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Silver nanoparticles green synthesis: A mini review

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Nanotechnology is a significant field of contemporary research dealing with design, synthesis, and manipulation of particle structures ranging from in the region of 1-100 nm. Nanoparticles (NPs) have broad choice of applications in areas such as fitness care, cosmetics, foodstuff and feed, environmental health, mechanics, optics, biomedical sciences, chemical industries, electronics, space industries, drug-gene delivery, energy science, optoelectronics, catalysis, single electron transistors, light emitters, nonlinear optical devices, and photo-electrochemical applications. Nano Biotechnology is a speedily mounting scientific field of producing and constructing devices, an important area of research in nano biotechnology is the synthesis of NPs with different chemical compositions, sizes and morphologies, and controlled dispersities. Silver nanoparticles (NPs) have been the subjects of researchers because of their unique properties (*e.g.*, size and shape depending optical, antimicrobial, and electrical properties). A variety of preparation techniques have been reported for the synthesis of silver NPs; notable examples include, laser ablation, gamma irradiation, electron irradiation, chemical reduction, photochemical methods, microwave processing, and biological synthetic methods. This assessment presents a general idea of silver nanoparticle preparation. The aim of this analysis article is, therefore, to replicate on the existing state and potential prediction, especially the potentials and limitations of the above mentioned techniques for industries.

Capsule Summary: Green methods for the synthesis of silver nanoparticles for different applications have been reviewed briefly.

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INTRODUCTION

Metal nanoparticles are intensely studied due to their unique optical, electrical and catalytic properties. To utilize and optimize chemical or physical properties of nano-sized metal particles, a large spectrum of research has been focused to control the size and shape, which is crucial in tuning their physical, chemical and optical properties (Bar et al., 2009; Coe et al., 2002; Bruchez et al., 1998). Various techniques, including chemical and physical means have been developed to prepare metal nanoparticles, such as chemical reduction (Tan et al., 2002; Petit et al., 1993; Vorobyova, A.I. Lesnikovich, 1999), electrochemical reduction (Liu and Lin, 2004; Sandmann et al., 2002), photochemical reduction (Keki et al., 2000; Mallick et al., 2005), heat evaporation (Bae et al., 2002; Smetana et al., 2005) and so on. In most cases, the surface passivator reagents are needed to prevent nanoparticles from aggregation. Unfortunately many organic passivators such as thiophenol, thiourea (Pattabi and Uchil, 2000; Ravindran et al., 1999), marcapto acetate (Lin et al., 2000) etc. are toxic enough to pollute the environment if large scale nanoparticles are produced. An array of physical, chemical and biological methods has been used to synthesize nanomaterials. Specific methodologies have been used to synthesize noble metal nanoparticles of particular size and shape. Although ultraviolet irradiation, aerosol technologies, lithography, laser ablation, ultrasonic fields, and photochemical reduction techniques have been used successfully to produce nanoparticles, they remain expensive and involve the use of hazardous chemicals. Therefore, there is a growing concern to develop simple, cost-effective, and sustainable methods. As nanoparticles of different compositions, sizes, shapes and controlled dispersity is an important aspect of nanotechnology, new cost-effective and eco-friendly procedures are being developed. Biological synthesis of nanoparticles is a green chemistry approach that interconnects nanotechnology and biotechnology (Absar et al., 2003). However, despite the stability, biological nanoparticles are not monodispersed and the rate of synthesis is slow. The concentration of synthesized macromolecules or components involved in the nucleation of particles varies with time and prolongs the nucleation period which causes the polydispersity of nanoparticles and subsequent decreased rate of synthesis. In order to overcome these problems, several methods such as microbial cultivation methods and the extraction techniques have to be optimized and the combinatorial approach such as photo biological methods may be used. Cellular, biochemical and molecular mechanisms that mediate the synthesis of biological nanoparticles should be studied in detail to increase the rate of synthesis and improve properties of nanoparticles. Owing to the rich biodiversity of plants and microbes, the potential as biological materials for nanoparticle synthesis is yet to be fully explored (Bönnemann and Richards, 2001).

