FACILE 'PHYTO' FABRICATION OF SILVER NANOPARTICLES OF DIVERSE GEOMETRIES WITH CONCOMITANT UTILIZATION OF A PERNICIOUS TERRESTRIAL WEED

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Abstract

We report, for the first time, shape-tuned and size-tuned synthesis of silver nanoparticles using extracts of the weed lantana (*Lantana camara*). The purity, crystal structure and possible biomolecules responsible for the nanoparticle formation were explored with SEM, Hr-SEM, TEM, EDAX, XRD, zetasizer and FTIR techniques. The distinguishing feature of the present study is that it enables the fabrication of silver nanoparticles with a non-hazardous, energy-saving, and cost effective method. Simultaneously the study enables gainful utilization of an obnoxious invasive weed, which is otherwise not only worthless but also seriously harmful to the environment.

Keywords- Bioinspired synthesis; terrestrial weed; whole plant; shape control; silver nanoparticles

I. INTRODUCTION

Nanotechnology is an umbrella term covering a wide range of technologies concerned with structures and processes on the nanometer scale [1]. As the realm of nanotechnology lies between the atomic and the mesocopic levels, it has the potential to solve many problems which the atomic or the mesoscale operations have failed to solve. It also has the potential to open up new fields of application. The trust of nanotechnology is built around nanoparticles. Hence synthesis of nanoparticles in an economical and eco-friendly manner forms the very basis of nanotechnology.

Nanoparticles can be synthesized by physical, chemical and biological means but the first two routes often entail the use of high energy inputs and/or high temperatures and pressures. Toxic chemicals are also often employed. In contrast biological method which use microorganisms, algae, or plant extracts to generate nanoparticles in a way it is done in nature-i.e. by biomimetics – are much cleaner and 'greener'. This aspect has bestowed great relevance to the field of biomimetic nanoparticles synthesis [2].

A number of living organisms are already well-known to elaborate nanostructure composites such as cyanobacteria, bacteria, fungi, actinomycetes, biomolecules and the use of plant extracts to extra-cellularly synthesize metallic nanoparticles is a recently developed approach. The plant species that have been explored, include, *Azadirachta indica*, *Emblica officinalis*, *Capsicum annum*, *Camellia sinensis*, *Parthenium hysterophorus*, *Argimone maxicana*, *Mimosa pudica*, *Syzygium cumini*, *Desmodium triflorum*, [3], and neem [4]. These plants encompass fruits, vegetables, cereals, spices, medicine and other foodstuff, etc, which already have well-established uses and entail substantial costs of production. Also process developed for silver nanoparticle synthesis using economically important plants and weeds was performed with few parts of the plant (e.g. Leaf, fruit, seed).

In contrast the present study utilizes different parts and whole plant of the weed lantana (*L. camara*), which is not only freely available in huge quantities but also worthless and harmful to the environment in general. In fact considerable expenditure is routinely incurred in removing these weeds or controlling them with herbicides. Moreover for morphology-controlled nanoparticle synthesis the reported processes had required rigorous controls, such as maintaining pH and temperature, and had other requirements such as agitation. In comparison the methods based on the present study are less complex, more versatile and much more cost-effective. The principle objective of this work was to study and optimize the process variables (for monodispersed and polydispersed silver nanoparticles) like bioagent proportion to that of metallic solution and their interaction time on the biomimetic synthesis of silver nanoparticles by the aqueous extract of the species *L. camara*.

L. camara, which belongs to the family Verbinaceae, is regarded as one of the worst weeds of the world. It has become a particularly serious problem in tropical countries, as it has invaded millions of hectares of land. Prolific seed production and easy dispersal helps it in colonizing vast tracts of land very quickly and becoming a pest. Its infestations have been so persistent that they have completely excluded other plants and have prevented all attempts of eradication. Its allelopathic properties further bolster its invasiveness.

II. MATERIALS AND METHODS

A. Preparation of plant extracts of L. camara

Lantana plant was collected from the region in Pondicherry University campus and was brought into the laboratory. The mature, fresh and disease-free plant parts (leaf, tender stem, hard stem, root and whole plant) were selected. Freshly collected plants were cleaned thoroughly in fresh water, followed by dipping in saline water (3 min) for surface sterilization. Then it was again rinsed thrice in de-ionized distilled water followed by blotting the water from surfaces of the plant. A known weight equivalent to 1g of dry weight (leaf – 5.60 g; tender stem – 5.88 g; hard stem – 3.24; root – 3.98 and whole plant – $1.40 + 1.47 + 0.81 + 1.0$ g in fresh weight) of samples were taken and cut into uniform sizes of $1\,\text{cm} \times 1\,\text{mm}$. Extracts were further prepared by transferring the cut portions into 250 ml Erlenmeyer flask and boiled with 100 ml of sterile distilled water for 3 min in water bath and named as leaf extract (LE), tender stem extract (TSE), hard stem extract (HSE), root extract (RE) and whole plant (WPE). The contents were decanted after cooling through nylon mesh and filtered through whatmann no.42 filter paper. Filtered extracts were then stored under refrigeration and were used with 3 days.

B. Synthesis of silver nanoparticle

Silver nitrate was procured from Merck chemicals. All glassware was cleaned with labolene and distilled water and dried in oven. Preliminary studies were performed by mixing varying the proportion of the $AgNO_3$ (1mM) aqueous solution and the plant extracts for synthesis of silver nanoparticles. At stoichiometric ratios differing in a fairly wide band, the nanoparticles formation began immediately on bringing the lantana extracts and the $AgNO_3$ solution together evidenced by the appearance of brownish yellow color characteristic of silver nanoparticles. The reaction mixtures were incubated at ambient temperature. The spectra of all the reaction mixtures were recorded using UV-visible spectrophotometer (Labindia 3000+) with 1 nm resolution.

C. Characterization of the synthesized silver nanoparticles

UV-visible spectrum gives us information about the nature, size and shape of the particles synthesized. It is generally recognized that UV–visible spectroscopy could be used to examine size-and shape-controlled nanoparticles in aqueous suspensions [5]. The plasmon absorption of the silver nanoparticles produced was monitored and periodic recording of the spectrum was done as a function of time at room temperature using a quartz cuvette with water as reference. It is reported that the absorption spectrum of spherical silver nanoparticles presents a maximum between 420 nm and 450 nm with a blue or red shift when particle size diminishes or increases, respectively. The stability of the peak wavelength, absorbance, change in color of the reaction mixture, type of peaks obtained etc., were noted. After the UV-visible spectral study, the selected reaction mixtures were centrifuged, at 12,000 rpm for 20 min using Remi C 24 centrifuge. The pellets obtained was washed thrice with distilled water to remove the excess un-reacted biomolecules and dispersed in distilled water for further characterization.

The morphology and size of as-formed silver were determined by SEM, employing a Hitachi, Model: S-3400N microscope. Samples for SEM studies were prepared by placing a drop of suspension on to carbon-coated SEM grid. Hr-SEM studies were performed using the instrument FEI Quanta FEG 200, by placing dry powder of palletized sample on carbon coated SEM grid. The corresponding EDAX (energy dispersive analysis of X-rays) spectrum was recorded in the spot-profile mode by focusing on the densely populated silver nanoparticle region. TEM analysis was performed using the instrument model: JEM-2100, by placing a suspension of synthesized silver nanoparticles.

The crystallinity of silver nanoparticles was characterized by XRD using X'Pert PRO X-ray diffractometer (PANalytical BV, The Netherlands) operated at a voltage of 40 kV and a current of 30mA

with Cu $K\alpha$ radiation in a $\theta - 2\theta$ configuration. High Score software was used for the search-match phase identification analyses. The crystallite domain size was calculated from the width of the XRD peaks, assuming that they are free from non-uniform strains, using the Scherrer formula,

$$D = 0.94\,\lambda/\beta\cos\theta$$

Where, D is the average crystallite domain size perpendicular to the reflecting planes, λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ is the diffraction angle [6]. The synthesized silver particles were also studied under particle size analyzer using the instrument Malvern Zetasizer. The purified suspension was completely oven dried. Finally, the dried nanoparticles were analysed and FTIR measurements were carried out to identify the possible biomolecules responsible for the synthesis of nanoparticles by the plant used. The Fourier Transform Infrared (FTIR) spectra were recorded using thermo Nicolet Model 6700 spectrometer in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets for a wave number range of 4000 to 400 in the mid-IR region.

