

RESEARCH PAPER

A Facile and Green Biosynthesis of Silver Nanostructures by Aqueous Extract of *Suaeda Acuminata* after Microwave Assisted Extraction

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ABSTRACT

In the present study, a simple, efficient and fast synthetic strategy was reported for the green biosynthesis of silver nanostructures (i.e. nanorods and Nanostructures) by the extract of *Suaeda Acuminata* plant, without any catalyst, template or surfactant. Aqueous extracts were obtained by maceration and microwave assisted extraction (MAE) methods. In MAE procedure, the effect of microwave power on the extracted compounds was studied at 90, 270 and 450 W. Colloidal nano-scaled silver samples were synthesized by reacting aqueous silver nitrate with *Suaeda Acuminata* leaf extract at non-photomediated conditions. Comparative characterizations of the prepared Ag nanostructures were carried out by different techniques including UV-Vis absorption spectroscopy, scanning electron microscopy, X-ray diffraction, and FT-IR spectroscopy. The SEM images showed that it can be synthesized Ag nanorods and Nanostructures with the average size of 132 nm and 73 nm, by maceration and MAE methods, respectively. According to UV-Vis absorption spectra, a broad absorption peak around 400 nm was observed for all prepared Ag nanostructure samples synthesized by maceration and MAE methods, at different reaction times and irradiation microwave powers. The band can be corresponded to the plasmon absorbance of nano-scaled silver samples.

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INTRODUCTION

Today, development of eco-friendly procedures for the synthesis of nanostructures or the green nanochemistry is interested [1]. The biosynthesis of Nanostructures, which represents a connection between biotechnology and nanotechnology, has received increasing consideration due to the growing need to develop environmentally friendly technologies for material syntheses [2]. Among noble metal Nanostructures, silver Nanostructures have wide area of interest as they have large number of applications such as in non-linear optics, spectrally selective coating for solar energy absorption, biolabelling, intercalation materials for electrical batteries as optical receptors, catalyst in chemical reactions and as antibacterial capacities [3]. Natural sources of reducing materials such as plants,

fungi, honey, bacteria, and yeast could be used for preparation of silver and gold Nanostructures [4].

On the other hands, microwave heating has been found to be a convenient source of energy in the chemical laboratories [5]. Conventional extraction methods are typically associated with high solvent consumption, longer extraction times and increased risk of degradation of thermo-labile constituents [6]. Up to date, a variety of plant and fruit extracts have been used for the synthesis of silver Nanostructures; however, there is no data in the literature about the usage of *Suaeda Acuminata* (Scheme 1) for silver Nanostructures synthesis. Therefore, the objectives of this study were to develop a green and fast procedure based on microwave method for the synthesis of Ag Nanostructures by aqueous extracts of *Suaeda Acuminata* plant.

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EXPERIMENTAL

Materials and Chemicals

Suaeda Acuminata was collected from Abadan, Iran, during August 2014. After being washed thoroughly, were dried in 40 °C, then smashed finely and the powder screened by 100-mesh sieve, finally stored for late use. All chemical reagents were analytical grade, prepared from Merck Company.

Apparatus

In MAE process, a microwave device (model of KOC-9N8T, DAEWOO Company, Korea) was used to carry out the extraction step. Optical absorption spectra were recorded using a Perkin-Elmer UV-Vis double beam LAMBADA-25 spectrophotometer. The X-ray diffraction (XRD) pattern was obtained using STOE-Stidy-mp Diffractometer with Cu K α source ($\lambda = 1.541786 \text{ \AA}$). Infrared spectra were studied using a JASCO FT/IR-680 plus spectrometer. SEM images were recorded on a Philips XL30 series instrument using a gold film for loading the dried particles on the instrument.

Biosynthesis of Ag Nanoroads and Nanostructures Using the Extracts of MAE and Maceration

Plant extracts are known to contain several small molecules which may have the potential to carry out reduction of Ag⁺ ions to Ag followed by their stabilization [7]. In maceration method, 5 g of aerial parts *Suaeda Acuminata* plant was macerated with 100 ml deionized water for 48 h in Meyer flask. After filtration, the final volume of the solution was diluted to 100 ml by deionized water. In MAE process, aqueous extracts were obtained after microwave heating of 5 g of the plant powder with 100 ml deionized water for 15 min in Round-

bottom flask with condenser connected at different power (*i.e.* 90, 270 and 450 W). The extracts were stored at room temperature in order to be used for further experiments.

