



Very rapid synthesis of highly efficient and biocompatible Ag₂Se QD phytocatalysts using ultrasonic irradiation for aqueous/sustainable reduction of toxic nitroarenes to anilines with excellent yield/selectivity at room temperature

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ABSTRACT

There are many problems associated with the synthesis of nanocatalysts and catalytic reduction of nitroarenes - e. g., high temperatures, costs, long reaction/synthesis process times, the toxicity of chemicals/solvents, undesirable byproducts, the toxic/harmful wastes, low efficiency/selectivity, etc. This study represents an attempt to overcome these challenges. To this purpose, biocompatible and highly efficient Ag₂Se quantum dots (QDs) catalysts with antibacterial activity were synthesized in a very rapid (30 sec, rt), simple, inexpensive, sustainable/green, and one-pot strategy in water using ultrasonic irradiation. Characterization of the QDs was performed using different techniques. UV-Vis absorption and fluorescence spectroscopic studies showed an absorption peak at 480–550 nm and a maximum emission peak around 675 nm, which confirmed the successful synthesis of Ag₂Se QDs via the applied biosynthetic method. Subsequently, catalytic reduction of nitroarenes by them was carried out under safe conditions (H₂O, rt, air atmosphere) in ~ 60 min with excellent yield and selectivity (>99%). Their catalytic activity in the reduction of various toxic nitroarenes to aminoarenes under green conditions was investigated. Thus, a rapid and safe ultrasound-based method was employed to prepare stable and green Ag₂Se QDs phyto-catalysts with unique properties, including exquisite monodispersity in shape (orthorhombic) and size (~7 nm), air-stability, and good purity and crystallinity. Importantly, instead of various toxic chemicals, the plant extract obtained by rapid ultrasonic method (10 min, rt) was used as natural reducing, capping, and stabilizing agents. Moreover, antibacterial assays results showed that Ag₂Se-QDs catalysts at low concentrations (ppm) have high activity against all tested bacteria, especially *E. coli* (MIC:31.25 ppm, MBC:125 ppm) which were significantly different from those of Fig extract (MIC = MBC:500 ppm). The data reflect the role of these bio-synthesized Ag₂Se-QDs catalysts in the development of versatile and very safe catalysts with biomedical properties.

1. Introduction

Nitroarenes have different hazardous effects on human health and the environment. They are common organic pollutants and harmful wastes found in industrial water [1]. Hydrogenation reactions of nitroarenes are key processes in the removal of toxic/carcinogenic nitro compounds from environmental matrices as well as in the chemical industry as they produce important and useful building blocks (anilines) for the production of fine/bulk chemicals, pharmaceuticals, dyes/pigments, agrochemicals/herbicides, etc. [2,3].

On an industrial scale, these materials are produced by catalytic hydrogenation with precious metal catalysts [4]. These conventional reduction techniques require the use of high pressures/temperatures, additional amounts of a reducing metal, reagents, and a flammable gas (H₂). In addition, strong reducing agents in these methods produce undesirable by-products [5]. Therefore, it is important to find a cost-effective, robust, and environmentally friendly catalytic method that does not use hazardous/expensive agents that generate by-products [6]. Sodium borohydride (NaBH₄) is a common reducing agent that could be used for such catalytic reductions. However, current methods usually

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require it to be used in >100-fold excess over the substrate. Therefore, it is important to search for suitable catalysts that can increase the catalytic efficiency with a minimal amount of NaBH_4 [7].

Nanocatalysts have high catalytic activity and reactivity because of their high surface area to volume ratio. However, many of these catalysts exhibit higher toxicity than comparable bulk catalysts [7–9]. Moreover, the easy uptake of these nanoparticles by living systems has led to concerns about their effects on human health and the environment [9]. Hence, the selection and synthesis of safe/eco-friendly nanocatalysts, especially with biomedical applications, using non-toxic/benign synthetic methods (i.e., sustainable chemistry) is of utmost importance [10,11].

One way to achieve this goal is to use plant-derived materials (plant extract) as natural reducing, stabilizing, and capping agents simultaneously with ultrasound-based methods for greener synthesis of eco-friendly nanocatalysts [10]. Ultrasound-based methods are green/eco-friendly and have important advantages, including simplicity, cost-effectiveness, increased efficiency, improved dispersion, enhanced safety, and easy assimilability with other methods [12,13]. In these methods, water is often used as a suitable green solvent, and nanoparticles with high surface area, high phase purity, and narrow size and shape distribution can be prepared [14,15].

One of the most important challenges in using nanocatalysts is their separation from the reaction mixture, because of their very small particle size [16]. Phyto-nanocatalysts coated with water-soluble plant organic compounds solve the challenge of catalyst recovery and recycling by allowing extraction in an aqueous biphasic system and simple phase separation with water, with the catalyst remaining in the water [17].

Silver selenide (Ag_2Se) or naumannite as a superionic conductor [18] has attracted great attention because of its useful and intriguing properties. These materials are non-toxic semiconductors with a narrow band-gap (0.07–0.15 eV) that can be used in fuel cells, thermochromic materials, batteries, electrocatalysis, solar cells, photosensitizers, solid-state electrochemical sensors, and magnetic field sensors [19–23]. They are also used for in vivo bio-imaging and sensing. Toxicity studies have shown that Ag_2Se QDs have high biocompatibility, high stability, and low toxicity both *in vitro* and *in vivo* because they have extremely low solubility product constants [$K_{sp}(\text{Ag}_2\text{Se}) = 2.0 \times 10^{-64}$]. Therefore, only a minimum of Ag^+ ions are released into biosystems [24,25] and the ions can thus be rapidly eliminated from the blood and via the kidneys without accumulating in organs [26].

Although anilines have already been synthesized with various nanocatalysts (Table 1), to the best of our knowledge, this is the first study dealing with the synthesis of Ag_2Se QD photocatalysts, as well as the reduction of aromatic nitro compounds by them under completely green conditions (water, rt, air atmosphere). To this purpose, green/robust/stable/reusable/safe Ag_2Se QD photocatalysts with plant coating were synthesized in a very fast, safe, and one-pot method (H_2O , rt, air atmosphere) by ultrasonic irradiation for the reduction of nitroarenes using a small amount of NaBH_4 (mild hydride donor) under green conditions (H_2O , rt, air) in a short time (~60 min) in > 99% yield and selectivity (Scheme 1).

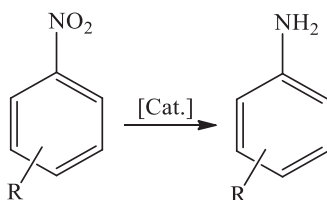
2. Experimental

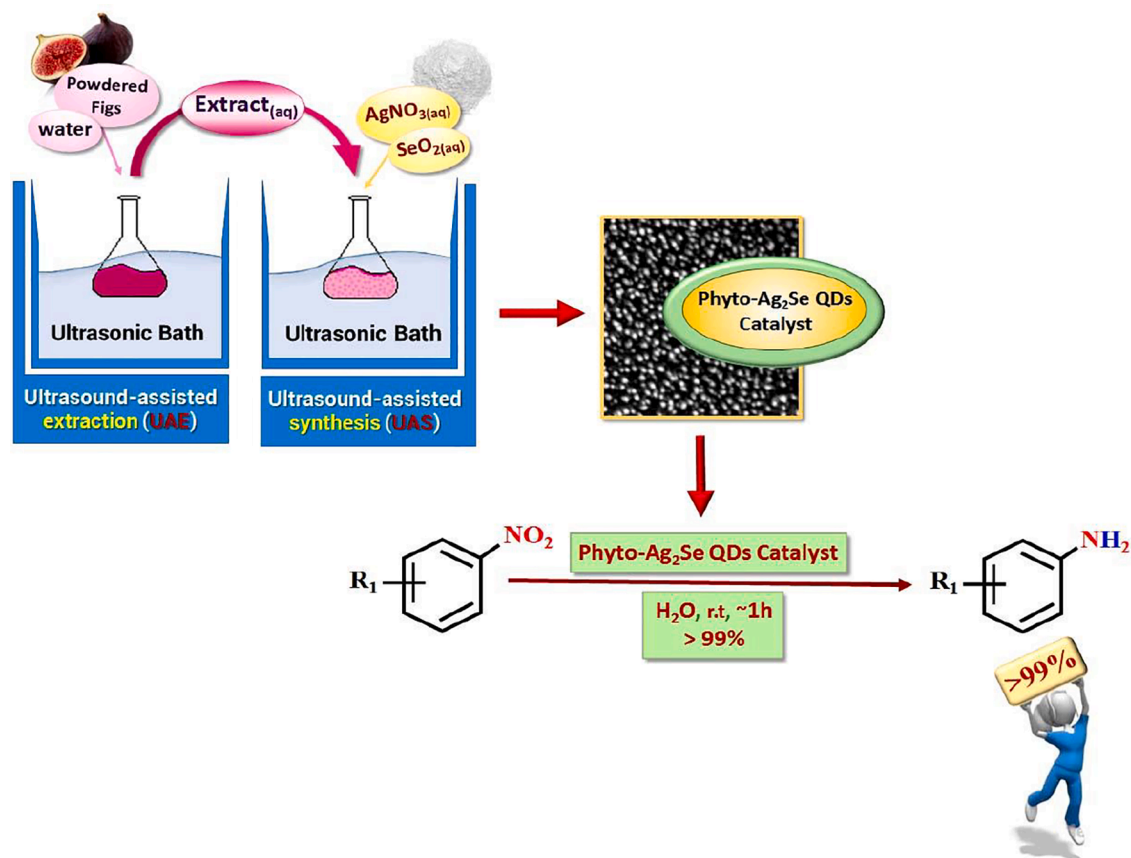
2.1. Materials and instruments

The ultrasonic irradiation was carried out using digital ultrasonic (WUC-D, Korea) to extract bioactive compounds from Fig fruits as well as phyto-synthesis of Ag_2Se QD phyto-catalysts. The preliminary characterization and light absorption of samples were studied using UV-2501PC (Shimadzu, Japan). Moreover, their functional groups and surface chemistry studies were performed by FT-IR spectrophotometer with a scanning range from 400 to 4000 cm^{-1} (Bruker Tensor 27, KBr wafer). The conductive materials (Au/Pd) onto the surface of the SEM samples were coated using the SEM sputter coater (Coxem SPT-20, South Korea). The scanning electron microscopy/energy dispersive X-Ray spectroscopy (SEM-EDS) was then utilized to investigate the catalyst's surface morphology, size, and elemental analysis (FEI ESEM Quanta 200, EDS Silicon Drift 2017, USA). The structural information and phase purity of obtained catalysts were studied using their X-ray diffraction (XRD) spectrum (PW1730, PHILIPS, Netherlands) with $\text{Cu K}\alpha$ source and $\lambda = 1.54056 \text{ \AA}$. Finally, biological data were read using the microplate reader BioTek (Epoch 2). The transmission electron microscopy (TEM- EM 208S) with a Tungsten filament (electron gun) and point resolution of 0.45 nm at an accelerating voltage of 100KV was used to obtain the information on the shape and size. Fig fruits (edible fruit of *Ficus carica L.*) with superior quality were procured from an herbal medicine shop in Ahvaz, Iran, and identified by the plant taxonomist Dr A. Sonboli. All chemicals used in the synthesis of catalyst and nitroarenes reduction were purchased from Sigma-Aldrich & Merck Co. and were used without any purification.