III. RESULTS AND DISCUSSION

A. UV-visible spectral studies

The onset of silver nanoparticle formation can be visually sensed by a gradual appearance of brownish

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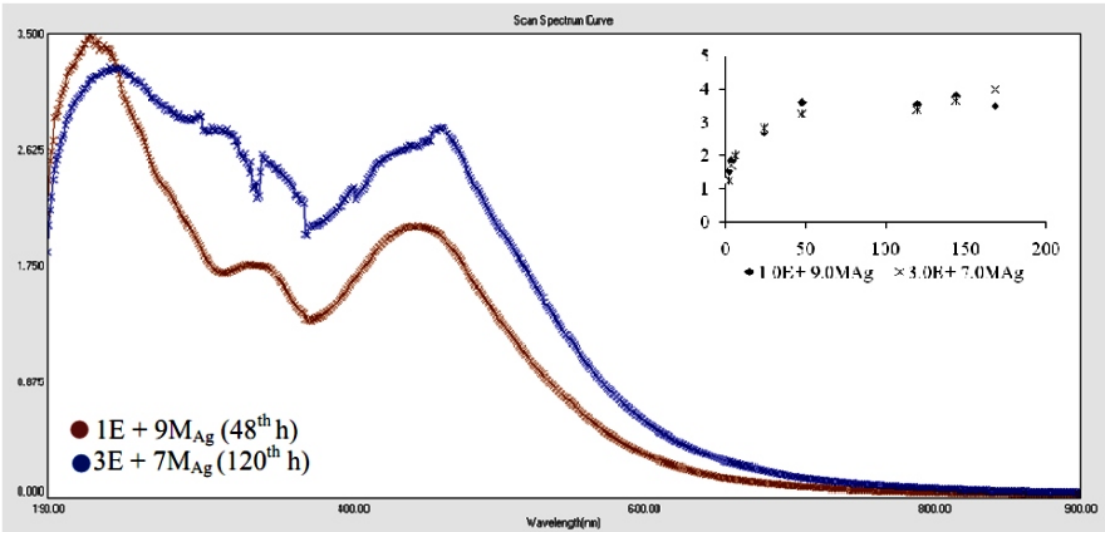

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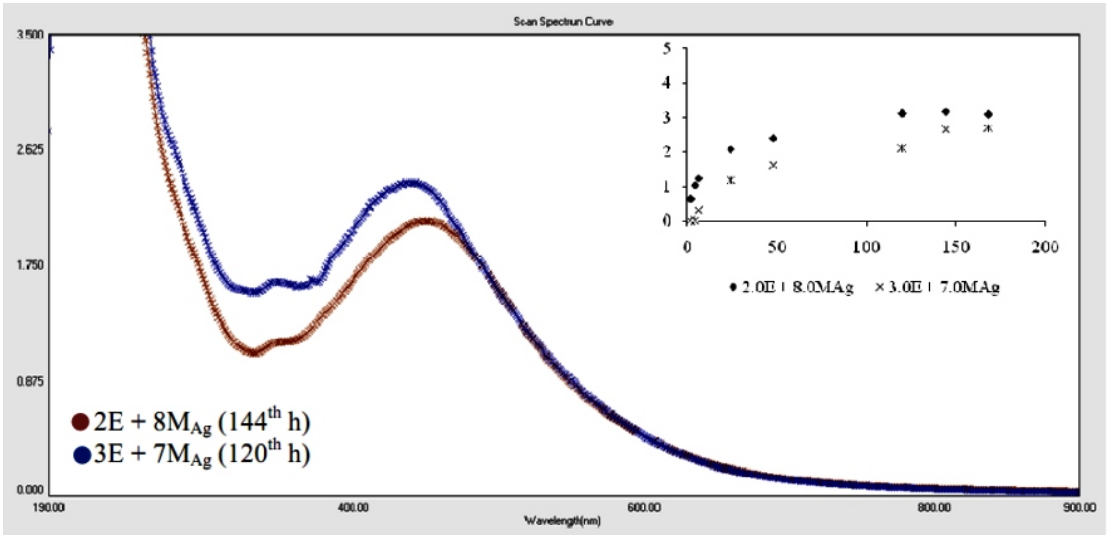

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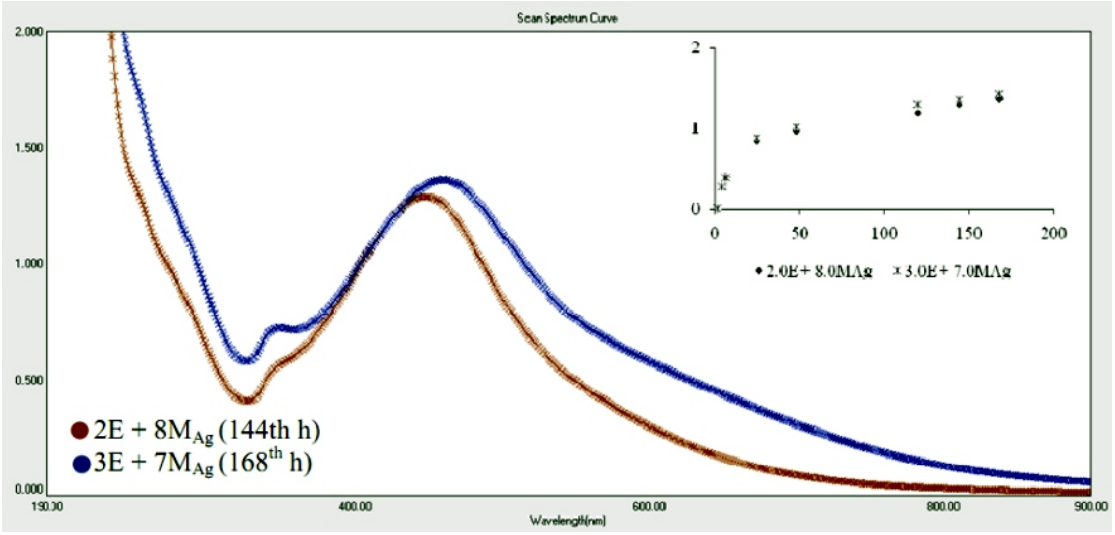

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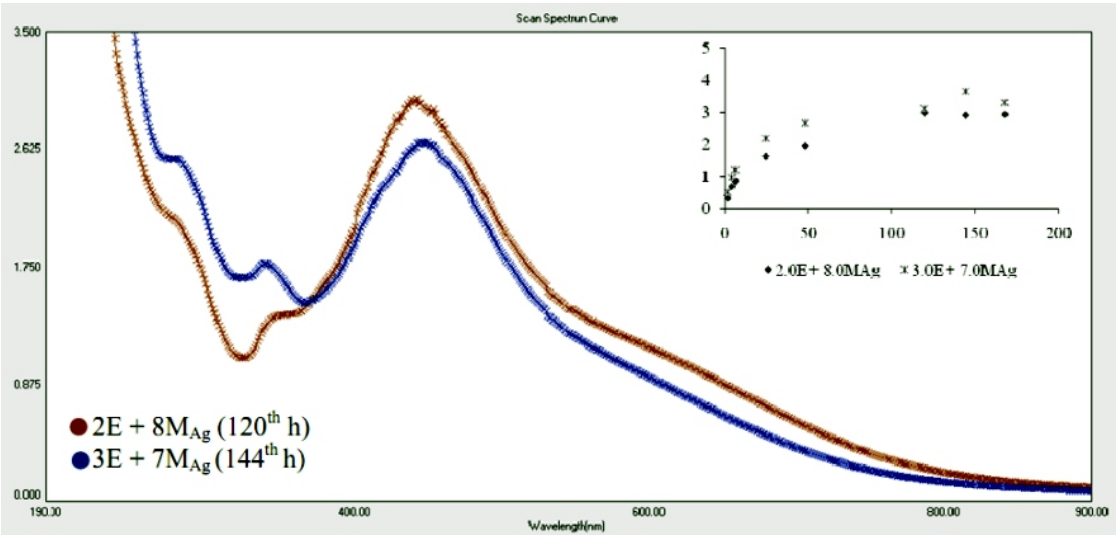