Recently, biosynthetic methods employing naturally occurring reducing agents such as polysaccharides, biological microorganism such as bacteria and fungus or plants extract, i.e. green chemistry, have emerged as a simple and viable alternative to more complex chemical synthetic procedures to obtain nanoparticles. With the increasing emphasis on green chemistry, it is becoming more important to develop an environmentally friendly, facile method for the synthesis of nanoparticles. It has been reported that template synthesis is one of the most promising methods for the preparation of monodispersed inorganic nanoparticles (Liu*et* et al., 2012) in which uniform void spaces of porous materials are used as hosts to confine the synthesized nanoparticles as guests (Guo et al., 2008 and 2010). In this present investigation we are going to report different green methods for the synthesis of nanoparticles from naturally occurring biological sources and their applications in various fields.

Highlights

Hui et al. (2006) have shown that green synthesis method for preparing pure (free of fly ash) and ordered MCM-41 materials from coal fly ash at room temperature (25°C) during 24 h of reaction. It was shown that the impurities in the coal fly ash were not detrimental to the formation of MCM-41 at the tested conditions. The experimental results showed that the amount of trace elements such as Al, Na, Ti and Fe incorporated into the sample increased with synthesis pH value. More aluminum species were incorporated with tetrahedral coordination in the framework under a high pH value. The particle size of the sample decreased with the synthesis pH value. Samples synthesized at high pH values had a larger pore size and were more hydrothermally stable than those at low pH values. From thermal analysis, it was observed that the synthesized MCM-41 samples showed a high thermal stability. These properties made the synthesized MCM-41 suitable for further processing into more useful materials in a wide range of applications like waste water treatment, catalysis, adsorption etc. This study demonstrates that converting coal fly ash into mesoporous materials not only eliminates the disposal problem of coal fly ash but also turns a waste material into a useful one. The proposed method provides another way of recycling coal fly ash (Hui and Chao, 2006).

Sarma et al. (2008) reported several synthetic methods for Ag NPs using inexpensive and nontoxic compounds under water environments were summarized and experimental approaches under different conditions were given to control the morphology of the Ag particles. Rapid and green synthetic methods using extracts of bio-organisms have shown a great potential in Ag NP synthesis. silver nanoparticles (Ag NPs) preparation by green synthesis approaches that have advantages over conventional methods involving chemical agents associated with environmental toxicity. Green synthetic methods include mixed-valence polyoxometallates, polysaccharide, Tollens, irradiation, and biological. The mixed-valence polyoxometallates method was carried out in water, an environmentally-friendly solvent. Solutions of AgNO3 containing glucose and starch in water gave starch protected Ag NPs, which could be integrated into medical applications. Tollens process involves the reduction of $Ag(NH_3)^{2+}$ by saccharides forming Ag NP films with particle sizes from 50–200 nm, Ag hydrosols with particles in the order of 20–50 nm, and Ag colloid particles of different shapes. The reduction of $Ag(NH3)^{2+}$ by HTAB (n-hexadecyltrimethylammonium bromide) gave Ag NPs of different morphologies: cubes, triangles, wires, and aligned wires. Ag NPs synthesis by irradiation of Ag^+ ions does not involve a reducing agent and is an appealing procedure. Eco-friendly bio-organisms in plant extracts contain proteins, which act as both reducing and capping agents forming stable and shape-controlled Ag NPs. The synthetic procedures of polymer-Ag and TiO2–Ag NPs are also given. Both Ag NPs and Ag NPs modified by surfactants or polymers showed high antimicrobial activity against Gram-positive and Gram-negative bacteria. The mechanism of the Ag NP bactericidal activity is discussed in terms of Ag NP interaction with the cell membranes of bacteria. Silver-containing filters are shown to have antibacterial properties in water and air purification. Finally, human and environmental implications of Ag NPs to the ecology of aquatic environment are briefly discussed (Sharma et al., 2009).