Table 1
Catalytic reduction of nitrobenzenes with diverse catalysts

	Fe-phen/C-800	cobalt oxide catalysts	Ni-phen@ SiO_2 -1000	(PNA-BIS-2) microgel-stabilized Ag NPs	Ag-rGO/g- C_3N_4	This work: Phyto- Ag_2Se QDs
	Science, (Jagadeesh et al., 2013)[2]	Nat. Chem, (Westerhaus et al., 2013)[27]	Science, (Ryabchuk et al., 2018)[4]	J. Hazard. Mater. (Begum et al., 2019) [28]	J. Hazard. Mater. (Kumar et al., 2020) [29]	
Catalyst synthesis conditions	Need for high temperatures, various toxic and expensive chemicals/organic solvents, N_2 or Ar atmosphere, special facilities and equipment, and involve several time-consuming reaction steps					AgNO_3 , SeO_2 , Aqueous Fig extract, sonication, rt, 30 sec
Reduction reaction conditions	H_2 (50 bar) $\text{H}_2\text{O}/\text{THF}$ 120 °C 12–24 h	H_2 (50 bar) $\text{H}_2\text{O}/\text{THF}$ 110 °C 4–12 h	10 bar $\text{H}_2\text{O}/\text{MeOH}$ 60 °C 20 h	NaBH_4 H_2O rt 3–9 h	N_2 , methanol, visible light ($\lambda > 400 \text{ nm}$) 4–6.5 h	NaBH_4 H_2O rt ~1h
yield	86–97%	53–99%	61–99%	75–95	89.2–98.2%	>99%





Scheme 1. Schematic representation of the method used for phyto-synthesis of Ag_2Se QDs catalysts using Fig extract and their use in the reduction reaction of anilines.

2.2. Ultrasound-assisted synthesis (UAS) of Ag_2Se QDs catalysts: (UAS/extract-capped Ag_2Se QDs)

Dried Figs were washed with distilled water to remove impurities and then powdered by a mechanical grinder. The ultrasound-assisted extraction (UAE) as a fast/green/easy method was used for Fig extraction. Hence, 10 g of dried fruit powder was mixed with 100 mL of distilled H_2O and was then sonicated (10 min, rt, 40 kHz). The content of the flask was filtered using Whatman filter paper to obtain a clear extract that was stored in a sealed container and refrigerated.

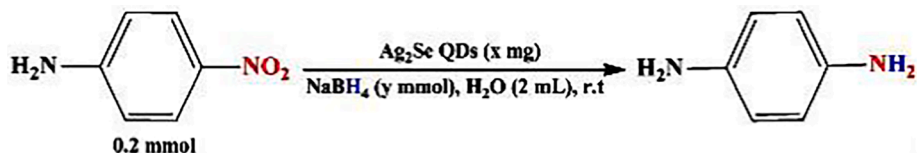
Afterwards, the aqueous extract (12.5 mL, PH = 8) and AgNO_3 solution (25 mL, 259×10^{-4} mol. L^{-1}) were mixed, and the container was placed in the ultrasonic bath (40 kHz, rt). Subsequently, during the

ultrasonic process, SeO_2 solution (25 mL, 129×10^{-4} mol. L^{-1}) was added to the mixture and subjected to ultrasonic irradiation (30 sec, rt). The observation of turbidity and rapid colour change in the reaction mixture indicates phyto-reducing ions and the production of UAS/phyto-synthesized Ag_2Se QD catalysts (extract-capped). The mixture was centrifuged (6000 rpm, 15 min), washed with distilled H_2O , and dried in vacuo (45°C , 24 h).

2.3. General procedure for nitrobenzenes reduction using Ag_2Se QD catalysts

The catalytic activity of phyto- Ag_2Se QDs (extract-capped) was evaluated using the reduction of a series of nitroarenes (Table 2). Briefly,

Table 2
Optimization of conditions of reduction reaction of nitrobenzenes.



Entry	Ag_2Se QDs (x mg)	NaBH_4 (y mmol)	t (min)	Aniline yield [%]
1	10 mg	1	60	>99
2	7 mg	1	120	55
3	5 mg	1	120	40
4	10 mg	0.5	60	75
5	–	1	120	0
6	10 mg	–	120	0

the desired nitroarene (0.2 mmol), NaBH_4 (1.0 mmol), water (2.0 mL), and Ag_2Se QD catalyst (10.0 mg, 0.7 mol% Ag) were mixed and stirred at room temperature. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, the crude mixture was diluted with water (5 mL), centrifuged, and worked up by EtOAc (2×10 mL), and then the organic phase was dried over MgSO_4 and evaporated under a vacuum to give the desired product, which was characterized by ^1H NMR and ^{13}C NMR spectroscopy in $\text{DMSO}-d_6$.

2.4. In vitro antibacterial activity

The *in vitro* antibacterial activity of the samples, including UAS/phyto- Ag_2Se QDs catalysts (extract-capped) synthesized by biological method and Fig extract, were evaluated against four bacterial strains including two Gram-negative bacteria species (*Pseudomonas aeruginosa* and *Escherichia coli*) and two Gram-positive bacteria species (*Bacillus subtilis* and *Staphylococcus aureus*) using disc diffusion method (DDM), minimum inhibitory concentration (MIC), and minimum bactericidal concentration (MBC) tests.

2.4.1. Antibacterial activities by disk diffusion test (DDM)

According to [30], the disk diffusion method (DDM) was utilized to determine the *in vitro* antibacterial activity of samples, with slight modifications. In this method, different concentrations of the samples (12.5, 25, and 50 mg/mL) as antibacterial compounds were prepared. Filter paper discs with a 6-mm diameter were impregnated with each known concentration of the tested sample solution and then placed on the surface of Mueller-Hinton agar (MHA) loaded with each of the desired organisms. Afterwards, they were incubated (24 h, 37 °C) and then the diameter (mm) of the zone of growth inhibition surrounding the discs was reported as antibacterial activities of the samples [30].

2.4.2. Antibacterial activities by minimum inhibitory concentration (MIC) test

The highest dilution of a sample or minimal inhibitory concentration (MIC) which inhibits the growth of a test microorganism, was evaluated by the broth dilution method [31,32], with some modifications. The serial dilution procedure as a common standard method gives the best reproducible results in MIC [31,32]. Briefly, different concentrations of the samples (0.488 to 1000 ppm) were prepared. Muller Hinton Broth and microorganisms were then added to each well containing a sample and then incubated (37 °C, 24 h). The concentration of the last well in the dilution series with no visible growth of bacteria or turbidity was recorded as the MIC value of each sample [33].

2.4.3. Antibacterial activities by minimum bactericidal concentration (MBC) test

According to previously reported [34], the minimum bactericidal concentration (MBC) of samples as complementary to the MIC assay was determined by sub-culturing wells with no visible turbidity/growth in MIC assay, on an area of Muller-Hinton agar (MHA) and incubation (24 h, 37 °C). The lowest sample concentration without visible growth of bacterial colonies on MHA was considered as MBC value in bacterial death (99.9%) [35].

3. Result and discussion

3.1. Synthesis and characterization of the UAS/extract-capped Ag_2Se QD catalysts

The use of biocompatible and safe quantum dots with high antibacterial activity as catalysts in the reduction reaction of toxic nitrorenes is interesting. In some published research, chemically synthesized Ag_2Se QDs have been used as biocompatible and safe QDs in in-vivo imaging [36,37]. Nevertheless, to increase safety, reduce costs, prevent the use of expensive/unsafe chemicals, and provide an eco-friendly

greener synthesis, biocompatible Ag_2Se QD phyto-catalysts were biosynthesized using only two chemicals: i.e., solutions of $\text{SeO}_2(\text{aq})$ and $\text{AgNO}_3(\text{aq})$, together with aqueous Fig extract (as a natural and cheap reducing/capping/stabilizing agents) and ultrasound irradiation.

In the plant-mediated synthesis of nanoparticles, plant extracts act as reducing, capping and stabilizing agents. Studies have shown that biomolecules and phytochemical content of plant extract (e.g. phenolics, terpenoids, phenolic acid, flavonoids, amino acids, glycosides, organic acids, polysaccharides, vitamins, and proteins) not only play a role in bio-reduction of the ions to nanoparticles but also play an important role in the capping and stabilizing of metal and metal oxide NPs [38,39].

It is noteworthy that the aqueous extract of Fig was obtained by ultrasound-assisted extraction (UAE) as a green method, which requires less energy, time, temperature, and solvent than conventional extraction methods [40,41]. This method increases extraction yield [42] using the acceleration of plant cell wall damage and the mass transfer of bioactive components (such as phenolic compounds) from the solid to the liquid phase [43] by maintaining the quality of the extract [40,42].