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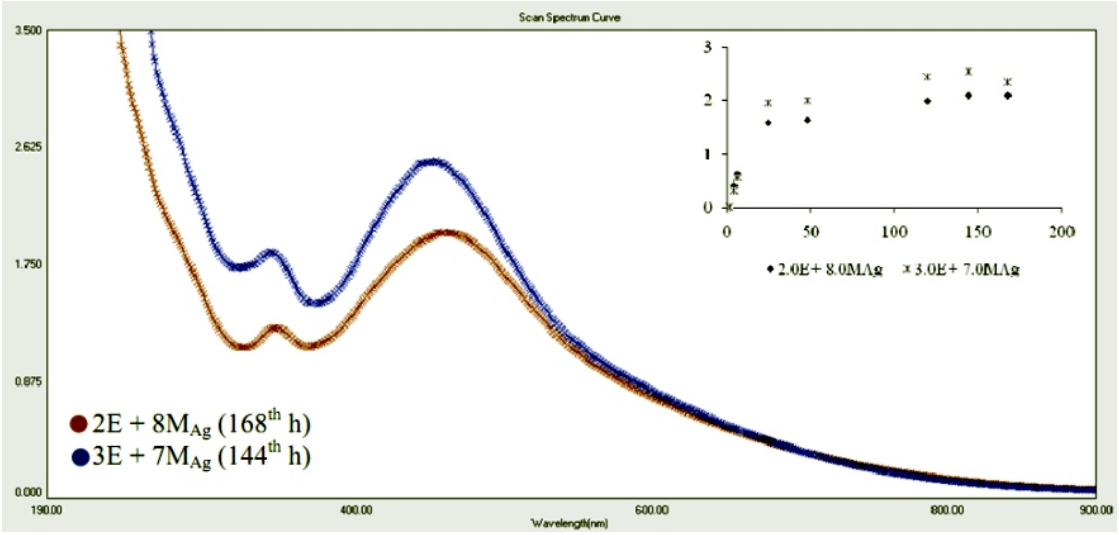
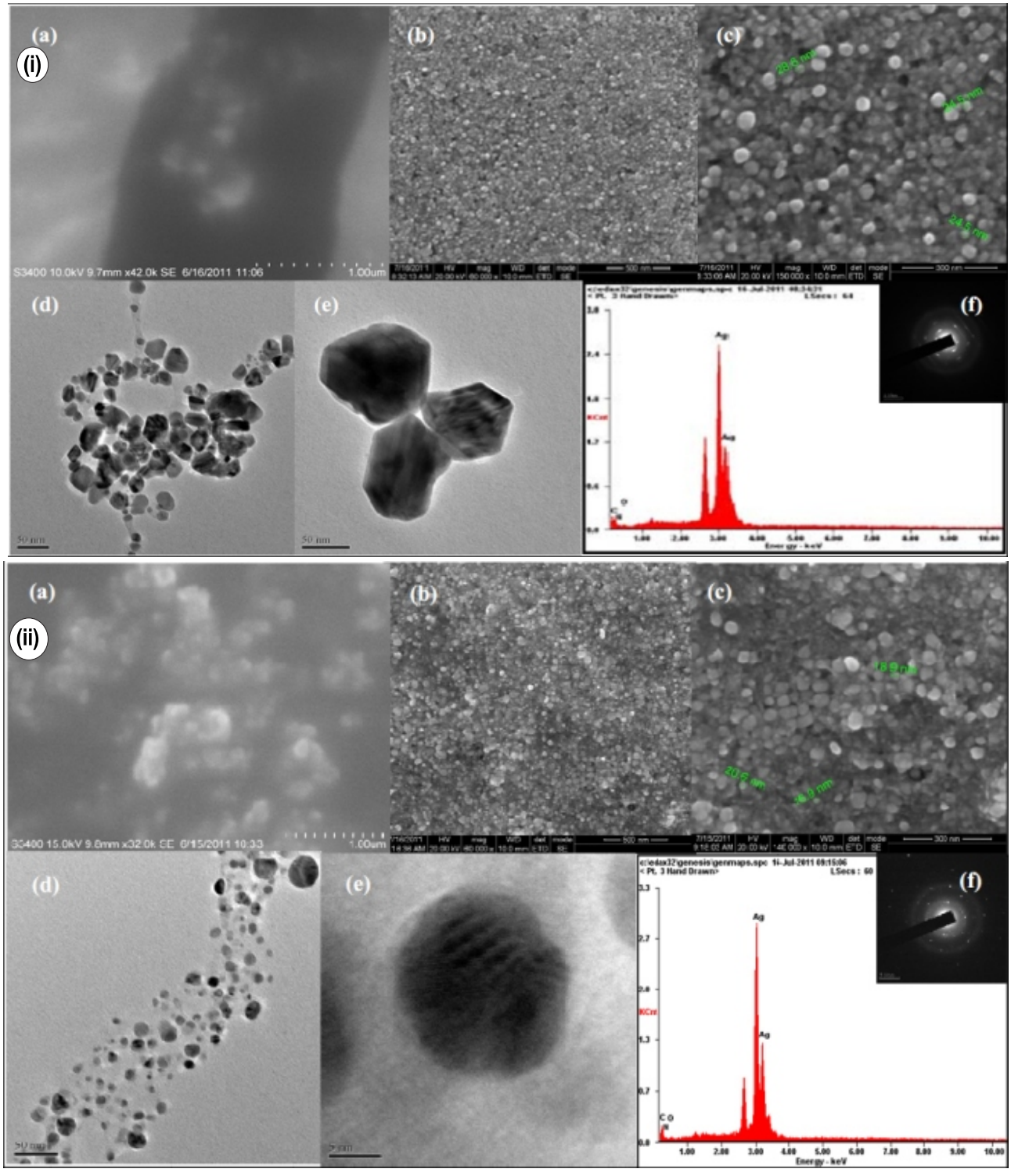


Fig. 1. UV-Visible spectra of silver nanoparticles synthesized using, (a) LE, (b) TSE, (c) HSE, (d) RE, and (e) WPE (Inset is the plot of the intensity of the surface plasmon resonances against the reaction time).

yellow to reddish brown color within 5 min as soon as the metallic solution was challenged with the plant extract. From the results obtained, the combinations with stable wavelength, maximum intensity were selected and further characterized. Figure 1 shows the UV-visible spectrum recorded for various combinations for the synthesized silver nanoparticles. The spectrum clearly shows the presence single peak, centered at 444 nm & 462 nm, 455 nm & 439 nm, 449 nm & 460 nm, 443 nm & 469 nm, and 461 nm & 454 nm for the combinations 1.0E + 9.0M_{Ag} & 3.0E + 7.0M_{Ag}; 2.0E + 8.0M_{Ag} & 3.0E + 7.0M_{Ag} in the studies performed with LE; TSE, HSE, RE and WPE respectively.