Kumar et al. (2009) discussed the exploitation of various plant materials for the biosynthesis of nanoparticles is considered a green technology as it does not involve any harmful chemicals. The present study reports the synthesis of silver (Ag) nanoparticles from silver precursor using the bark extract and powder of novel *Cinnamon zeylanicum*. Water-soluble organics present in the plant materials were mainly responsible for the reduction of silver ions to nano-sized Ag particles. The pH played a major role in size control of the particles. Bark extract produced more Ag nanoparticles than the powder did, which was attributed to the large availability of the reducing agents in the extract. Zeta potential studies showed that the surface charge of the formed nanoparticles was highly negative. The EC50 value of the synthesized nanoparticles against *Escherichia coli* BL-21 strain was 11±1.72 mg/L. Thus *C. zeylanicum* bark extract and powder are a good bio-resource/biomaterial for the synthesis of Ag nanoparticles with antimicrobial activity. For large-scale productivity of Ag nanoparticles to be even more economical and eco-friendly, using silver ions from wastewaters may be an alluring technique (Sathishkumar et al., 2009). Bar et al (2009) presented an idea about Silver nanoparticles were successfully synthesized from AgNO3 through a simple green route using the latex of *Jatropha curcas* as reducing as well as capping agent. Synthesis of metallic nanoparticles using green resources like Jatropha latex is a challenging alternative to chemical synthesis, since this novel green synthesis is pollutant free and eco-friendly synthetic rote for silver nanoparticles. We anticipate that the smaller particles are mostly stabilized by the cyclic octapeptide, i.e. curcacycline A and cyclic nonapeptide, i.e. curcacycline B. On the other hand the larger and uneven shape particles are mainly stabilized by the curcain, an enzyme present in the latex. Further experiments for the size selective synthesis of silver and gold nanoparticles using the cyclic peptide present in the latex are in progress (Bar et al., 2009a). Bar et al. (2009b) also studied an eco-friendly process for rapid synthesis of silver nanoparticles has been reported using aqueous seed extract of *Jatropha curcas*. Here Jatropha seed extract which is environmentally benign and renewable, act as both reducing and stabilizing agent. Particles are mostly spherical in shape. Size of the particles can be controlled by varying the concentration of $AgNO_3$. Ag nanoparticles prepared in this process are quiet stable and remain intact for nearly two months if it protected under light proof conditions [25]. Top down and bottom up methods are available for nanoparticle synthesis. Various types of synthesis are also available like vapours phase, liquid phase etc are dicussed by René Overney (2010). Abou El-Nour et al. (2010) reported that nano-size particles of less than 100 nm in diameter are currently attracting increasing attention for the wide range of new applications in various fields of industry. Most of the unique properties of nanoparticles require not only the particles to be of nano-sized, but also the particles be dispersed without agglomeration. Discoveries in the past decade have clearly demonstrated that the electromagnetic, optical and catalytic properties of silver nanoparticles are strongly influenced by shape, size and size distribution, which are often varied by varying the synthetic methods, reducing agents and stabilizers. Accordingly, this review presents different methods of preparation silver nanoparticles and application of these nanoparticles in different fields (Kholoud et al., 2010).