Because of the benefits of ultrasonic irradiation, it was also used for fast bio-reduction of ions and synthesis of Ag_2Se QDs phyto-catalysts. This method was surprisingly useful because it produced Ag_2Se QDs catalysts with extremely small size (~7 nm), good purity, very uniform shape and size, and without aggregation, in a short time (30 sec). The synthesis of nanoparticles with these properties is important because the size, dimensions, shape, crystallinity, composition, and structure greatly affect their physicochemical properties [44].

These obtained UAS/phyto- Ag_2Se QDs catalysts (extract-capped) were then used to reduce nitrobenzenes under completely green conditions (H_2O , rt) and produced anilines selectively with a very high yield (>99%). Therefore, the comparison of this study with previously published researches (Table 4) shows the use of simple, fast and completely green methods (water, rt), safe materials and biocompatible catalyst, without the use of special equipment at all stages including nanocatalyst synthesis as well as the reduction reaction of toxic nitrorenes. For this purpose, all steps were performed in water and ambient temperature without the use of unsafe chemicals and special equipment with excellent efficiency and without toxic by-products. Characterization of the UAS/phyto- Ag_2Se QDs catalysts was then performed with different methods, including Fourier-transform infrared spectroscopy (FT-IR), UV-Vis spectrophotometry, X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), and coupled plasma optical emission spectroscopy (ICP-OES).

The formation of QDs (extract-capped) was initially monitored through the visual color change from clear red to turbid pink under ultrasound irradiation. It was confirmed that the turbidity/color change was due to the phyto-reduction of ions by the biomolecules present in the extract and the formation of Ag_2Se QDs in the reaction mixture. Preliminary characterization and optical properties of QDs were investigated using UV-Vis absorption spectra in the range of 250–700 nm (Fig. 1A). The absorption of light by semiconductor nanoparticles excites the electron and transfers it from the valence band to the conduction band, creating a continuous and wide absorption peak [45]. Because the concentration, pH, distribution, morphology, size, and adsorption of electrophile or nucleophile to the surface of the nanoparticles affect the position of the absorption signal and optical properties of nanoparticles [46–48], the appearance of a wide peak at 480–550 nm, confirmed the formation of Ag_2Se QD catalysts in the reaction mixture [48,49].

Quantum dots can be excited and emit fluorescence after absorbing (a) certain wavelength(s) of light [50]. Fig. 1B shows the photoluminescence (PL) spectra of extract capped- Ag_2Se QDs catalysts. The emission micrograph shows a maximum PL intensity (a clear and symmetric emission peak) at $\lambda_{\text{max}} = 676$ nm. Furthermore, the calculated full width at half-maximum (FWHM) of this emission peak does not exceed 15 nm, which clearly indicates the monodispersed and pristine biosynthesized Ag_2Se quantum dots with a very narrow particle size

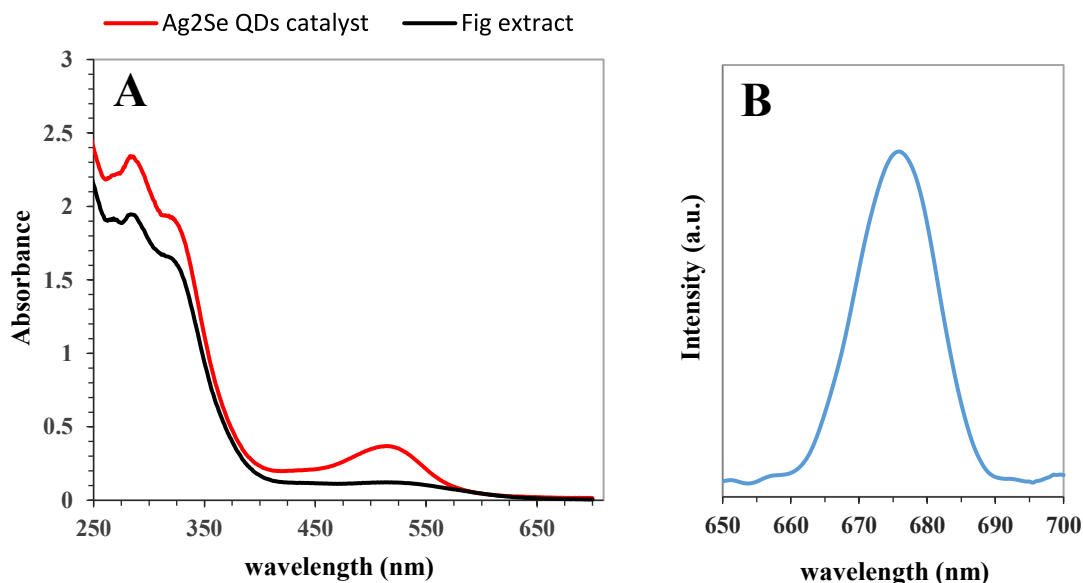


Fig. 1. The UV-Vis absorption (A) and PL spectra (B) of the extract-capped Ag_2Se QDs catalysts.

distribution [51]. Moreover, since the sharp emission intensity is related to the lower density of defect sites, these safe Ag_2Se quantum dots can be used to improve photovoltaic performance as QDs inbuilt by low-defect and PL emission with high quality [52].

It is found that the optical properties of semiconductors depend on their structure, as well as the nature and amount of impurities in the structure [53]. The value of optical band gap energy (E_g) of the bio-synthesized semiconductor Ag_2Se QDs can be calculated by Tauc's plot method using following equation: $\alpha h\nu = \alpha_0 (h\nu - E_g)^{1/2}$.

where α , ν , h , and E_g are the absorption coefficient, frequency, Planck's constant, and band gap of the nanoparticles, respectively [54,55]. According to the results, the optical band gap energy of Ag_2Se QDs was obtained (2.4 eV) which was higher than the value of 0.15 eV reported for bulk Ag_2Se at room temperature [56]. Therefore, this increase in band gap compared to its bulk value can be due to a decrease in particle size, which is the result of the quantum size confinement effect [54,57,58]. The size quantization increases the effective bandgap due to the creation of a series of discrete states in the valence and conduction

bands [59]. It should be noted that when materials are extremely small like quantum dots, their optical and electronic properties are significantly distracted from their bulky materials [60].

Fourier Transform Infrared (FT-IR) spectrum brings valuable information about the surface chemistry of bio-synthesized nanoparticles [48] because the stabilizing/capping agents are bound to the surface of Ag_2Se QDs change the FT-IR spectrum [61]. Therefore, this analysis can be used to detect the presence of possible phytochemicals in the aqueous Fig extract that is responsible for the capping and stabilization of Ag_2Se QDs [62]. Fig. 2 shows the FT-IR spectra of Fig extract (black line) and Fig capped Ag_2Se QDs (red line). The FT-IR spectra of Fig extract showed a strong, broadband at 3414 cm^{-1} , which is attributed to the stretching vibration of the OH groups and the formation of intra- and intermolecular hydrogen bonds. The peak at 2925 is due to the C-H symmetric- and asymmetric stretching of the methyl/methylene band. The C=O of ester or carboxylic acid and protein secondary structure (amides I and II) was predominantly observed at 1626 cm^{-1} , while the absorption band at 1406 cm^{-1} was ascribed to the C-O bonds of ether/ester groups and CH_2

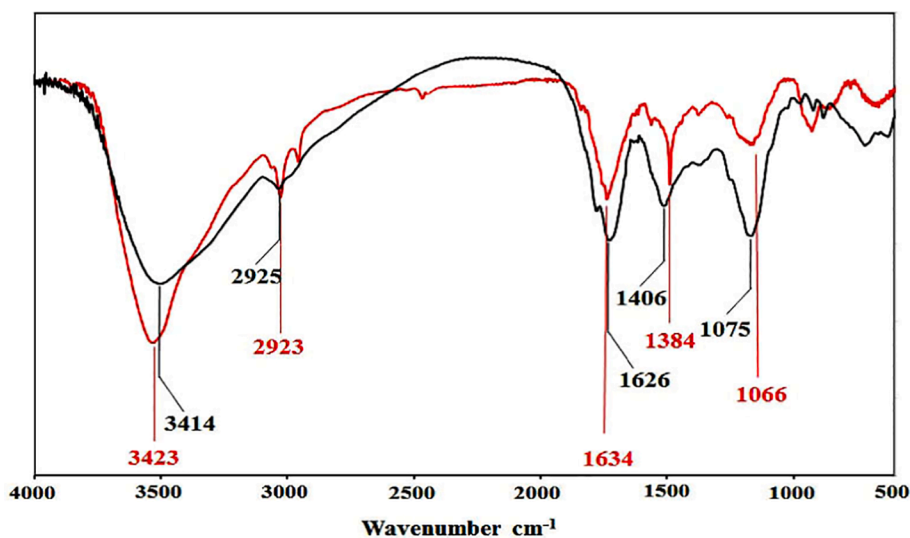


Fig. 2. The FT-IR spectra of UAS/phyto- Ag_2Se QDs (red) and Fig extract (black) by UAE method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

bending. Moreover, the absorption peak at 1075 cm^{-1} corresponds to the C–O/C–N of aliphatic amines or alcohol/phenol [63–65]. These absorption bands showed a shift after the reaction with Ag_2Se QDs to 3423, 2923, 1634, 1384, and 1066 cm^{-1} , respectively. All these peaks show the presence of phytochemicals in extract including polyphenolics, flavonoids, amino acids, etc. which contain different functional groups as phyto-reducing/phyto-capping/phyto-stabilizing agents in the synthesis of Ag_2Se QDs, preventing aggregation of nanoparticles [66]. The results confirmed interactions of Fig extract amino- and hydroxyl groups with Ag_2Se QD catalyst surface. This means that Fig extract has the ability to bind metals and can act as a capping agent for stabilizing the nanocatalysts.

The size details, morphology, size distribution, and elemental

composition of the Ag_2Se QDs were determined using SEM-EDS (scanning electron microscopy/energy dispersive spectroscopy) and TEM analysis, as depicted in Fig. 3 (A–D). The resulting images showed the presence of a large number of very fine spherical nanoparticles with a very narrow size distribution, without any aggregation, which had an average diameter of $\sim 7\text{ nm}$. To our knowledge, there are no phyto-synthesized Ag_2Se QDs using ultrasonic with a very uniform, extremely fine, and very good monodispersity in shape and size in the literature.