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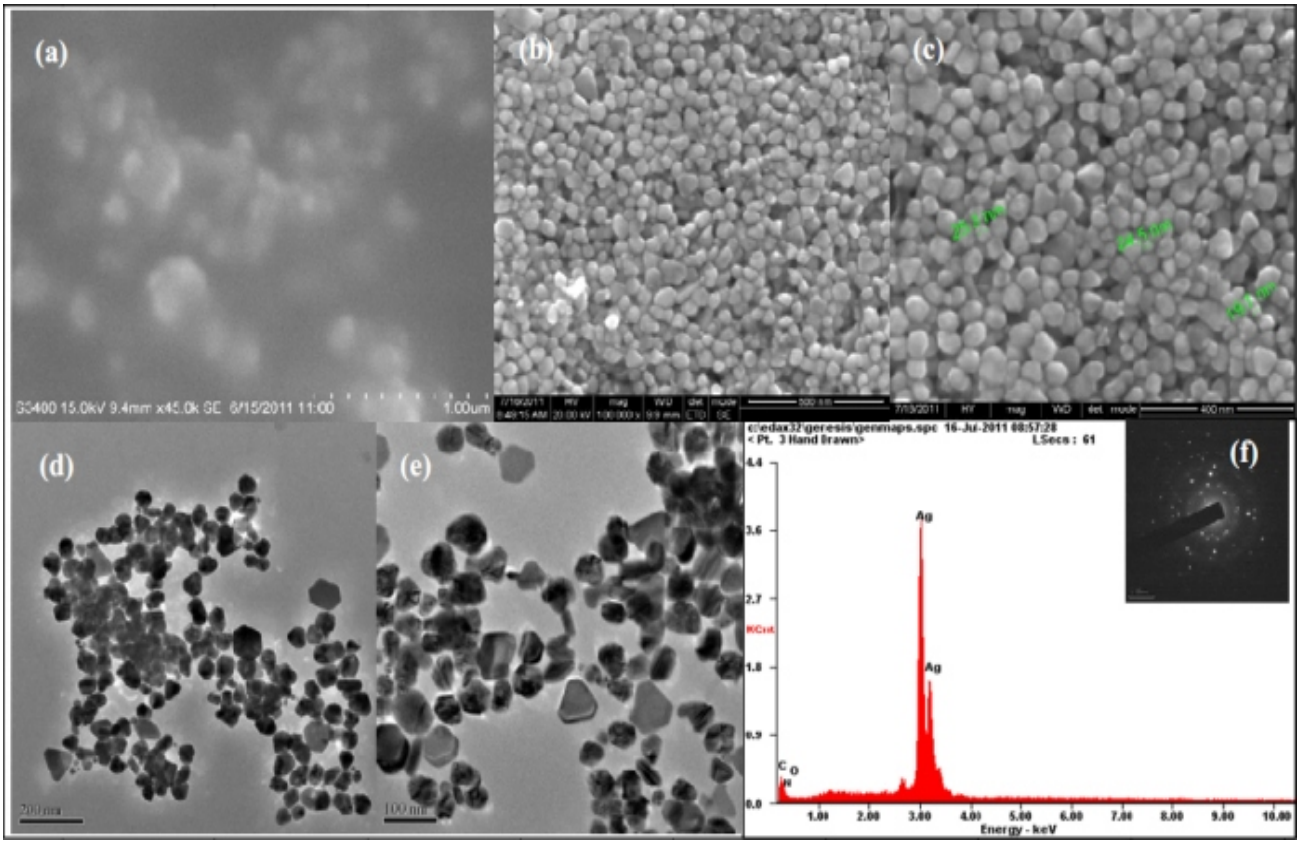

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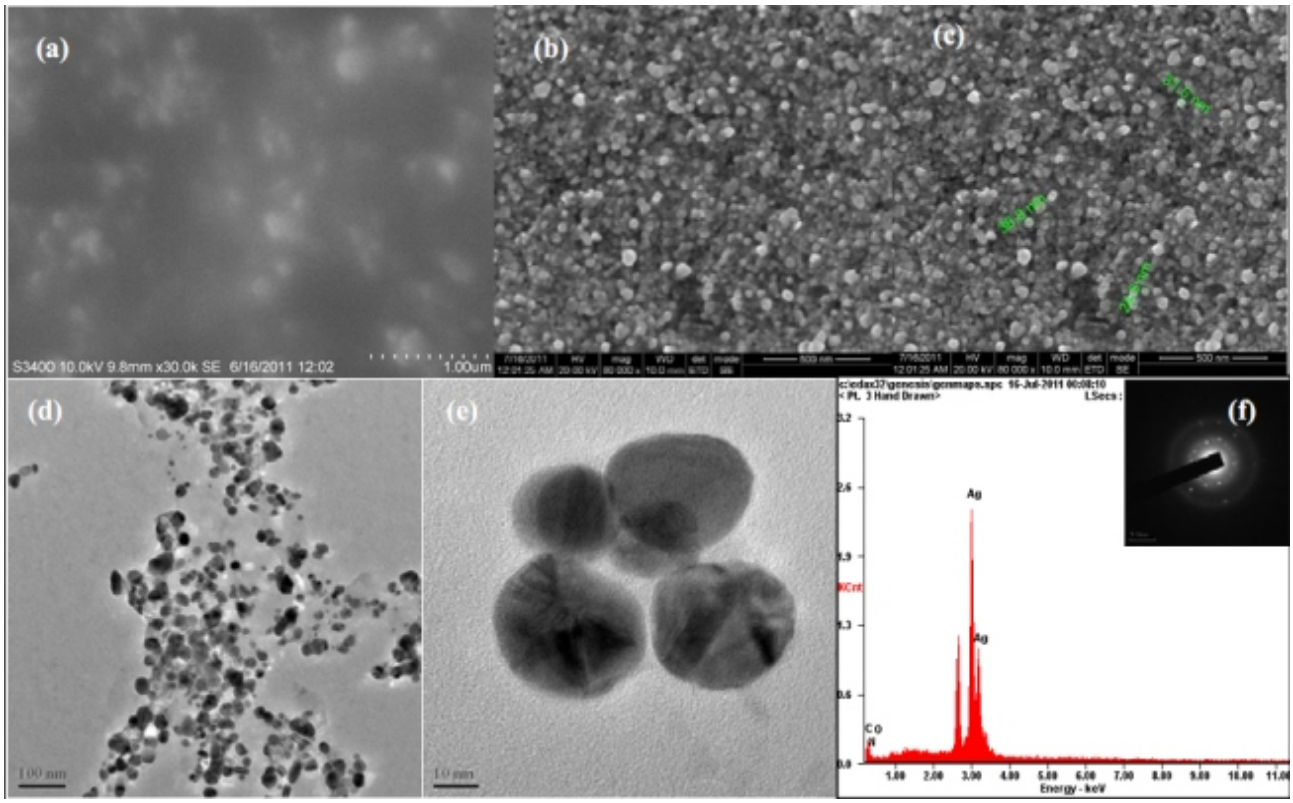