Dubey et al. (2010a) have shown spanking new and simple method for biosynthesis of silver and gold nanoparticles offers a valuable contribution in the area of green synthesis and nanotechnology without adding different physical and chemical steps. Tansy fruit extract was prepared and successfully employed for the development of silver and gold nanoparticles with spherical and triangular shapes. Powder diffraction study showed the face-centered cubic lattice of both AgNPs and AuNPs. The average crystal of AgNPs and AuNPs are 16 and 11nm estimated from Scherrer method. This simple, low cost and greener method for development of silver and gold nanoparticles may be valuable in environmental, biotechnological and biomedical applications (Dubey et al. 2010b). Biological systems, especially those using microorganisms, have the potential to offer cheap, scalable and highly tunable green synthetic routes for the production of the latest generation of nanomaterials. Recent advances in the biotechnological synthesis of functional nano-scale materials are described. These nanomaterials range from catalysts to novel inorganic antimicrobials, nanomagnets, remediation agents and quantum dots for electronic and optical devices. Where possible, the roles of key biological macromolecules in controlling production of the nanomaterials are highlighted, and also technological limitations that must be addressed for widespread implementation are discussed by Lloyd et al. (2011). Narayanan and Sakthivel (2011) reported the modulation of size and shape can be achieved by varying the ratio of gold salt and the cell-free filtrate of fungus *S. rolfsii*. The production of anisotropic and isotropic gold nanoparticles is quite stable in aqueous solution for 2months. This simple, efficient, eco-friendly process is very rapid and completes in 10–15 min. unraveling the exact biochemical mechanism underpinning the modulation of size and shape of nanoparticles is underway. The applications of gold nanoparticles vary with its shape and size. The NIR absorbance of nano triangles has interesting applications in cancer hyperthermia. To the best of our knowledge, this is the rapid synthesis of gold nanoparticles using a microbial component (Narayanan and Sakthivel, 2011). Machida et al. (2011) presented industrial processes and emerging technologies that use supercritical fluids are highlighted. Supercritical fluids are being used in transcritical cycles for heat transfer due to their favorable thermo physical properties and their environmental compatibility. Supercritical water is being proposed as a reaction solvent for zinc silicate industrial phosphors, since it allows production of luminescent materials at low temperatures (400 °C) and with less energy than industrial solid-state methods that require high temperatures (1200 °C). Supercritical CO_2–ionic liquid systems have much potential as biphasic systems for reactions and separations; however, when used for chiral separations, the selectivity of these systems is not well understood yet. The use of supercritical CO_2 for viscosity reduction in ionic liquid reaction systems seems to be a favorable research area with conversion of d-fructose to 5-hydroxymethylfurfural in high yields (>90%) being an example. Systems to convert biomass to energy by direct oxidation in supercritical water are under development. Many opportunities exist for developing green chemical processes with supercritical fluids[31]. Biosynthesis of gold nanoparticles with small size and biostability is very important and used in various biomedical applications. There are lot of reports for the synthesis of gold nanoparticles by the addition of reducing agent and stabilizing agent. In the present study we have synthesized gold nanoparticles, with a particle size ranging from 5 to 15 nm, using *Zingiber officinale* extract which acts both as reducing and stabilizing agent. *Z. officinale* extract is reported to be a more potent anti-platelet agent than aspirin. Therefore, green synthesis of gold nanoparticles with Z. officinale extract, as an alternative to chemical synthesis, is beneficial from its biological and medical applications point of view, because of its good blood biocompatibility and physiological stability. Gold nanoparticles synthesized using citrate and *Z. officinale* extract demonstrated very low protein adsorption. Both nanoparticles were non platelet activating and non-complement activating on contact with whole human blood. They also did not aggregate other blood cells, however, nanoparticles synthesized with *Z. officinale* extract was highly stable at physiological condition compared to citrate capped nanoparticles, which aggregated. Thus the usage of nanoparticles, synthesized with *Z. officinale* extract, as vectors for the applications in drug delivery, gene delivery or as biosensors, where a direct contact with blood occurs is justified by Kumar et al. (2011). Smuleac et al. (2011) has shown that membranes containing reactive nanoparticles (Fe and Fe/Pd) immobilized in a polymer film (polyacrylic acid, PAA-coated polyvinylidene fluoride, PVDF membrane) are prepared by a new method. The current study reports for the first time the synthesis of Fe and bimetallic Fe/Pd nanoparticles on a membrane support, using a “green” reducing agent – tea extract, which acts as both reducing and capping agent. The latter ensures a high nanoparticle longevity and resistance to oxidation. We have successfully demonstrated a membrane-based approach for the reductive destruction of a model toxic chlorinated organic, a common pollutant, TCE. The dechlorination can be performed in convective mode, using pump and treat approach or in batch mode, when membrane-immobilized NPs can be injected underground. For all cases, the surface area normalized reaction rates were quantified (Smuleaca et al., 2011). Ngo et al. (2011) briefly discussed an overview of the properties of gold, silver and titania nanoparticles which contribute to the major applications of nanoparticles functionalized paper. Different preparation methods of the nanoparticles-functionalized paper are reviewed, focusing on their ability to control the morphology and structure of paper as well as the spatial location and adsorption state of nanoparticles which are critical in achieving their optimum applications. In addition, main applications of the nanoparticles-functionalized papers are highlighted and their critical challenges are discussed, followed by perspectives on the future direction in this research field. Whilst a few studies to date have characterized the distribution of nanoparticles on paper substrates, none have yet optimized paper as a nanoparticles' substrate. There remains a strong need to improve understanding on the optimum adsorption state of nanoparticles on paper and the heterogeneity effects of paper on the properties of these nanoparticles (Ngo et al., 2011). Hsu et al. (2011) reported about Chitosan nanocomposites were prepared from chitosan and gold nanoparticles (AuNPs) or silver nanoparticles (AgNPs) of 5 nm size. Transmission electron microscopy (TEM) showed the NPs in chitosan did not aggregate until higher concentrations (120–240 ppm). Atomic force microscopy (AFM) demonstrated that the nanocrystalline domains on chitosan surface were more evident upon addition of AuNPs (60 ppm) or AgNPs (120 ppm). Both nanocomposites showed greater elastic modulus, higher glass transition temperature (Tg) and better cell proliferation than the pristine chitosan. Additionally, chitosan-Ag nanocomposites had antibacterial ability against Staphylococcus aureus. The potential of chitosan-Au nanocomposites as haemostatic wound dressings was evaluated in animal (rat) studies. Chitosan-Au was found to promote the repair of skin wound and hemostasis of severed hepatic portal vein. This study indicated that a small amount of NPs could induce significant changes in the physicochemical properties of chitosan, which may increase its biocompatibility and potential in wound management (Hsu et al., 2011).