The EDX spectrum (Fig. 3E) displays peaks corresponding to Ag and Se, which confirmed the successful synthesis of UAS/phyto- Ag_2Se QDs. It is noteworthy that the extract phytochemicals, which capped the surface of the QDs, generate other signals that can be seen in Fig. 3E

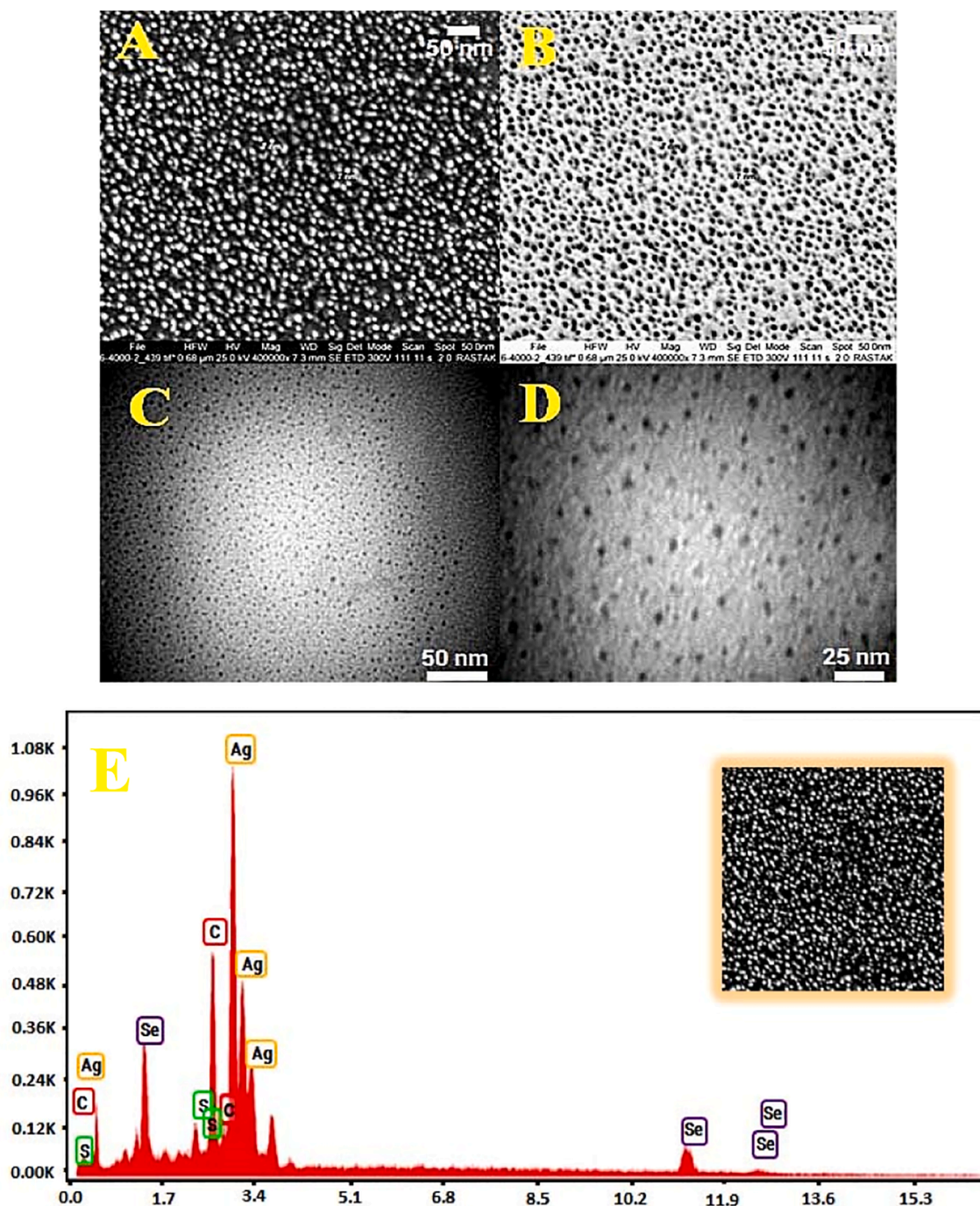


Fig. 3. SEM images (A&B), TEM images (C&D), and EDX pattern (E) of phyto-synthesized Ag_2Se QDs by UAS method.

[66]. Furthermore, the results of inductively coupled plasma optical emission spectroscopy (ICP-OES) exhibited that Ag content in Ag_2Se QDs was 1.5 wt%.

The phase purity and crystal structure of the Ag_2Se was investigated by the x-ray diffraction (XRD) method. The X-ray diffractogram is shown in Fig. 4 in the 2θ range from 15° to 80° , which was assigned with Miller indices (hkl) values to each reflection peak. The X-ray diffraction peaks were identical and matched with those reported in the appropriate literature database (reference code: 96–223-0973). The successful synthesis of Ag_2Se QDs phyto-catalysts could be made evident from the appearance of the characteristic peaks of Ag_2Se in the XRD pattern [67]. As shown (Fig. 4), some peaks corresponding to orthorhombic Ag_2Se were observed at the position (2θ) of 23.05° , 26.90° , 31.07° , 32.88° , 33.63° , 34.90° , 37.09° , 40.15° , 42.76° , 45.14° , 46.86° , 48.71° , 50.07° , 53.38° , 55.20° , 57.41° , 59.29° , 62.52° , 65.92° , 69.61° , 71.33° , 75.28° , and 79.21° which were attributed to (002), (111), (102), (120), (112), (121), (013), (031), (113), (032), (004), (014), (132), (114), (222), (042), (231), (204), (301), (125), (151), (322), and (243) crystallographic planes, respectively. The results revealed the pure phase of the Ag_2Se QDs had an orthorhombic crystal structure.

3.2. Catalytic selectivity and activity

Different industries, including those associated with pharmaceuticals and fine chemicals, use many toxic, hazardous chemicals and chemical processes and produce relatively much more waste, which have adverse effects on nature, the environment, and human health [68]. Therefore, the use of green chemistry and safe materials and processes such as the use of water, recyclable/biocompatible catalysts, and the prevention and minimal use of chemicals, etc. are very important.

Water as green, inexpensive, non-toxic, abundant, non-flammable, and the available solvent is the ideal solvent. In addition, because of its high polarity, new reactivity and selectivity can be expected for organometallic catalysis in water [17].

Importantly, the use of the biocompatible/green catalyst (phyto-synthesized Ag_2Se QDs) coated with water-soluble plant organic compounds solved the problem of catalyst recovery and recycling by extraction in an aqueous biphasic system and by simple phase separation, using water with the catalyst remaining in the water.

The use of plant extracts to prevent the use of chemicals in nanocatalysts synthesis is also significant. The complexity and synergistic effect of all the components of plant extracts have increased their therapeutic effects and have caused them to act simultaneously as reducing, stabilizing, and capping agents with a natural origin in the synthesis of eco-friendly nanoparticles [69].

To demonstrate the applicability of UAS/phyto-synthesized Ag_2Se

QDs as biocompatible/green catalysts, the catalytic hydrogenation of industrially important substrates (nitrobenzenes) under completely green conditions was tested.

To find the optimal conditions for the greenest, easiest, and most environmentally friendly hydrogenation of nitroarenes with the highest possible efficiency as well as to evaluate the selectivity and activity of Ag_2Se -Qs phyto-catalysts, 4-nitroaniline was selected as a model substrate. Thus, optimization of catalytic reduction reactions was performed under completely green conditions (H_2O , rt), and other common parameters such as the amount of Ag_2Se QD catalysts and NaBH_4 were tested. Initially, this reaction was tested by decreasing the amount of nano-catalyst. The Ag_2Se QD catalyst (rt, 60 min) in the presence of NaBH_4 (1 mmol) as the mild hydrogen donor was able to reach exclusively dianiline as the product in a $> 99\%$ yield, selectively (Table 2, entry 1). Moreover, reaction efficiency in the presence of 7 and 5 mg catalyst was significantly dropped to 55% and 40%, respectively (Table 2, entries 2 and 3). It was also found that by reducing the amount of NaBH_4 (0.5 mmol), the reaction efficiency decreased to 75% (Table 2, entry 4). Nevertheless, blank runs showed that in the absence of the Ag_2Se QD catalyst or NaBH_4 , no reaction occurred, and the starting 4-nitroaniline was recovered (Table 2, entries 5 and 6). This suggested that both Ag_2Se QD phyto-catalysts and NaBH_4 have important roles in the reduction of 4-nitroaniline.

As a result, the best catalytic activity was obtained using the Ag_2Se QD phyto-catalyst (10 mg) and NaBH_4 (1 mmol) under green conditions (H_2O , rt) which provided the product with excellent yield and selectivity ($>99\%$). It should be noted that under these conditions, the reduction reaction was carried out more rapidly by the Ag_2Se QD catalyst ($\sim 1\text{h}$) than previously reported similar reactions [28,29,70–72]. Thus, this phyto-nanocatalyst plays an important role in the green/environmentally friendly catalytic reduction with the excellent yield and selectivity.

Next, to reach a deeper understanding of the generality and limitations of the catalytic system as well as the ability of UAS/phyto- Ag_2Se QD catalysts in eco-friendly hydrogenation of nitrobenzene under green optimal reaction conditions, hydrogenations of diverse nitrobenzenes were investigated (Table 3). Corresponding anilines were characterized by ^1H NMR and ^{13}C NMR. As shown in Table 3, nitroarenes substituted with electron-withdrawing and electron-donating groups including NH_2 , OH , CH_3 , Cl , Br , $-\text{COCl}$, $-\text{CHO}$, $-\text{OCOCH}_3$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{Br}$, $-\text{CHCHCHO}$, etc. were readily hydrogenated to the targeted anilines in excellent selectivity and yield ($>99\%$) without any byproduct. It was also found that both carbonyl and nitro groups in the aqueous medium were reduced (Table 3, 7–10).