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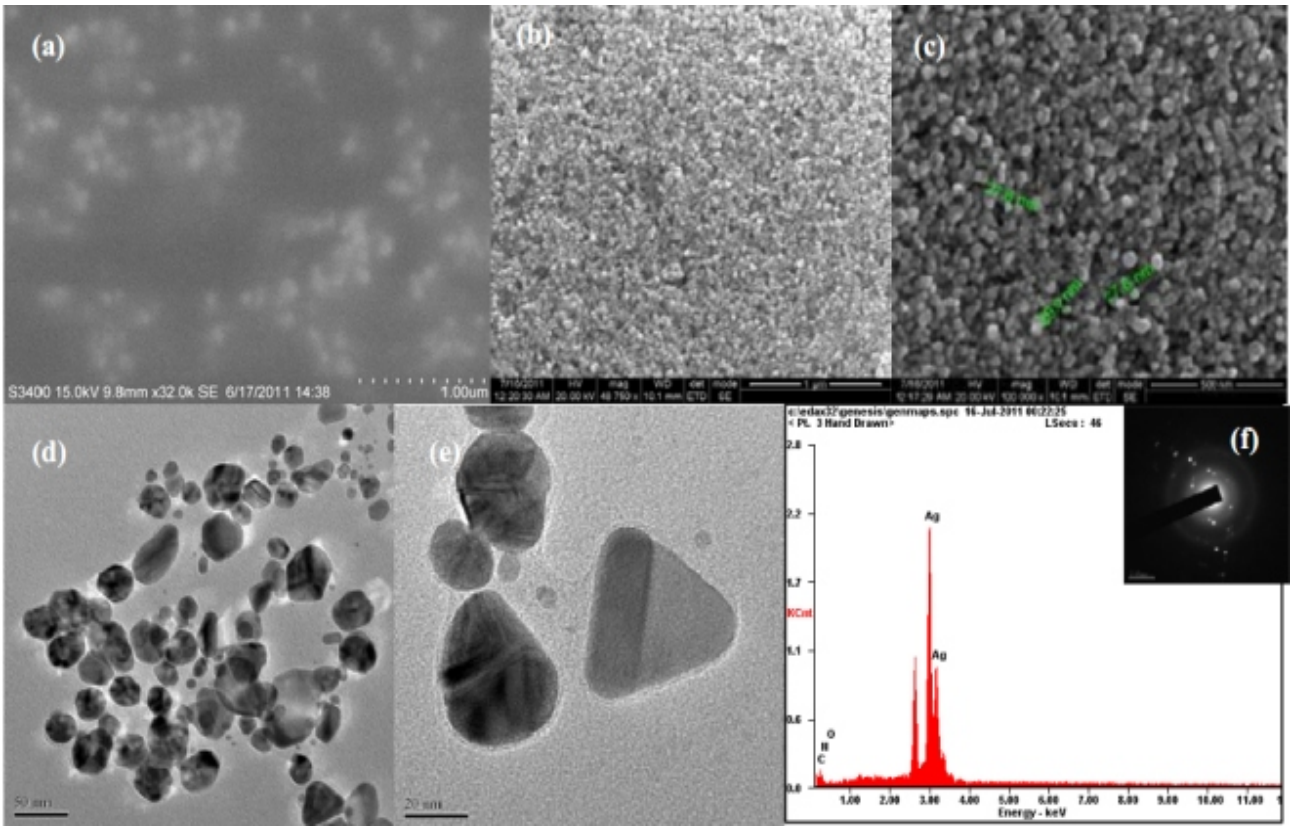

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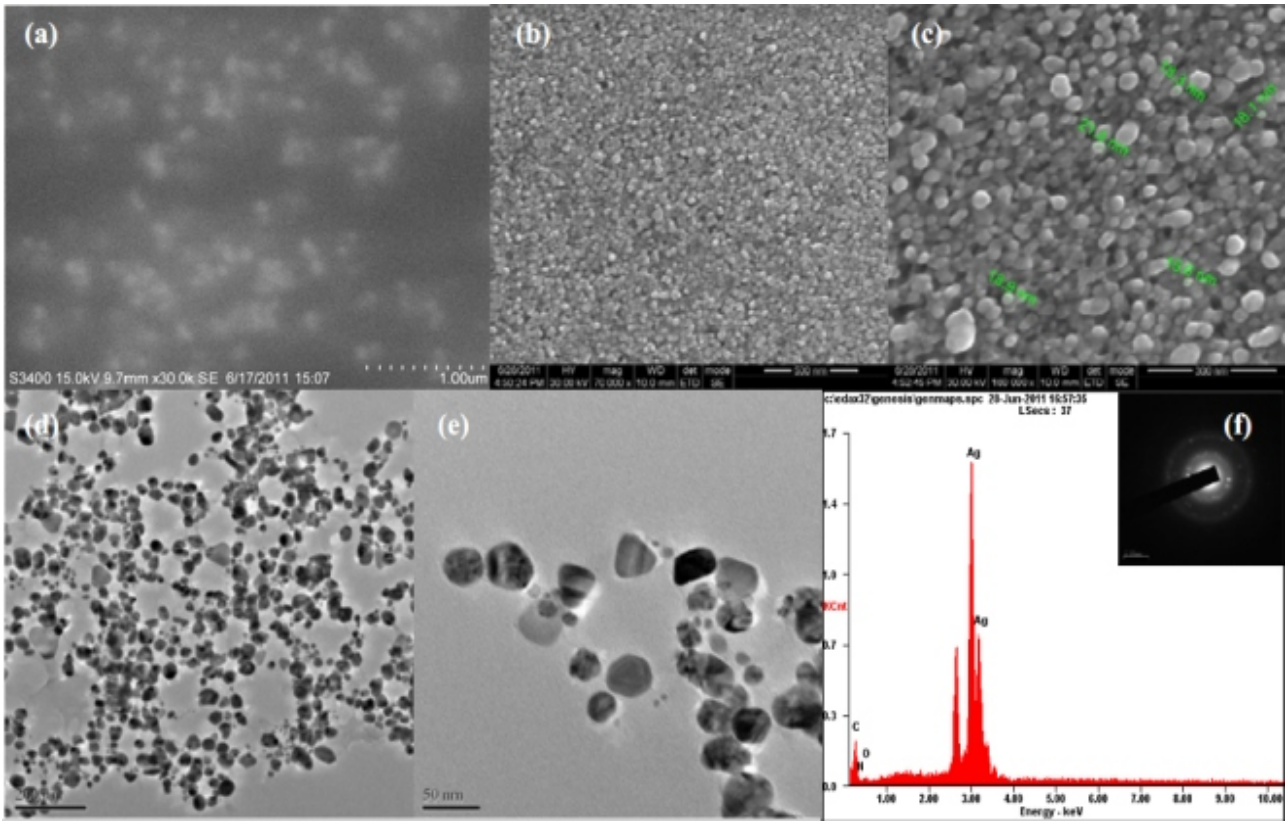

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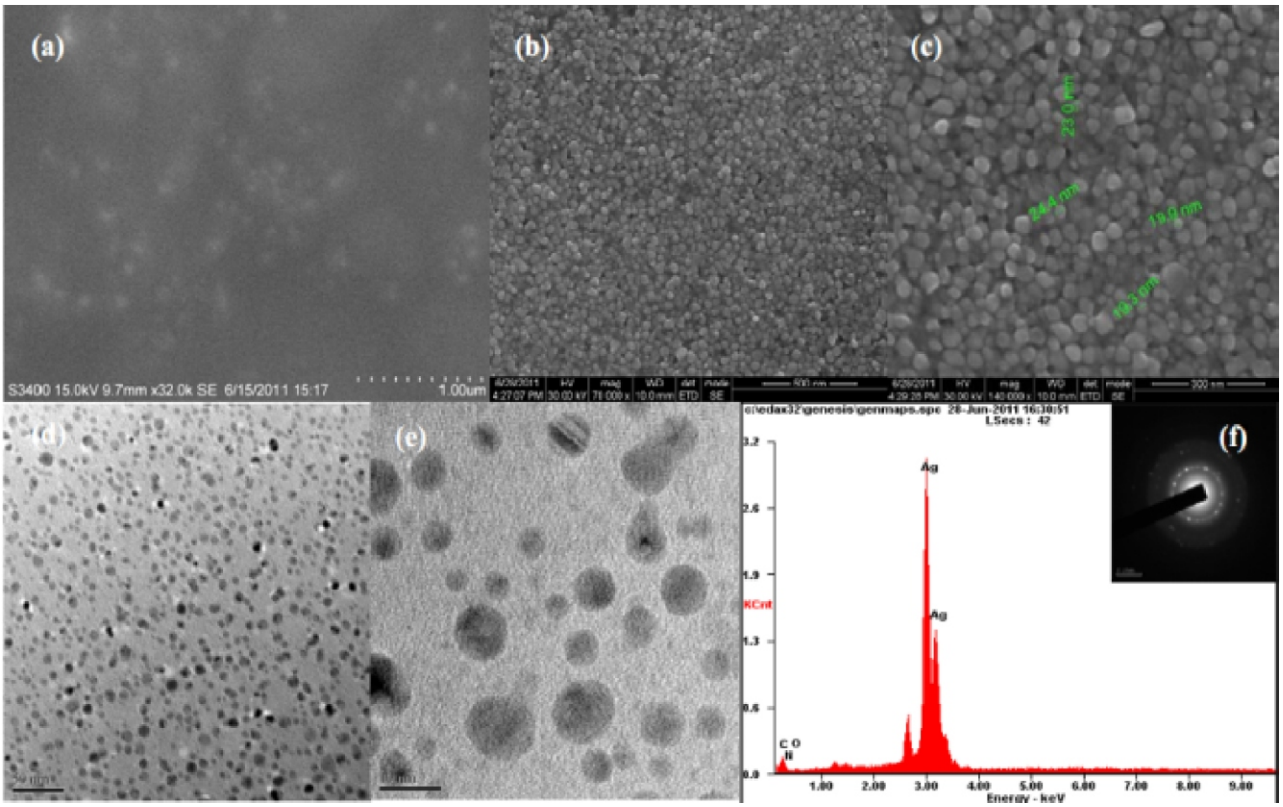