In addition, the obtained extracts by both method was used as reducing precursor for the biosynthesis of silver Nanostructures, while the volume ratio of extract, silver solution, and ammonia solution were 4, 2 and 1, respectively [8]. In a typical reaction procedure, 10 ml of aqueous extract added to a Meyer flask, in the presence of 2.5 ml of concentrated ammonia. After it, 5 ml of 0.001 M aqueous solution of silver nitrate was added drop-wise to the above solution for 45 min, under magnetic stirring and nitrogen atmosphere. The color of the solution changed immediately from yellowish-brown to dark-brown after the extract was added. The obtained samples were centrifuged at 4000 rpm for 10 min, subsequently washed three times and dispersed in deionized water to eliminate the non-coordinated materials.

RESULTS AND DISCUSSION

Colorimetry and Scanning Electron Microscopy (SEM)

Reduction of Ag⁺ into Ag during exposure to water extract of *Suaeda Acuminata* could be followed by the color change. The fresh suspension of *Suaeda Acuminata* was yellow in color (Fig. 1). However, after addition of AgNO₃ and stirring at room temperature, the emulsion turned to dark brown (Fig. 1). The color changes in aqueous solutions are due to the surface plasmon resonance phenomenon. The result obtained in this investigation is found to be interesting because it can serve as a foundation in terms of identification of potential forest plants for synthesizing Ag nanostructures.



Scheme 1. Photographical images of Suaeda Acuminata plant

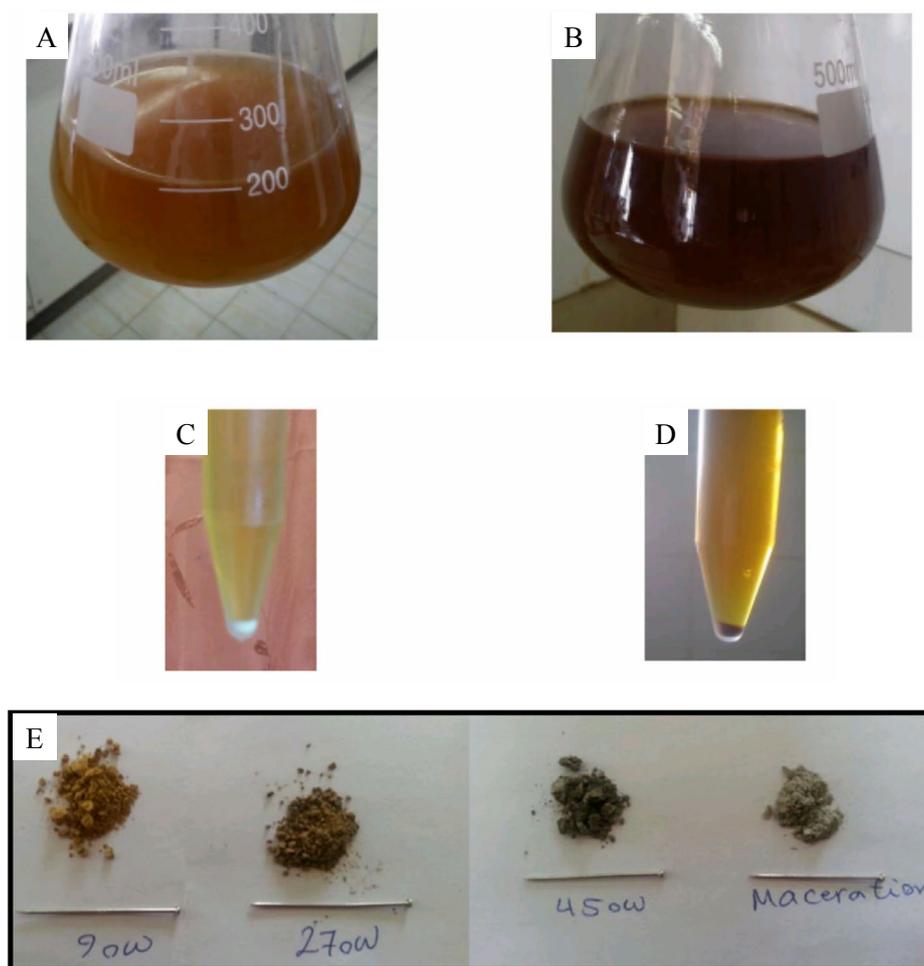


Fig. 1. Colorimetric results of the prepared Ag samples. Color of aqueous extract (A) before and (B) after addition of silver nitrate. Color of the prepared samples after (C) 10 min and (D) 1 h, and (E) image of the dried Ag samples in different synthetic conditions.