The synthesis conditions of Ag_2Se QD phyto-catalysts as well as their performance (effectiveness) in the reduction of nitroarenes were compared to those obtained for other catalytic systems containing Ag

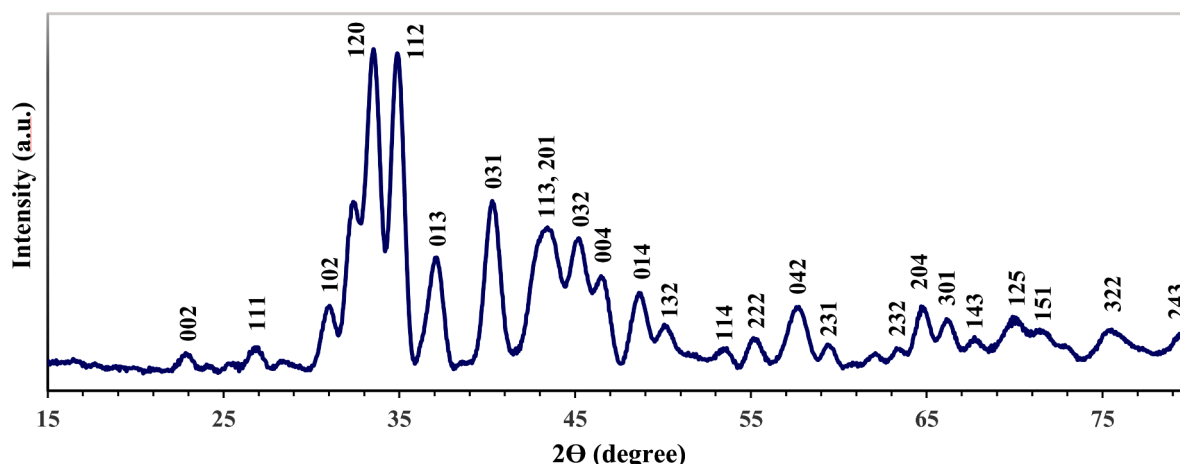


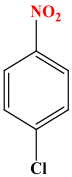
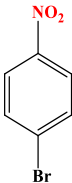
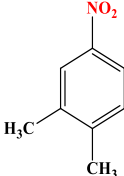
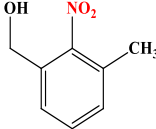
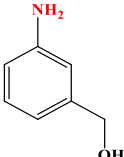
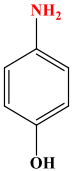
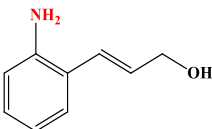
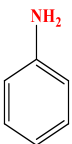
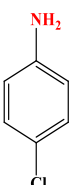
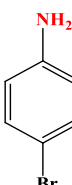
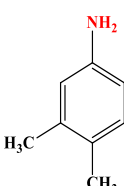
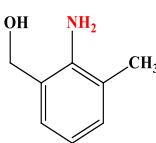
Fig. 4. XRD patterns of phyto- Ag_2Se QDs using ultrasound assisted synthesis (UAS).

Table 3
Substrate scope for the hydrogenation of nitroarenes.

Entry	Sub.	Product	t (min)	Conv. [%]	Sel. [%]
1			60	>99	>99
2			60	>99	>99
3			75	>99	>99
4			70	>99	>99
5			60	>99	>99
6			55	>99	>99
7			60	>99	>99
8			55	>99	>99
9			55	>99	>99
10			70	>99	>99

(continued on next page)

Table 3 (continued)

Entry	Sub.	Product	t (min)	Conv. [%]	Sel. [%]
11			60	>99	>99
12			65	>99	>99
13			65	>99	>99
14			60	>99	>99
15			75	>99	>99
					

reported in the literature (Table 4). The results showed that not only was the synthesis of the Ag₂Se QD catalysts performed much faster, easier, with minimal use of toxic chemicals, and in completely green conditions than other catalysts in the previous literature; also, they are highly active in the catalytic reduction of various nitroarenes. It was surprisingly found that Ag₂Se QD-catalyzed hydrogenation of nitroarenes under green conditions (rt, H₂O) could be performed within ~ 60 min in excellent yield and selectivity (>99%).

3.3. Gram scale experiment

Because of the excellent reduction results obtained for the reduction of nitrobenzenes into corresponding arylamines on small scale, the usability of this procedure in the gram scale experiment was investigated. To this purpose, a gram-scale catalytic reduction of 4-nitroaniline (10 mmol) to 1,4-diaminobenzenes as the model reaction was chosen. This reaction was carried out using the phyto-Ag₂Se QD catalyst and NaBH₄ in water (green solvent) with a good yield. 1,4-Diaminobenzene as the reaction product was then isolated and purified. This method demonstrates the technical feasibility of replacing precious metal catalysts with inexpensive biocompatible catalysts, and it is expected that this protocol will expand the use of these catalysts in the hydrogenation of

nitroarenes.

3.4. Catalyst recycling experiments

The recyclability and stability of the phyto-Ag₂Se QD catalyst is one of the important properties of the catalyst, and performance metrics for its use in cost-effective industrial processes, for use in consecutive runs, was also assessed. To this purpose, after diluting each reduction reaction mixture with water, it was centrifuged (6000 rpm, 35 min), and worked up with ethyl acetate for use in the next run. The Ag₂Se QD catalyst remained in the aqueous phase. The aqueous mixture containing nanocatalyst was reused again under identical reaction conditions. The results of recycling tests are shown in Fig. 5. The catalyst recycling results showed that they were surprisingly usable in five consecutive 4-nitroaniline reduction cycles, without loss of selectivity and need for reactivation (Fig. 5). As shown in Fig. 5, the targeted aniline was formed with excellent efficiency in the first five runs, but from the sixth cycle onwards, the reaction was performed with reduced efficiency. Recyclability of the catalyst is due to its good stability, obtained from covering its surface with plant phytochemicals. These phyto-Ag₂Se QD catalysts are completely safe for humans and the environment. Unlike Raney Ni, it is an eco-friendly catalyst and can be easily used under an

Table 4

Comparison of the catalytic activity of phyto-Ag₂Se QDs with some previously reported catalytic for the reduction of nitroarenes.

Catalyst	Catalyst synthesis conditions	diam (nm)	Reaction reduction conditions	Time	Yield (%)	Ref.
Nanoporous Al ₇₅ Ag ₂₅	1) pure Al, pure Ag, Ar _(g) , High-frequency induction melting furnace, Single roll melt spinning machine 2) NaOH, r.t, 24 h	ligament size: ~30 nm.	NaBH ₄ , H ₂ O, rt	1–12 h	91–99	(Li et al., 2015) [71]
(PNA-BIS-2) microgel-stabilized Ag NPs	1) SDS, NiPAM, AAm, BIS, water, N ₂ , 30 min, rt, and then 70 °C, 20 min 2) APS, N ₂ , 70 °C, 4.5 h 3) dialysis: 5 days 4) microgel, water, N ₂ , rt, 30 min 5) AgNO ₃ (aq), NaBH ₄ , N ₂ , rt, 1 h 6) dialysis: 30 min	10–20 nm	NaBH ₄ , H ₂ O, rt	3–9 h	75–95	(Begum et al., 2019)[28]
Ag NPs-MPAT-1	1) SDS, TAA, TEMED, water, conc. HCl (12 N) 2) APS, water, 1 h, then at 348 K, 3 days 3) AgNO ₃ , water, TRIS, 2 min 4) NaBH ₄ , 10 min 5) Template-free MPAT-1, TRIS-stabilized Ag-NPs, rt, 1 h	15–20 nm	<i>i</i> -PrOH, NaOH, N ₂ , 80 °C	5–12 h	81–98	(Salam et al., 2014) [72]
Ag@C/ZrPP-500R	1) ZrOCl ₂ ·8H ₂ O, reflux, H ₃ PO ₄ , 100 °C, 24 h and drying at 65 °C, 24 h 2) AgNO ₃ , ethanol, phenylacetylene, 1,3-bis(diphenylphosphino) propane, CH ₂ Cl ₂ 3) NaBH ₄ , ethanol, rt, 12 h 4) α-ZrP, DMF, ultrasonic for 30 min 5) Ag cluster ([Ag ₇₄ (C≡CPh) ₄₄ (NO ₃) ₂), DMF, 100 °C, 5 h and drying (vacuum, 80 °C, 4 h) 6) 750 °C (2 °C/min), N ₂ , 3 h 7) 500 °C, 1 h 8) N ₂ , 10% H ₂ , 300 °C, 2 h	1.0–2.0 nm	H ₂ (4 MPa), THF, 160 °C	1–2 h	94.5–100	(Gong et al., 2019) [70]
Ag/Fe ₂ O ₃ nanocatalyst	1) sodium salicylate, NaOH, Iron(III) nitrate, water, pH = 8, 3 h 2) 200 °C, 72 h, washed (water and ethanol), extracted (acid-ethanol) 3) S200-BTO (-Fe ₂ O ₃) nanocrystal, water, sonication 4) AgNO ₃ , ice bath, 30 min 5) NaBH ₄ , ice bath, 3 h and rt, 12 h. washed (water, methanol)	α-Fe ₂ O ₃ nanocrystals (length × width × height: 310 × 220 × 150 nm) and Ag NPs (4–6 nm)	NaBH ₄ (10 eq), H ₂ O, r.t	30 min	20.1–99.5	(Patra et al, 2017) [73]
HS-Alginate-Ag/Fe ₃ O ₄	1) halloysite (HS), water, 15 min 2) iron(III) chloride, iron (II), N ₂ , 70 °C 3) ammonia, N ₂ , 70 °C, 1 h 4) halloysite/Fe ₃ O ₄ , water, 20 min, alginate, 5 h 5) HS-Alginate/Fe ₃ O ₄ , water, 25 °C, 90 min, AgNO ₃ 6) hydrazine hydrate, water, 25 °C, 24 h	41–52 nm	NaBH ₄ , H ₂ O, 50 °C	20 min- 2 h	92–100	(Mohammadi et al., 2021) [74]
Ag@MTC	1) glucose, NaOH, water, ice bath, 12 h 2) chloroacetonitrile, isopropanol, 65 °C, 12 h 3) ethanol, dried at 65 °C, 12 h 4) cyanomethyl glucose, zinc chloride, 400 °C, 40 h 5) water, hydrochloric acid solution, 24 h and then washing with water, THF, acetone and drying in a vacuum at 100 °C. 6) glucose mesoporous, water, silver nitrate, NaBH ₄ , rt, 12 h	16–22 nm	NaBH ₄ , H ₂ O, 75 °C	20 min- 4 h	80–100	(Vahedi-Notash et al., 2020) [75]
Ag-rGO/g-C ₃ N ₄	1) dicyandiamide, thiourea, ball mill (300 rpm min – 1, 50 min), calcination (rt to 550 °C, 4 h) 2) graphene oxide (GO), water, formic acid, sonication, AgNO ₃ , 80 °C, 6 h, NaHCO ₃ 3) g-C ₃ N ₄ , water, 180 °C, 24 h	10–12 nm	methanol, N ₂ , visible light irradiation (λ > 400 nm)	4–6.5 h	89.2–98.2	(Kumar et al., 2020) [29]
Phyto-Ag ₂ Se QDs	1) Washing with ethanol and drying, 80 °C, 12 h Aqueous Fig extract, AgNO ₃ , SeO ₂ , sonication, rt, 30 Sec	~ 7 nm	NaBH ₄ , H ₂ O, rt	~60 min	~100	This work

air atmosphere without any danger or deactivation.