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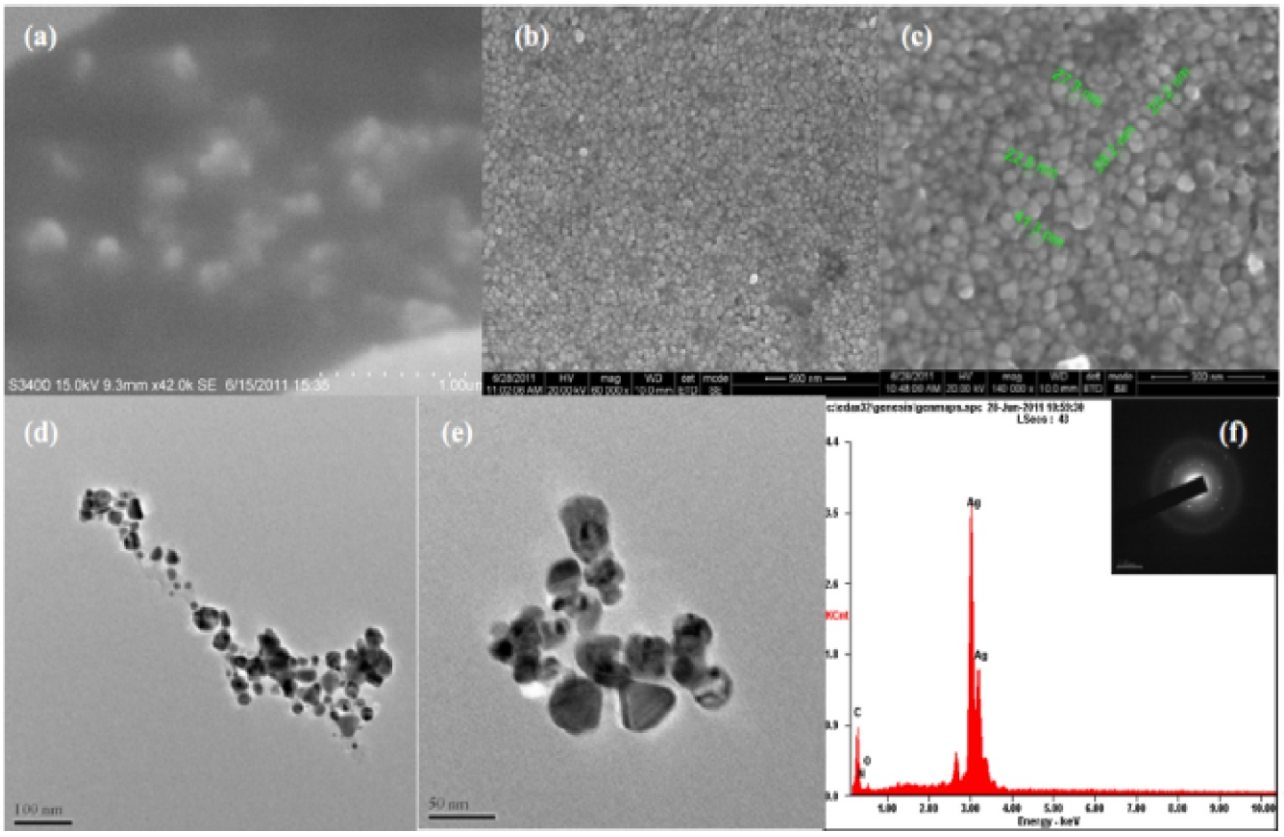