The SEM micrograph provided further information about the morphological characteristics of the particles synthesized. The SEM images of the nano-scaled Ag samples prepared by maceration and MAE methods, at a magnification of 20.0 K were presented in Fig. 2. SEM images (Figs. 2A, B) show silver nanorods and agglomerated silver Nanostructures, respectively. However, the agglomeration of the particles may be due to some parameters such as: particle size, particle size distribution, macroscopic particle shape, and microscopic shape (surface configuration). We suggest that this change in particle morphology can be due to the type, efficiency, and amount of the major reductant compounds in the aqueous extract obtained by different methods for biosynthesis of silver nanostructures. However, it can be

concluded that both maceration and MAE aqueous extracts of *Suaeda Acuminata* contain the suitable bioreductant for biosynthesis of the nanometer-sized silver particles and rods. From SEM images, the average size of Ag samples obtained by maceration and MAE methods were observed to be 132 nm and 73 nm, respectively.

UV-Vis Absorption Spectroscopic Analyses

UV-Vis spectroscopy is a powerful tool to observe the formation of metal Nanostructures [7]. To investigate the absorption pattern of biosynthesized silver Nanostructures, the samples were periodically recorded by UV-Vis spectrophotometer between 300 and 600 nm. It is well known that silver Nanostructures exhibit lovely red colors, this color arises due to the excitation of surface plasmon

vibrations in the silver Nanostructures [9]. As shown in Fig. 3, the formation of silver Nanostructures was confirmed by the presence of an absorption peak at visible region, around 420 nm. This pattern is in good agreement with the reported spectra in the literature for the silver Nanostructures [7-11].

It is worth to note that metallic Nanostructures (such as silver) possess the free electrons abundance, which they could move through conduction and

valence band. These free electrons are responsible for surface plasmon resonance (SPR) absorption band of the metal Nanostructures [10]. The peak is consigned to a surface plasmon phenomenon for various metal Nanostructures with sizes ranging from 2-100 nm [11]. Meanwhile, the obtained spectra from silver sample revealed that increasing the reaction time leads to changing the intensity of the silver peaks at 420 nm.

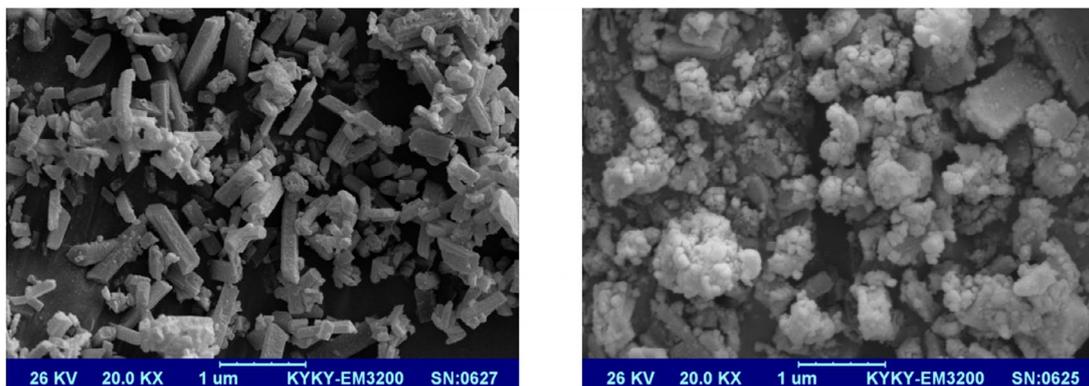


Fig. 2. SEM images of the Ag Nanostructures prepared by (A) maceration and (B) MAE methods, at a magnification of 20.0 K.