3.5. Evaluation of antibacterial properties using DDM, MIC, and MBC assays

The antibacterial activities of phyto-synthesized Ag₂Se QDs catalysts under UAS (UAS/phyto-Ag₂Se QDs), as well as UA-based Fig extract,

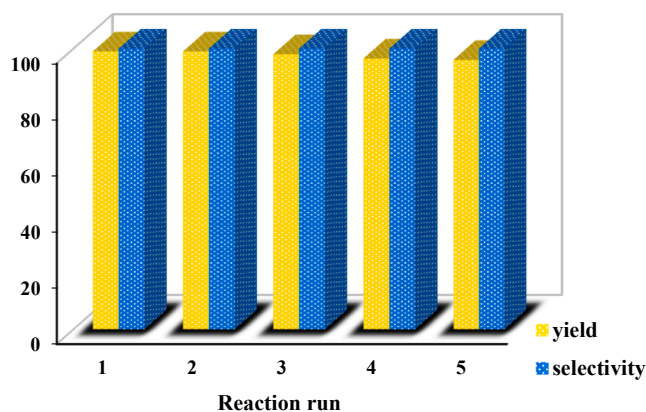


Fig. 5. Catalyst recycling experiments.

were also investigated against the following important microorganisms: *P. aeruginosa*, *E. coli*, *B. subtilis*, *S. aureus* bacteria by disk diffusion (DDM), MIC, and MBC assays.

The antibacterial results of samples at different concentrations (12.5, 25, and 50 mg/ml) were recorded as the diameter of the inhibition zone (mm) of bacterial growth using the DDM method (Fig. 6). A comparison between the *in vitro* antibacterial activity data by the DDM method showed that the tested samples have different effects on preventing the growth of bacteria and UAS/phyto- Ag_2Se QDs catalyst had more antibacterial activity (inhibition zone) than Fig extract against all selected bacteria. Also, there is a direct relationship between the concentration of samples and their antibacterial activity. Hence, the UAS/phyto- Ag_2Se QDs catalyst at 50 mg/mL concentration had the highest effect against both tested gram-positive and gram-negative bacterial strains (Fig. 6). As found, the samples showed the most antibacterial activity against *E. Coli* bacteria, which is attributed to the structure of their cell wall structure and the permeability of the samples to their cell wall [76].

Moreover, to further investigate the antibacterial properties of these phyto-nanocatalysts and corresponding Fig extract, the minimal inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) assays were performed at lower samples concentrations (1000 to 0.488 ppm) on four different bacteria strains (Table 5).

The MIC and MBC values showed that there is a considerable difference in antibacterial activities of samples against tested bacteria as well as the UAS/phyto- Ag_2Se QDs catalyst coated with Fig phytochemicals (plant-coated) is the most active sample with maximum antibacterial effect against all tested bacteria, especially *E. coli* bacteria (MIC:31.25 ppm, MBC:125 ppm).

Therefore, biological results showed that the UAS/phyto- Ag_2Se QDs

catalysts in very low concentrations have antibacterial activities. This could be due to their high available surface area, extremely small size as well as the Fig extract coating on their surface, which enhances the friction and contact between the phytochemicals in extract coating and microorganisms' cells and thus facilitates their penetration into the cell and causes cell death [77,78].

4. Conclusion

Ag_2Se QD was previously synthesized and used in various industries, e.g., as a non-toxic/safe agent in in-vivo imaging. For the first time, the rapid/one-pot synthesis of stable/biocompatible Ag_2Se QD phyto-catalysts (30 sec) with high antibacterial activity (ppm), as well as the hydrogenation of nitroarenes by these catalysts (~60 min) were carried out in very high yields under completely green conditions (H_2O , rt, air atmosphere) by simpler/faster/safer/cheaper methods than other reported works, without the need for high pressure equipment or N_2/Ar atmosphere as well as without the use or production of hazardous/toxic substances and by-products. For a greener/faster synthesis of Ag_2Se QD phyto-catalyst, a combination of facile plant-mediated and sonochemical methods was used. Importantly, the present method did not need organic solvents nor unsafe and expensive chemicals; instead, aqueous Fig extract was used as capping, reducing, stabilizing agents, and water was used as a green and low-cost solvent. The use of green ultrasound irradiation greatly accelerated cell wall destruction and the extraction (10 min) as well as the synthesis of Ag_2Se QDs phyto-catalyst (30 sec) and simultaneously improved catalyst properties. This means that the obtained nanocatalysts were highly monodisperse, fine (~7 nm), with good crystallinity and purity, and were generated without aggregation. A safe, silver selenide-catalyzed reduction of nitroarenes under absolutely green conditions (H_2O , rt, air atmosphere) in ~ 60 min with excellent selectivity and yield (>99%) was performed. The catalytic activity results showed that these stable/biocompatible/eco-friendly Ag_2Se QD catalysts exhibit high activity in nitroarene reduction. Moreover, the product and this reusable catalyst can be easily separated from the reaction mixture by simple extraction. Hence, this safe phyto-catalyst offers direct access to a variety of anilines (important building in chemicals, pharmaceutical, and agrochemical industries) from toxic nitroarenes with excellent selectivity and yield as well as they can be used as reusable and efficient catalysts with good antibacterial activity to remove toxic nitroarenes from environmental effluents, intending to create a cleaner environment for sustainable development. With their operational simplicity and absolutely green conditions, they could enable wide applications in research and industries.

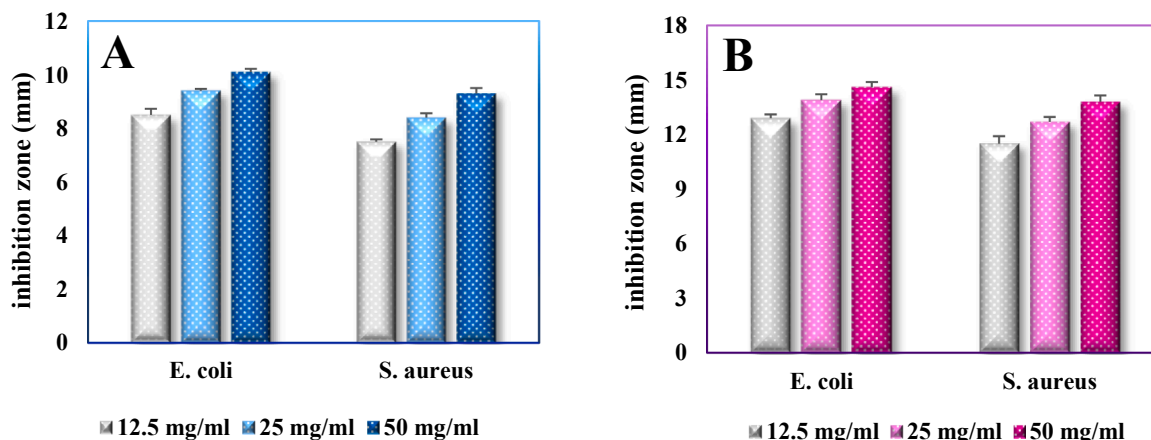


Fig. 6. Antibacterial studies result of Fig extract (A) and phyto- Ag_2Se QDs catalysts samples (B) using disc diffusion method (DDM).

Table 5

MIC and MBC of UAE-based *Fig* extract (ppm) and Ag₂Se QDs (ppm) against Gram-positive/negative bacterial strains.

Samples	<i>S. aureus</i>		<i>B. subtilis</i>		<i>E. coli</i>		<i>P. aeruginosa</i>	
	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MBC
UAS/phyto-Ag ₂ Se QDs catalysts	500	>1000	62.5	125	31.25	125	125	500
<i>Fig</i> extract	>1000	>1000	250	500	500	500	1000	>1000