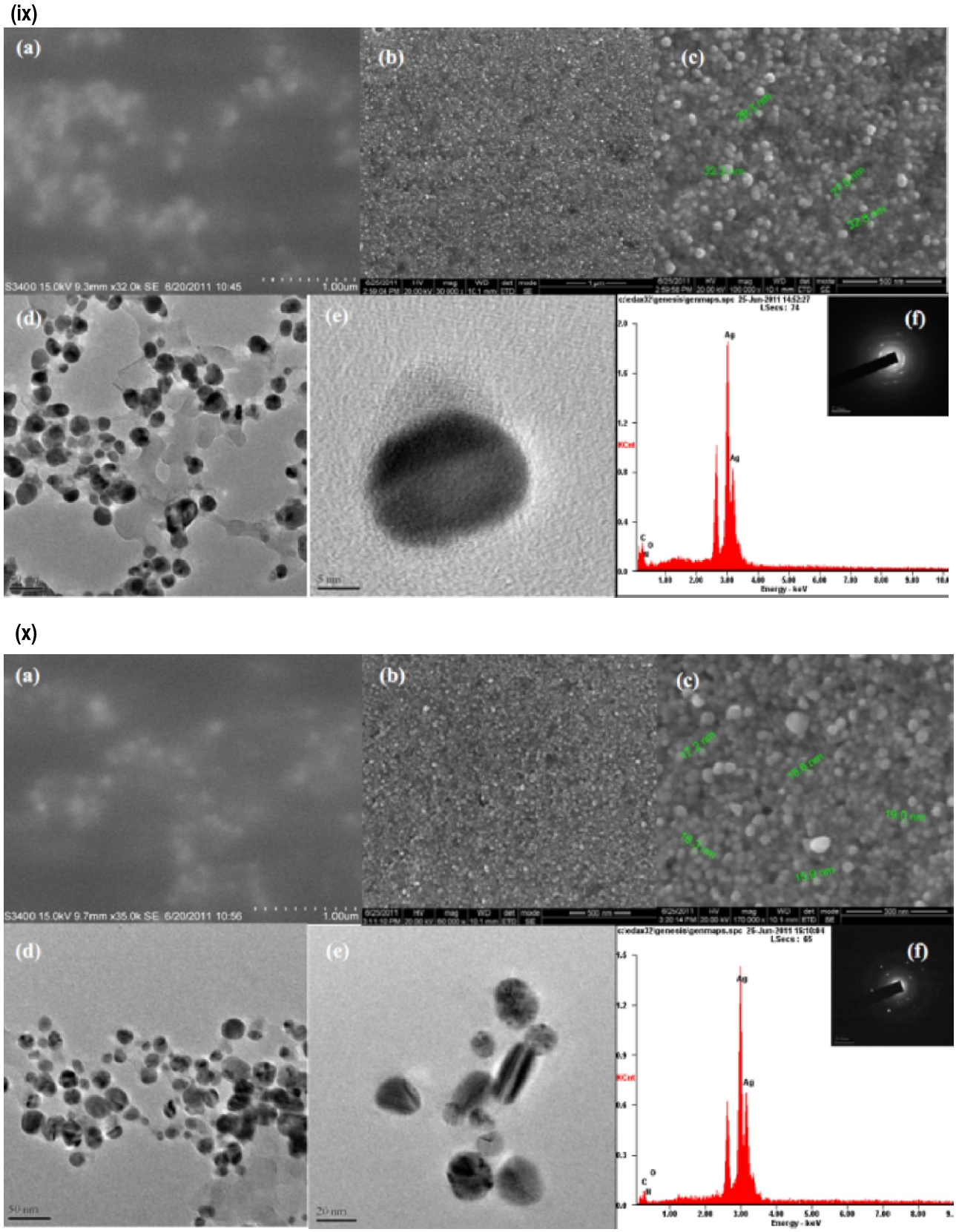
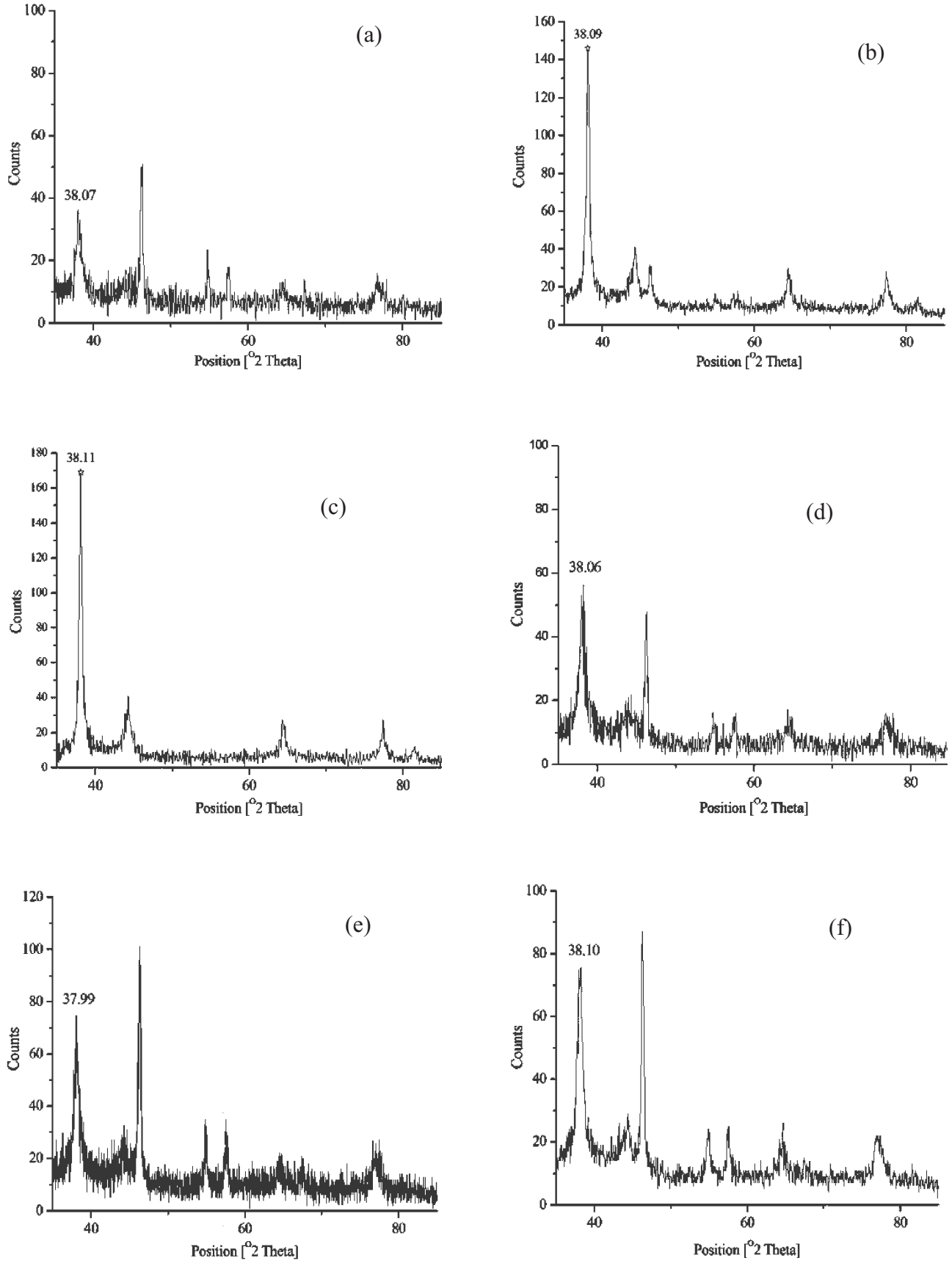


Fig. 2. Each visual is a composite of (a) Scanning electron micrograph; (b) & (c) High resolution electron micrographs; (d) & (e) Transmission electron micrographs; (f) EDX spectrum (Inset is the SAED pattern).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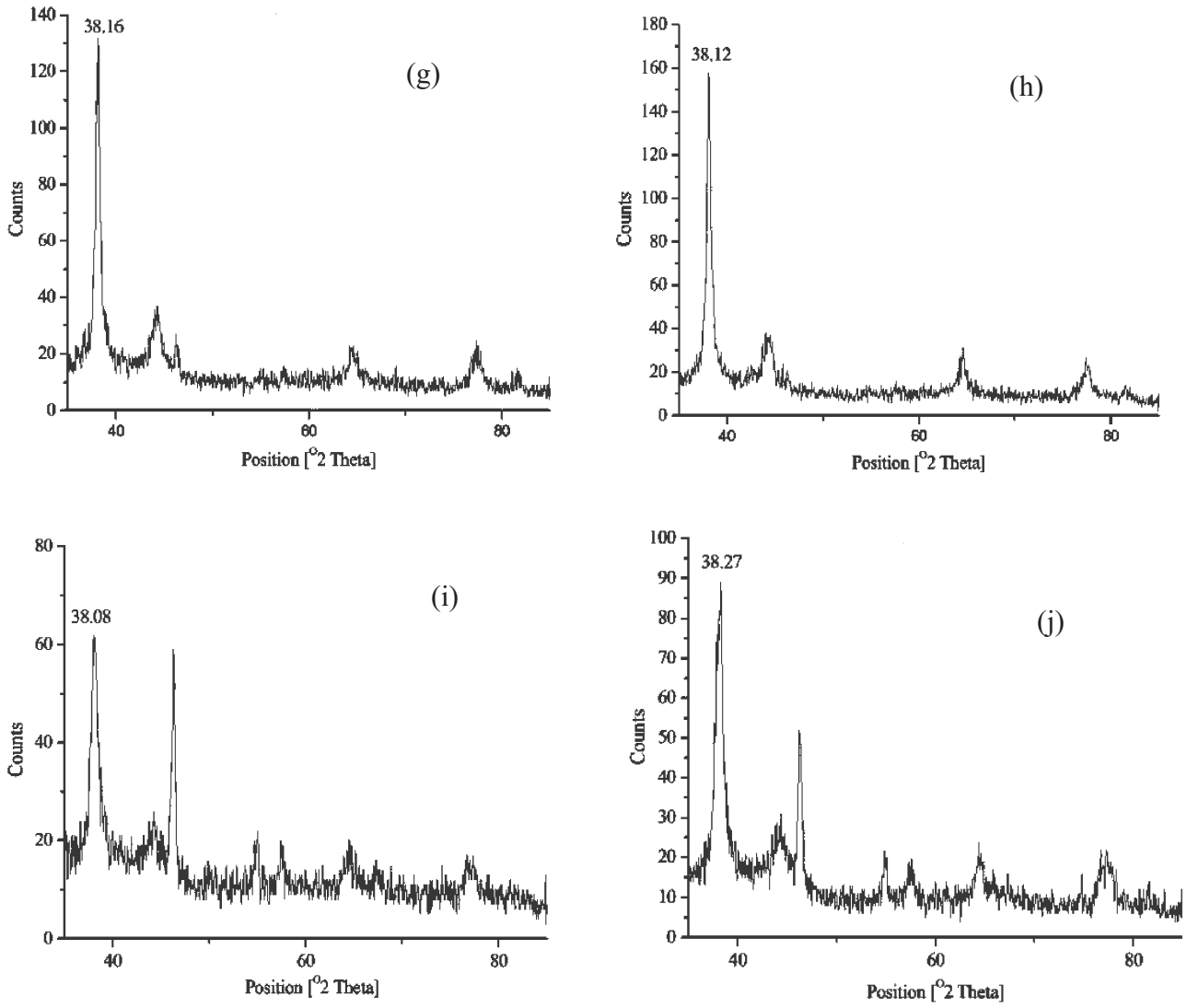

Fig. 3. X-ray diffractograms of the silver nanoparticles synthesized using LE (a and b), TSE (c and d), HSE (e and f), RE (g and h), and WPE (i and j).