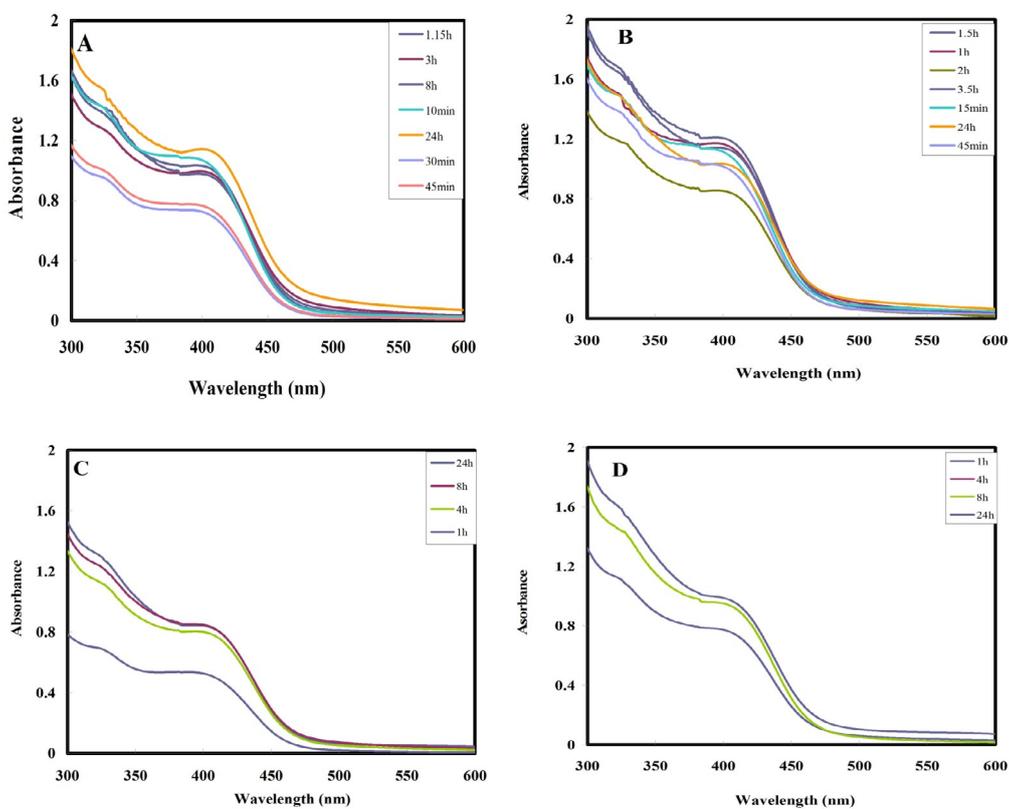


Fig. 3. UV-Vis absorption spectra of the Ag nanostructures prepared at different conditions: (A) 90 W, (B) 270 W, (C) 450 W irradiation power, (D) maceration.

FT-IR Spectra of the Prepared Ag Nanostructures

The FT-IR spectra of Ag nanostructures with obvious peaks around 3400, 2950, 1600, 1000 and 770 cm^{-1} were observed (Fig. 4). The spectra obtained to characterize the interaction between silver nitrate and the plant extract obtained by maceration and MAE methods with different irradiation power. These peaks corresponds to C-H group (stretch strong), C-H group (variable), C=O group (strong), C=C group (strong), CH_2 group

(variable), reflecting its complex nature. A peak at 3417 cm^{-1} results due to the stretching of the N-H bond of amino groups. Moreover, the highest absorption peak 3417 reflects that the bonded hydroxyl (-OH) group might be responsible for the educing property of the extract [12].

XRD Results

X-ray diffraction studies were performed to confirm the crystalline structure of Ag