A novel green method of silver nanoparticles synthesis using *Dillenia indica* fruit extract. *D. indica* is an edible fruit widely distributed in the foothills of Himalayas and known for its antioxidant and further predicted for cancer preventive potency. The maximum absorbance of the colloidal silver nanoparticle solution was observed at 421 nm when examined with UV-Vis spectrophotometer (Sing et al., 2012). The biological synthesis of gold nanoparticles (AuNPs) of various shapes (triangle, hexagonal, and spherical) using hot water olive leaf extracts as reducing agent is reported. The size and the shape of Au nanoparticles are modulated by varying the ratio of metal salt and extract in the reaction medium. The high phenolic content of the hot water extract of olive leaves having strong anti-oxidant properties helped in the reduction of gold cations to AuNPs. The characterization of AuNPs revealed that the morphology of the AuNPs depends on the extract concentration and pH of the used medium. At higher concentration of the extract and basic pH, the pseudo-spherical particles are capped by phytochemicals. This method for AuNP synthesis does not use any toxic reagent and thus has a great potential for the use in biomedical applications and will play an important role in future opto-electronic and biomedical device applications (Khalil et al., 2012). Indulkar et al. (2012) discussed about nano zinc oxide (Nano-ZnO) was explored as a reusable catalyst for the enamination of 1,3-dicarbonyls using diverse amines. To make the process environmentally viable, the reaction was carried out under solvent-free conditions and found to give good yield of desired products. The catalyst was found to be reusable up to four catalytic cycles without any appreciable loss in activity. They have reported a procedure for the enamination of carbonyl compounds with nano ZnO as a green, cost effective, and reusable catalyst [38]. A green synthesis method for the preparation of mesoporous a-Fe2O3 nanoparticles has been developed using the extract of green tea (camellia sinensis) leaves. The method is one-step and scalable for highly crystallized mesoporous a-Fe2O3 nanoparticles. The as-prepared nanoparticles have about 4 times higher surface area compared to commercial a-Fe2O3 nanoparticles and two time higher photocatalytic activity in terms of hydroxyl radical formation under visible light irradiation. Also, the as prepared nanoparticles were successfully applied in wet-type solar cell (Ahmmad et al., 2012).

Edison and Sethuraman (2012) have shown a novel green approach for the synthesis and stabilization of silver nanoparticles (AgNPs) using water extract of Terminalia chebula (T. chebula) fruit under ambient conditions is reported. The study has demonstrated that AgNPs could be prepared instantly by making use of aqueous extract of myrobalan. The phytoconstituents such as hydrolysable tannins, gallic acid, chebulic acid, chebulic ellagitannins and gallate esters act as reducing agents for the preparation of AgNPs and the capping of AgNPs by the phytoconstituents provide stability to AgNPs as evident from FT-IR and EDS studies. The synthesized AgNPs were found to have a crystalline structure with face centered cubic geometry as studied by XRD method. The HR-TEM images and DLS studies had shown that the synthesized AgNPs are having the size around 25 nm. The synthesized AgNPs act through the electron relay effect and influence the degradation of methylene blue by myrobalan extract (Edison and Sethuraman, 2012).