B. Scanning Electron microscopy, High resolution Scanning Electron Microscopy, Transmission Electron Microscopy and Energy dispersive X-ray analysis

Electron microscopic studies revealed the presence of monodispersed (Spherical) and polydispersed (Truncated triangles, triangles, polygons, and rods) silver nanoparticles for the samples synthesized using, LE (i and ii), TSE (iii and iv), HSE (v and vi), RE (vii and viii), and WPE (ix and x) (figure 2).

Sizes of the silver nanoparticles were in the range of 16 – 30 nm (spherical) and 25 – 75 nm (Truncated triangles, triangles, polygons, and rods). The EDX spectrum recorded for the synthesized nanoparticles showed strong peaks for silver atom at 3 keV position. Hence the presence of Ag^0 nanoparticles was confirmed and the presence of silver was found to be always more than 75% in all cases.

C. X-ray diffraction analysis

The X-ray diffractogram (figure 3) showed several peaks at 2θ equivalent to 38.09°, 44.31°, 64.65°, 77.35°, and 81.71° characteristic to face-centered cubic (FCC) silver. These peaks corresponds to [111], [200],

[220], [311] and [222] orientation of silver nanoparticles [7]. The crystallite grain size of the silver nanoparticles as calculated using Scherrer formula of the Bragg's angle at 38° were in the range of 14 – 31 nm in all the cases. A few additional, unassigned peaks were also noticed in vicinity of the characteristic peaks of silver nanoparticles. These peaks might have resulted from some bioorganic compounds/proteins present in the plant extract. The recorded XRD patterns were matching with the database of JCPDS file No. 01-089-3722. The Bragg's reflection peaks obtained during these studies proves the crystalline nature of the synthesized silver nanoparticle.

D. Particle size analysis (zetasizer)

The size distribution of particles in the solution was studies on the basis of intensity (%) under particle size analyser. It gives an idea of the distribution of particles in colloidal suspension which are in constant Brownian movement. An intense single peak and an intense peak with a shoulder was seen which might be due to the presence of monodispersed and polydispersed particles respectively. It was observed that the intensity upto 100% was due the presence of particles with width between 16 and 35 nm and in size ranging 25 – 100 nm (Spectral records not presented).

E. FTIR Spectral studies

FTIR measurements were carried out to identify the potential functional group of the biomolecules found in the lantana extracts responsible for the reduction of the silver ions and also the capping agent responsible for the stability of the phyto-fabricated silver nanoparticles. The FTIR spectra of extract and silver nanoparticles are depicted in figure 4.

The plant extracts show medium or strong absorption bands about at 3394, 2925, 1606, 1413, and 1074 cm^{-1}. The strongest absorption band can be assigned to C-N stretching vibrations (at 1413 cm^{-1}) of aromatic and aliphatic amines [8]. Bands originating from hydroxyl group (free water and/or alcohols) at ~ 3300 and 1080cm^{-1}, as well as medium band at 1606 cm^{-1} indicating presence of amide/amine groups, as would be expected due to plant-origin of these samples.

Comparison between spectra of extract (a) to the silver nanoparticles samples (b) reveals only minor

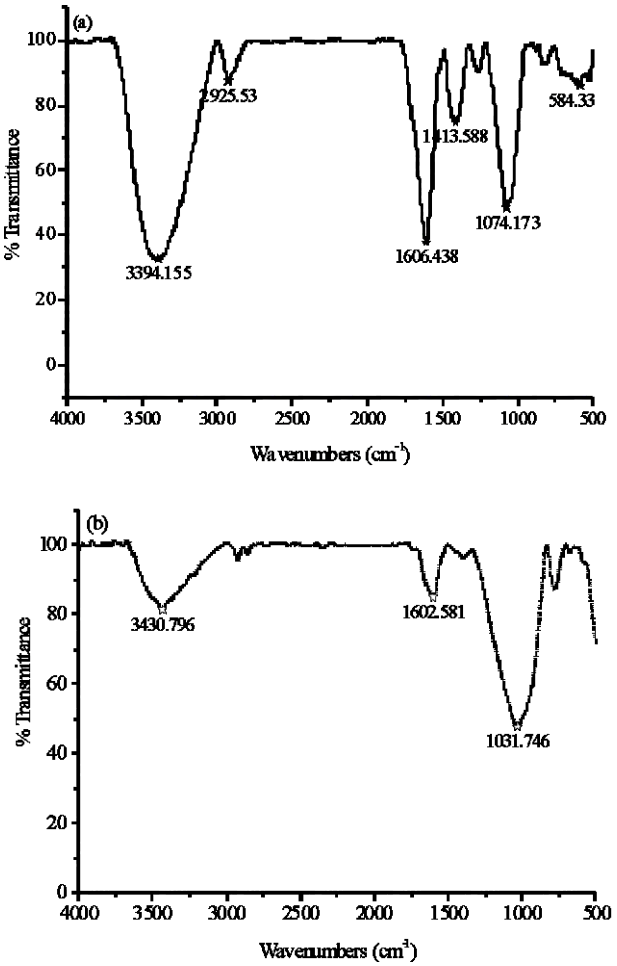

Fig. 4. FTIR spectra of plant extract (a) and silver nanoparticles (b).

changes in the positions as well as on the magnitude of the absorption bands. With closer examination, the spectrum of silver nanoparticles show somewhat stronger absorption and minor shift at 3430 (N-H stretch) and 1602 cm^{-1} (due to $C=O$ stretch) bands confirms the presence of amides. Hence, it can be inferred that these biomolecules had interacted with the silver nanoparticles for reduction and stabilization.

IV. CONCLUSION

The present process of phyto-fabrication of silver nanoparticles was achieved successfully by utilizing the highly pernicious and invasive weed *L. camara* (L.). Here we reported shape, and size tuned synthesis of silver nanoparticles using *L. camara* plant extracts (i.e. leaf, stem (Tender stem) and (Hard stem), root and whole plant) of 1 g TS. With this process it is possible to obtain mono and poly dispersed silver nanoparticles of desired size and shape. The synthesized

nanoparticles were characterized for their size, shape, purity, crystal structure and to identify the possible biomolecules responsible for the reduction and stabilization, by employing SEM, Hr-SEM, TEM, EDAX, XRD, zetasizer and FTIR techniques. The results obtained from electron microscopic studies were in concordance with the results determined from XRD and zetasizer. Amides were found to be the biomolecules responsible for the biocompatible synthesis of silver nanoparticles. The present study is an eco-friendly and 'green', one pot, synthesis route which leads to shape and size-tuneable, silver nanostructures under benign process conditions. Additionally it enables, on one hand, fabrication of silver nanoparticles with a non-hazardous, energy-saving, and cost effective method, and on the other hand, the study enables gainful utilization of the obnoxious invasive weed, which is otherwise not only worthless but also harmful to the environment in general and to just keep them in check enormous costs are incurred with risks to environment from herbicide use.

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