CRediT authorship contribution statement

Maryam Shahzad Shirazi: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Alireza Foroumadi:** Validation, Resources. **Iraj Saberikia:** Software, Formal analysis. **Mahdi Moridi Farimani:** Conceptualization, Validation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] M. Niakan, M. Masteri-Farahani, Ultrafine and well-dispersed Pd-Ni bimetallic catalyst stabilized by dendrimer-grafted magnetic graphene oxide for selective reduction of toxic nitroarenes under mild conditions, *J. Hazard. Mater.* 424 (2022), 127717.
- [2] R.V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, Nanoscale Fe₂O₃-based catalysts for selective hydrogenation of nitroarenes to anilines, *Science* 342 (2013) 1073–1076.
- [3] R.K. Sharma, S. Yadav, S. Dutta, H.B. Kale, I.R. Warkad, R. Zboril, R.S. Varma, M. B. Gawande, Silver nanomaterials: Synthesis and (electro/photo) catalytic applications, *Chem. Soc. Rev.* (2021).
- [4] P. Ryabchuk, G. Agostini, M.-M. Pohl, H. Lund, A. Agapova, H. Junge, K. Junge, M. Beller, Intermetallic nickel silicide nanocatalyst—A non-noble metal-based general hydrogenation catalyst, *Sci. Adv.* 4 (2018) eaat0761.
- [5] N. Sakai, K. Fujii, S. Nabeshima, R. Ikeda, T. Konakahara, Highly selective conversion of nitrobenzenes using a simple reducing system combined with a trivalent indium salt and a hydrosilane, *Chem. Commun.* 46 (2010) 3173–3175.
- [6] R.V. Jagadeesh, G. Wienhöfer, F.A. Westerhaus, A.E. Surkus, H. Junge, K. Junge, M. Beller, A Convenient and General Ruthenium-Catalyzed Transfer Hydrogenation of Nitro- and Azobenzenes, *Chemistry—A, European Journal* 17 (2011) 14375–14379.
- [7] Z. Zhang, C. Shao, Y. Sun, J. Mu, M. Zhang, P. Zhang, Z. Guo, P. Liang, C. Wang, Y. Liu, Tubular nanocomposite catalysts based on size-controlled and highly dispersed silver nanoparticles assembled on electrospun silica nanotubes for catalytic reduction of 4-nitrophenol, *J. Mater. Chem.* 22 (2012) 1387–1395.
- [8] K. Hemalatha, G. Madhumitha, A. Kajbafvala, N. Anupama, R. Sompalle, S. Mohana Roopan, Function of nanocatalyst in chemistry of organic compounds revolution: an overview, *Journal of Nanomaterials* 2013 (2013).
- [9] Y. Zheng, L. Hou, M. Liu, S.E. Newell, G. Yin, C. Yu, H. Zhang, X. Li, D. Gao, J. Gao, Effects of silver nanoparticles on nitrification and associated nitrous oxide production in aquatic environments, *Sci. Adv.* 3 (2017) e1603229.
- [10] R.P. Chauhan, C. Gupta, D. Prakash, Methodological advancements in green nanotechnology and their applications in biological synthesis of herbal nanoparticles, *International Journal of Bioassays (IJB)* (2012).
- [11] X. Li, H. Xu, Z.-S. Chen, G. Chen, Biosynthesis of nanoparticles by microorganisms and their applications, *Journal of Nanomaterials* 2011 (2011).
- [12] K.B. Louie, S.M. Kosina, Y. Hu, H. Otani, M. de Raad, A.N. Kufin, N.J. Mouncey, B. P. Bowen, T.R. Northen, Mass spectrometry for natural product discovery, (2020).
- [13] I. Pacheco-Fernández, V. Pino, Extraction with ionic liquids-organic compounds, Elsevier, Liquid-phase extraction, 2020, pp. 499–537.
- [14] H. Duan, D. Wang, Y. Li, Green chemistry for nanoparticle synthesis, *Chem. Soc. Rev.* 44 (2015) 5778–5792.
- [15] M.-R. Gao, Y.-F. Xu, J. Jiang, S.-H. Yu, Nanostructured metal chalcogenides: synthesis, modification, and applications in energy conversion and storage devices, *Chem. Soc. Rev.* 42 (2013) 2986–3017.
- [16] J.A. Glaser, *Green chemistry with nanocatalysts*, Springer, 2012.
- [17] R.A. Sheldon, Green solvents for sustainable organic synthesis: state of the art, *Green Chem.* 7 (2005) 267–278.
- [18] X. Jiang, Y. Xie, J. Lu, L. Zhu, W. He, Y. Qian, In-situ interface self-assemblies of nanocrystalline Ag₂E (E = S, Se, or Te) via chalcogen directional transfer agents, *J. Mater. Chem.* 11 (2001) 584–588.
- [19] K. Bhardwaj, S. Pradhan, S. Basel, M. Clarke, B. Brito, S. Thapa, P. Roy, S. Borthakur, L. Saikia, A. Shankar, Tunable NIR-II emitting silver chalcogenide quantum dots using thio/selenourea precursors: Preparation of an MRI/NIR-II multimodal imaging agent, *Dalton Trans.* 49 (2020) 15425–15432.
- [20] M. Jafari, M. Salavati-Niasari, F. Mohandes, Synthesis and characterization of silver selenide nanoparticles via a facile sonochemical route starting from a novel inorganic precursor, *J. Inorg. Organomet. Polym. Mater.* 23 (2013) 357–364.
- [21] K. Li, X. Liu, H. Wang, H. Yan, Rapid synthesis of Ag₂Se nanocrystals by sonochemical reaction, *Mater. Lett.* 60 (2006) 3038–3040.
- [22] A. Sahu, L. Qi, M.S. Kang, D. Deng, D.J. Norris, Facile synthesis of silver chalcogenide (Ag₂E; E = Se, S, Te) semiconductor nanocrystals, *J. Am. Chem. Soc.* 133 (2011) 6509–6512.
- [23] S.-Y. Zhang, C.-X. Fang, W. Wei, B.-K. Jin, Y.-P. Tian, Y.-H. Shen, J.-X. Yang, H.-W. Gao, Synthesis and electrochemical behavior of crystalline Ag₂Se nanotubes, *The Journal of Physical Chemistry C* 111 (2007) 4168–4174.
- [24] R. Gui, H. Jin, Z. Wang, L. Tan, Recent advances in synthetic methods and applications of colloidal silver chalcogenide quantum dots, *Coord. Chem. Rev.* 296 (2015) 91–124.
- [25] H. Tang, S.-T. Yang, D.-M. Ke, Y.-F. Yang, J.-H. Liu, X. Chen, H. Wang, Y. Liu, Biological behaviors and chemical fates of Ag₂Se quantum dots in vivo: the effect of surface chemistry, *Toxicol. Res.* 6 (2017) 693–704.
- [26] X.-L. Ge, Z.-L. Zhang, Z.-X. Xie, R. Cui, D.-W. Pang, Revealing the biodistribution and clearance of Ag₂Se near-infrared quantum dots in mice, *New J. Chem.* 41 (2017) 12721–12725.
- [27] F.A. Westerhaus, R.V. Jagadeesh, G. Wienhöfer, M.-M. Pohl, J. Radnik, A.-E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis of molecularly defined complexes, *Nat. Chem.* 5 (2013) 537–543.
- [28] R. Begum, Z.H. Farooqi, A.H. Aboo, E. Ahmed, A. Sharif, J. Xiao, Reduction of nitroarenes catalyzed by microgel-stabilized silver nanoparticles, *J. Hazard. Mater.* 377 (2019) 399–408.
- [29] A. Kumar, B. Paul, R. Boukherroub, S.L. Jain, Highly efficient conversion of the nitroarenes to amines at the interface of a ternary hybrid containing silver nanoparticles doped reduced graphene oxide/graphitic carbon nitride under visible light, *J. Hazard. Mater.* 387 (2020), 121700.
- [30] J. Hudzicki, Kirby-Bauer disk diffusion susceptibility test protocol, *American Society for Microbiology*, 2016.
- [31] L. Scorzoni, T. Benaducci, A.M.F. Almeida, D.H.S. Silva, V.D.S. Bolzani, M.J.S. M. Gianinni, The use of standard methodology for determination of antifungal activity of natural products against medical yeasts *Candida* sp and *Cryptococcus* sp, *Brazilian Journal of Microbiology* 38 (2007) 391–397.
- [32] Z.M. Alvand, H.R. Rajabi, A. Mirzaei, A. Masoumiasl, Ultrasonic and microwave assisted extraction as rapid and efficient techniques for plant mediated synthesis of quantum dots: green synthesis, characterization of zinc telluride and comparison study of some biological activities, *New J. Chem.* 43 (2019) 15126–15138.
- [33] S. Ravikumar, R. Gokulakrishnan, K. Selvanathan, S. Selvam, Antibacterial activity of metal oxide nanoparticles against ophthalmic pathogens, *Int J Pharm Res Dev* 3 (2011) 122–127.
- [34] Y. Liu, P. She, L. Chen, L. Xu, Y. Li, S. Liu, Z. Li, Z. Hussain, Y. Wu, Antimicrobial, antibiofilm, and anti-persister activities of penfluridol against *Staphylococcus aureus*, *Frontiers in Microbiology*, 2313.
- [35] S. Hebel-Gerber, A. García-Cancino, A. Urbina, M.J. Simirgiotis, J. Echeverría, L. Bustamante-Salazar, K. Sáez-Carrillo, J. Alarcón, E. Pastene-Navarrete, Chilean *Rhubarb*, *Gunnera tinctoria* (Molina) Mirb. (Gunneraceae): UHPLC-ESI-Orbitrap-MS Profiling of Aqueous Extract and its Anti-*Helicobacter pylori* Activity, *Front. Pharmacol.* 11 (2020).
- [36] Y.-P. Gu, R. Cui, Z.-L. Zhang, Z.-X. Xie, D.-W. Pang, Ultrasmall near-infrared Ag₂Se quantum dots with tunable fluorescence for in vivo imaging, *J. Am. Chem. Soc.* 134 (2012) 79–82.
- [37] H. Tang, S.-T. Yang, Y.-F. Yang, D.-M. Ke, J.-H. Liu, X. Chen, H. Wang, Y. Liu, Blood clearance, distribution, transformation, excretion, and toxicity of near-infrared quantum dots Ag₂Se in mice, *ACS Appl. Mater. Interfaces* 8 (2016) 17859–17869.
- [38] M. Nasrollahzadeh, S.M. Sajadi, Z. Issaabadi, M. Sajadi, Biological sources used in green nanotechnology, Elsevier, Interface science and technology, 2019, pp. 81–111.
- [39] H.R. Rajabi, F. Sajadiasl, H. Karimi, Z.M. Alvand, Green synthesis of zinc sulfide nanophotocatalysts using aqueous extract of *Ficus Johannis* plant for efficient photodegradation of some pollutants, *J. Mater. Res. Technol.* 9 (2020) 15638–15647.