Vijayaraghavan et al. (2012) reported a novel biosynthesis route for silver nanoparticles (Ag-NPs) was attempted in this present investigation using aqueous extracts of Trachyspermum ammi and Papaver somniferum. The main constituents in T. ammi are thymol, p-cymene and _-terpinene, while P. somniferum consists of morphine and codeine. The essential oil in T. ammi was found to be a good reducing agent than the alkaloids present in P. somniferum for the formation of biocompatible Ag-NPs. The effectiveness of both the extracts was investigated by using same dosage of extract in the synthesis of silver nanoparticle. The results showed that for the same dosage of extracts the T. ammi synthesized various size triangular shaped nanoparticles measuring from 87 nm, to a fewer nanoparticles having a size of 998 nm diagonally. P. somniferum resulted in almost spherical shaped particle ranging in size between 3.2 and 7.6 _m diagonally (Vijayaraghavan et al., 2012).

This study shows that cationic CTAB surfactant can be used efficiently to the synthesis of Ag-nanoparticles having different morphology (spherical, quantum dots, hexagonal and polyhedral) during the bio-reduction of Ag+ ions by Neem leaf extract. The synthesized aqueous solution of Ag-nanoparticles were found to be stable in room temperature for more than a month due to the presence of natural products, such as flavanones, terpenoids, proteins and reducing sugars. The nanoparticles were crystalline in nature. Pre- and post-micellization are responsible to the anisotropic growth of the particles. The desired morphology of Ag-nanoparticles would be achieved by using suitable [CTAB] which acts as an excellent template to regulate the nanoparticle growths. The role of CTAB to alter the shape ofnanoparticles as observed in this study opens up the exciting possibility of synthesizing advanced by using natural biological sources by Khan et al. (2012).

Khan et al. (2012) have shown a simple, bio-reductive, green and room temperature method was reported to the preparation of Ag-nanoparticles using ascorbic acid and soluble starch. The effects of various parameters such as [reductant], [oxidant], [stabilizer], pH and reaction- time were studied and discussed. TEM analysis showed the presence of amylose on the surface of nanoparticles which acted as a probable stabilizer and/or capping agent. The hydrophilic poly –OH groups were mainly responsible for the adsorption of amylose onto the surface of nanoparticles through electrostatic interactions. The size dispersity of quasi-spherical, triangular nano-plates and nano-rods of pure crystalline metallic silver could be synthesized in presence of starch (Khan et al., 2012). $(Bu4N)7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]^{-}TiO_2$ nanocomposite have been synthesized at low temperature via sol–gel method under oil-bath condition. Fixing of

$(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ into TiO_2 decreases the particle size of crushed nano leaf of anatase phase. The $(Bu_4N)_7H_3[P_2W_{18}Cd_4]$–$TiO_2$ nanocomposite was very active catalyst systems for the model compound oxidation, while unmodified$(Bu_4N)_7H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ much less active. The oxidation reaction is selective as only sulfone was detected. For this polyoxometallates/ H_2O_2 system, oxidation reactivity decreased according to the following order: DBT>4,6-DMDBT>BT (Rezvani et al., 2012). Gan et al. (2012) discussed biosynthesis of AuNps using POME was demonstrated to be a simple, low-cost and non-toxic method. The AuNps synthesized were predominantly spherical with an average size of 18.75 nm. The morphology and size of AuNps could be controlled by varying the reaction conditions such as initial pH of the $HAuCl_4$ solution and reaction temperature. Bioactive compounds involved in the biosynthesis are most likely proteins and water soluble polyphenols in POME that contains amine and carbonyl groups. Interaction of biosynthesized AuNps with Hg(II) was investigated which demonstrates the chemical reactivity of these nanoparticles.

CONCLUSIONS

Silver NPs have gained substantial attention since, their unique properties, and proven applicability in diverse areas such as medicine, catalysis, textile engineering, biotechnology, nanobiotechnology, bio-engineering sciences, electronics, optics, and water treatment. These NPs have noteworthy inhibitory effects against microbial pathogens, and are widely used as antimicrobial agents in a diverse range of products.

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