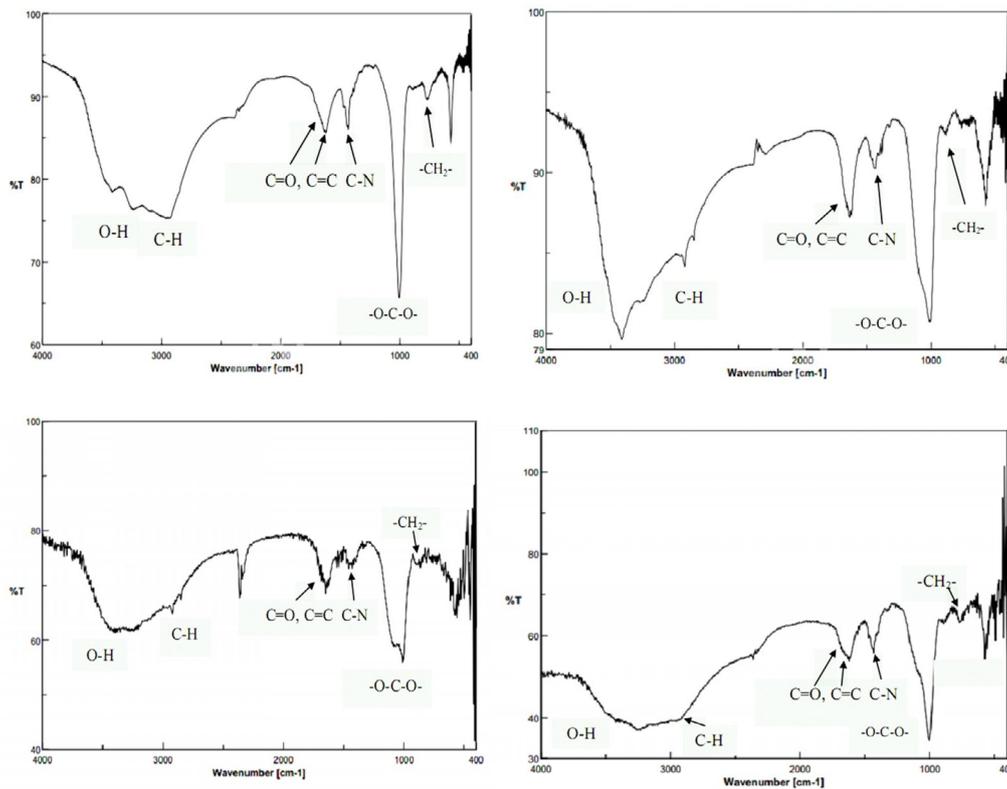


Fig. 4. FT-IR results of the Ag nanostructures prepared at different conditions: (A) 90 W, (B) 270 W, (C) 450 W irradiation power, (D) maceration

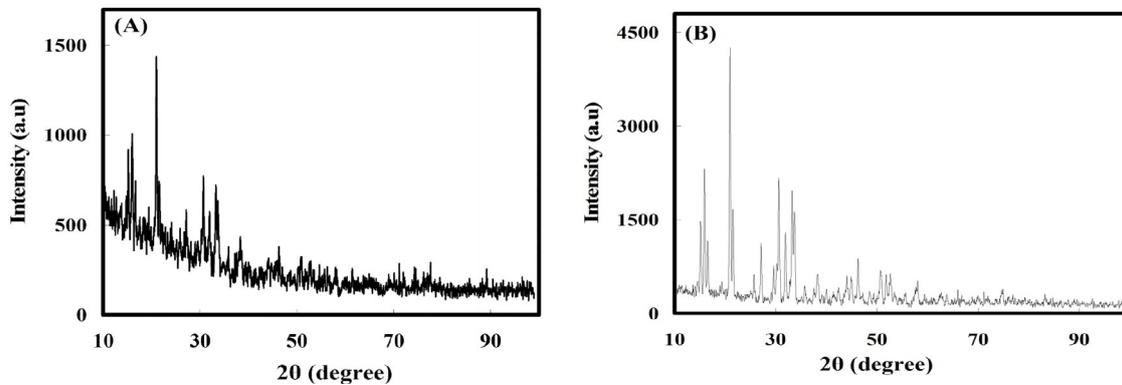


Fig. 5. XRD results of the Ag nanostructures prepared by (A) maceration and (B) MAE methods.

nanostructures synthesized by aqueous extracts obtained by maceration and MAE methods. It showed distinct diffraction peaks which could be assigned to (1 1 1), (2 0 0) and (2 2 0) of nano-scaled Ag samples, respectively and were in agreement with the database of Joint Committee on Powder Diffraction Standards (JCPDS No. 04-0784) [13]. Moreover, the XRD results thus show that the silver Nanostructures formed are crystalline (Fig. 5). The unidentified crystalline peaks are also observed in many works, which are due to the presence of organic compounds in the extracts [14].

CONCLUSIONS

In the present work, we have demonstrated, for the first time, extracellular green synthesis of Ag nanostructures using aqueous extract of *Suaeda Acuminata*. The aqueous extracts were obtained by maceration and MAE methods and were used for the reduction of Ag⁺ ions to Ag species with morphology of Nanostructures. The development of nanostructures was monitored by UV-Vis spectroscopy and its results showed that most of the particles were formed during the first hour of green synthesis reaction. This study exhibits the potential of *Suaeda Acuminata* aqueous extract for the simple and green synthesis of silver nanostructures with several advantages such as low cost, compatibility for medical and pharmaceutical applications as well as potential for large scale production.

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