- [40] K. Kumar, S. Srivastav, V.S. Sharanagat, Ultrasound assisted extraction (UAE) of bioactive compounds from fruit and vegetable processing by-products: A review, *Ultrason. Sonochem.* 70 (2021), 105325.
- [41] Z.M. Alvand, H.R. Rajabi, A. Mirzaei, A. Masoumiasl, H. Sadatfaraji, Rapid and green synthesis of cadmium telluride quantum dots with low toxicity based on a plant-mediated approach after microwave and ultrasonic assisted extraction: Synthesis, characterization, biological potentials and comparison study, *Mater. Sci. Eng., C* 98 (2019) 535–544.
- [42] J. Quintero Quiroz, A.M. Naranjo Duran, M. Silva Garcia, G.L. Ciro Gomez, J.J. Rojas Camargo, Ultrasound-assisted extraction of bioactive compounds from annatto seeds, evaluation of their antimicrobial and antioxidant activity, and identification of main compounds by LC/ESI-MS analysis, *International journal of food science*, 2019 (2019).
- [43] S. Al Jitan, S.A. Alkhoori, L.F. Yousef, Phenolic acids from plants: extraction and application to human health, *Stud. Nat. Prod. Chem.* 58 (2018) 389–417.
- [44] C.C. Yang, Y.-W. Mai, Thermodynamics at the nanoscale: A new approach to the investigation of unique physicochemical properties of nanomaterials, *Materials Science and Engineering: R: Reports* 79 (2014) 1–40.
- [45] F. Karimi, H.R. Rajabi, L. Kavoshi, Rapid sonochemical water-based synthesis of functionalized zinc sulfide quantum dots: study of capping agent effect on photocatalytic activity, *Ultrason. Sonochem.* 57 (2019) 139–146.
- [46] R.F. Elsupikhe, K. Shamel, M.B. Ahmad, N.A. Ibrahim, N. Zainudin, Green sonochemical synthesis of silver nanoparticles at varying concentrations of κ -carrageenan, *Nanoscale Res. Lett.* 10 (2015) 1–8.
- [47] V. Popov, I. Hinkov, S. Diankov, M. Karsheva, Y. Handzhiyski, Ultrasound-assisted green synthesis of silver nanoparticles and their incorporation in antibacterial cellulose packaging, *Green Process. Synth.* 4 (2015) 125–131.
- [48] P. Sibiya, M. Moloto, EFFECT OF PRECURSOR CONCENTRATION AND pH ON THE SHAPE AND SIZE OF STARCH CAPPED SILVER SELENIDE (Ag 2 Se) NANOPARTICLES, *Chalcogenide letters* 11 (2014).
- [49] D.W. Ayele, A facile one-pot synthesis and characterization of Ag₂Se nanoparticles at low temperature, *Egyptian Journal of Basic and Applied Sciences* 3 (2016) 149–154.
- [50] J. Ke, X. Li, Q. Zhao, Y. Hou, J. Chen, Ultrasensitive quantum dot fluorescence quenching assay for selective detection of mercury ions in drinking water, *Sci Rep* 4 (2014) 1–6.
- [51] Q. Cao, R. Che, Synthesis of near-infrared fluorescent, elongated ring-like Ag 2 Se colloidal nanoassemblies, *RSC Adv.* 4 (2014) 16641–16646.
- [52] N. Singh, V. Murugadoss, J. Rajavedhanayagam, S. Angaiah, A wide solar spectrum light harvesting Ag₂Se quantum dot-sensitized porous TiO₂ nanofibers as photoanode for high-performance QDSC, *J. Nanopart. Res.* 21 (2019) 1–10.
- [53] M. Shamsipur, H.R. Rajabi, Study of photocatalytic activity of ZnS quantum dots as efficient nanoparticles for removal of methyl violet: effect of ferric ion doping, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 122 (2014) 260–267.
- [54] H.R. Rajabi, M. Farsi, Study of capping agent effect on the structural, optical and photocatalytic properties of zinc sulfide quantum dots, *Mater. Sci. Semicond. Process.* 48 (2016) 14–22.
- [55] H.R. Rajabi, M. Farsi, Effect of transition metal ion doping on the photocatalytic activity of ZnS quantum dots: synthesis, characterization, and application for dye decolorization, *J. Mol. Catal. A: Chem.* 399 (2015) 53–61.
- [56] B. Ramezanloo, M. Molaie, M. Karimipour, Red emissive Ag₂Se quantum dots (QDs) with room-temperature synthesis of both orthorhombic and superionic cubic phases via stirring approach, *J. Lumin.* 204 (2018) 419–423.
- [57] H.R. Rajabi, H. Arjmand, H. Kazemdehdashti, M. Farsi, A comparison investigation on photocatalytic activity performance and adsorption efficiency for the removal of cationic dye: quantum dots vs. magnetic nanoparticles, *J. Environ. Chem. Eng.* 4 (2016) 2830–2840.
- [58] H.R. Rajabi, F. Karimi, H. Kazemdehdashti, L. Kavoshi, Fast sonochemically-assisted synthesis of pure and doped zinc sulfide quantum dots and their applicability in organic dye removal from aqueous media, *J. Photochem. Photobiol., B* 181 (2018) 98–105.
- [59] B. Pejova, M. Najdoski, I. Grozdanov, S.K. Dey, Chemical bath deposition of nanocrystalline (111) textured Ag₂Se thin films, *Mater. Lett.* 43 (2000) 269–273.
- [60] M. Jafari, M. Salavati-Niasari, A. Sobhani, Silver selenide nanoparticles: synthesis, characterisation and effect of preparation conditions under ultrasound radiation, *Micro & Nano Letters* 8 (2013) 508–511.
- [61] W.M. Shume, H. Murthy, E.A. Zereffa, A review on synthesis and characterization of Ag₂O nanoparticles for photocatalytic applications, *J. Chem.* 2020 (2020).
- [62] S.F. Hashemi, N. Tasharofi, M.M. Saber, Green synthesis of silver nanoparticles using Teucrium polium leaf extract and assessment of their antitumor effects against MNK45 human gastric cancer cell line, *J. Mol. Struct.* 1208 (2020), 127889.
- [63] L. Hssaini, R. Ouaabou, R. Razouk, J. Charafi, H. Hanine, K. Houmanat, S. Ennahli, R. Lahlali, ATR-FTIR Spectroscopy Combined with the In Vitro Antioxidant Activity and Chromaticity for Rapid Discrimination of Fig (*Ficus carica* L.) Cultivars, *Journal of Analysis and Testing* 5 (2021) 270–285.
- [64] H.M. Ibrahim, Green synthesis and characterization of silver nanoparticles using banana peel extract and their antimicrobial activity against representative microorganisms, *J. Radiat. Res. Appl. Sci.* 8 (2015) 265–275.
- [65] V. Manikandan, P. Velmurugan, J.-H. Park, W.-S. Chang, Y.-J. Park, P. Jayanthi, M. Cho, B.-T. Oh, Green synthesis of silver oxide nanoparticles and its antibacterial activity against dental pathogens, *J. Biotech* 7 (2017) 1–9.
- [66] K. Steffy, G. Shanthi, A.S. Maroky, S. Selvakumar, Synthesis and characterization of ZnO phytonanocomposite using *Strychnos nux-vomica* L. (Loganiaceae) and antimicrobial activity against multidrug-resistant bacterial strains from diabetic foot ulcer, *J. Adv. Res.* 9 (2018) 69–77.
- [67] S. Chand, P. Sharma, Synthesis and characterization of Ag-chalcogenide nanoparticles for possible applications in photovoltaics, *Materials Science-Poland* 36 (2018) 375–380.
- [68] S. Talaviya, F. Majmudar, Green chemistry: A tool in Pharmaceutical Chemistry, *NHL Journal of Medical Sciences* 1 (2012) 7–13.
- [69] R.C. Fierascu, A. Ortan, S.M. Avramescu, I. Fierascu, Phyto-nanocatalysts: Green synthesis, characterization, and applications, *Molecules* 24 (2019) 3418.
- [70] H. Gong, L. Lin, X. Zhao, H. Li, D. Li, Z. Xu, M. Chen, R. Huang, Z. Hou, Atomically precise Ag nanoclusters intercalated in zirconium pyrophosphate for efficient hydrogenation of nitroaromatics, *Appl. Catal. A* 574 (2019) 1–9.
- [71] Z. Li, X. Xu, X. Jiang, Y. Li, Z. Yu, X. Zhang, Facile reduction of aromatic nitro compounds to aromatic amines catalysed by support-free nanoporous silver, *RSC Adv.* 5 (2015) 30062–30066.
- [72] N. Salam, B. Banerjee, A.S. Roy, P. Mondal, S. Roy, A. Bhaumik, S.M. Islam, Silver nanoparticles embedded over mesoporous organic polymer as highly efficient and reusable nanocatalyst for the reduction of nitroarenes and aerobic oxidative esterification of alcohols, *Appl. Catal. A* 477 (2014) 184–194.
- [73] A.K. Patra, N.T. Vo, D. Kim, Highly robust magnetically recoverable Ag/Fe₂O₃ nanocatalyst for chemoselective hydrogenation of nitroarenes in water, *Appl. Catal. A* 538 (2017) 148–156.
- [74] P. Mohammadi, M. Heravi, M. Daraie, Ag nanoparticles immobilized on new magnetic alginate halloysite as a recoverable catalyst for reduction of nitroaromatics in aqueous media, *Sci. Rep.* 11 (2021) 1–10.
- [75] N. Vahedi-Notash, M.M. Heravi, A. Alhampour, P. Mohammadi, Ag nanoparticles immobilized on new mesoporous triazine-based carbon (MTC) as green and recoverable catalyst for reduction of nitroaromatic in aqueous media, *Sci. Rep.* 10 (2020) 1–9.
- [76] S. Vinay, H. Sumedha, G. Nagaraju, S. Harishkumar, N. Chandrasekhar, Facile combustion synthesis of Ag₂O nanoparticles using cantaloupe seeds and their multidisciplinary applications, *Appl. Organomet. Chem.* 34 (2020) e5830.
- [77] A. Nouri, M.T. Yarak, A. Lajevardi, Z. Rezaei, M. Ghorbanpour, M. Tanzifi, Ultrasonic-assisted green synthesis of silver nanoparticles using *Mentha aquatica* leaf extract for enhanced antibacterial properties and catalytic activity, *Colloid Interface Sci. Commun.* 35 (2020), 100252.
- [78] H.R. Rajabi, R. Naghihi, M. Kheirizadeh, H. Sadatfaraji, A. Mirzaei, Z.M. Alvand, Microwave assisted extraction as an efficient approach for biosynthesis of zinc oxide nanoparticles: synthesis, characterization, and biological properties, *Mater. Sci. Eng., C* 78 (2017) 1109–1118.