, but the cells in both groups exhibited much better spreading morphologies compared with that in the nanoparticles group, which indicated the worse inhibition effect on Bel-7402 cells activity.

Chen et al[7] measured the cellular cytotoxicity of biosynthesized Ag_2S NPs in vitro by tetrazolium based colorimetric assay (MTT test). For this purpose, pure Ribonuclease-A (RNase-A) and RNase-A capped Ag_2S NPs were cultured with normal human embryonic kidney cell line HEK 293T cells for 24 h. Very low cytotoxicity of RNase-A-Ag_2S NPs, which was similar to pure RNase-A value was observed (cell viability: pure RNase-A 97.473.7%, RNase-A-Ag_2S NPs 93.676.3%). It was suggested that for *in vivo* molecular imaging the biosynthesized Ag_2S quantum dot cluster was suitable for further applications.

Suresh et al[40] evaluated the toxicity impact of the biogenic Ag_2S NPs using *E. coli*, *B. subtilis* and *S. Oneidensis* bacterial Species and mouse lung epithelial (C 10) and macrophage (RAW 264.7) cell systems also. Experimental results revealed that the NPs were non-inhibitory and non-cytotoxic to any of these systems.

CuS: Zhou et al[54] evaluated the efficiency of the biosynthesized CuS NPs as a phtothermal therapeutic agent by applying it on A549 cells. The experimental results showed that the prepared CuS NPs could be effectively utilized as a photothermal therapy agent under the irradiation of 1064 nm.

Conclusion

The green route for the synthesis of nanomaterials using biogenic sources is an alternative, less toxic, energy efficient, and easy process towards synthesis. Biobased sources act as both reducing and stabilizing agents during the fabrication of nanostructured materials and control the shapes and sizes of the nanomaterials. This review summarizes the literature with the aim that it may help future researchers to get an idea about the biosynthesis of silver sulphide and copper sulphide NPs and also to understand the current status of the use of the said green synthesized NPs for photocatalytic and biomedical applications.

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