RESEARCH PAPER

Microwave-Assisted Synthesis of Alumina Nanoparticles Using Some Plants Extracts

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ABSTRACT

In present study we used five green plants for microwave assisted synthesis of Alumina nanoparticles from Aluminum nitrate. Structural characterization was studied using x-ray diffraction that showed semi- crystalline and possibly, amorphous structure. Fourier infrared spectroscopy was used to determine Al-O bond and functional groups responsible for synthesis of nanoparticles. FTIR confirmed existence of Al-O band and bio-functional groups, originated from plant extract. Morphology and size of nanoparticles were investigated using scanning electron microscopy, transmission electron microscopy and atomic force microscopy techniques. It was observed that nanoparticles have near-spherical shape. Average size of clusters of nanoparticles varied with different routes from of 60 nm to 300 nm. AFM images showed that Individual nanoparticles were less than 10 nm.

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INTRODUCTION

Nanoparticles are synthesized with various methods; each of them provides a certain level of controllability of properties such as: structure, morphology and purity. Synthesis methods can be categorized in to three main parts as follows: Liquid phase methods, gas phase synthesis and methods basing on surface growth under vacuum conditions [1].

Cunha et al. [2], utilized sol gel method with natural organic matter to produce Alumina particles of diameter 52nm ±1. Toshio Itoh et al. [3], prepared γ-Al_2O_3 with polyol method using PVP. Optimized amount for reflux temperature and PVP molecular weight was investigated to control particles' size. γ-Al_2O_3 with particles size of 142 nm to 1.0μm was successfully synthesized and α-Al_2O_3 was produced with subsequent annealing. Tahmasebpour et al. [4], investigated polyacrylamide sol–gel method to produce α-Al_2O_3nanoparticles. They found that with low heating rates, phase transformation is delayed and as a consequence finer particles are resulted. It was also revealed that, particle size is independent of solution concentration. Zaki et al. [5, 6], used pechini method, a modified sol-gel method, to develop α-Al_2O_3 nanoparticles. The main disadvantage of these conventional methods is long duration of preparation or reaction time, which is rectified by new developed methods such as microwave hydrothermal assisted synthesis. Microwave radiation can be used as a powerful heat source for synthesis of nanoparticles from liquid phase in short time.

Kiranmala Laishram et al. [7], Developed a combustive method for synthesis of α-Al_2O_3 via microwave heating. In their experiment Aluminum nitrate and urea, prepared 1:2.5ratios, were dissolved in D/W to form a clear solution and subsequently heated with 900W for 3-5 minutes. After evaporation of the water, urea acts as a fuel and subsequent combustion synthesizes the

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Alumina nanoparticles. Nanoparticles of 18-20 nm were produced which is comparable to peer practices such as low-temperature combustion synthesis. No calcination needed for α to γ phase transformation. Leyla Sharifi et al. [8], investigated sol-gel microwave synthesis of Aluminum nitrate with microwave irradiation. They prepared gel from bohemite sol and dried gel was calcined in microwave with 900W. They found that in short time heating, first γ -Al_2O_3 nucleates and by increasing the irradiation time, more α-Al_2O_3 is produced. After 10 minutes of irradiation α-Al_2O_3 is the dominant phase. Sutradhar et al.[9], used polyol components in plant extracts to synthesize Alumina nanoparticles.50-200 nm particles were produced from tea and coffee and 200-400 nm particles were produced from triphala. Elimination of capping agent or stabilizer and using green routs lays foundation for biological usage of nanopowders.

In further studies in microwave assisted synthesis of nanoparticles, Sahu et al. [10], produced LaAlO3, Ragupathi et al. [11], synthesized Nickel Aluminate with plant extract and BaTiO3 was prepared by Katsuki et al. [12]. Nano composites of nHAp (nano-hydroxyapatite)–alumina and alumina–zirconia were produced in researches by radha etal. [13], and Benavente et al. [14], respectively.

In present study, we used microwave irradiation, as a powerful source for heating and used green routs, to maximize the purity and minimize chemical impurities in the product. Microwave-assisted synthesis using green extracts have been studied previously by plant extracts such as coffee, tea and triphala [9], Sesame [11], Biophytum sensitivum [15], Aerva lanata [16], bamboo hemicelluloses and glucose [17], Euphorbia nivulia [18]. In current research few plant extracts are used as reducer, without stabilizer, and effect of plant type on size and morphology of nanoparticles is investigated.

MATERIALS AND METHODS

Extract preparation

Syzygium aromaticum [19], Origanum vulgare [20], Origanum majorana [21], Theobroma cacao [22] and Cichorium intybus [23]were selected based on preliminary studies. 20 gr of mentioned plants were mixed with 100 ml of deionized water and boiled for 2h. After cooling in ambient temperature, they were centrifuged for 10 minutes and washed subsequently. Plant extracts were stored in 20-25 °C. Alumina nanoparticles synthesized with mentioned plant extracts are labeled according to Table 1.

Table 1. Labeling of nanoparticles

Plant type	label
Syzygium aromaticum	ALNP-1
Origanum vulgare	ALNP-2
Origanum majorana	ALNP-3
Theobroma cacao	ALNP-4
Cichorium intybus	ALNP-5

Synthesize procedure

Aluminum nitrate (>98%, Daejung, South Korea) and plant extracts were mixed with 1:4 weight ratios and then stirred for 10 minutes at room temperature. 850W LG microwave model No: MS1040SM/00v with 2.45 GHz frequency was used as heat source and solution was irradiated for 10 minutes at 610W. Irradiated solutions were centrifuged and washed with ethanol and deionized water for 10 minutes. To reduce agglomeration, powders were dissolved in deionized water and treated by ultrasonic vibration with 150 W for 5 minutes.

Characterization

X-ray Diffraction (XRD) measurements were recorded using a “XPERT” diffractometer with a Co Kα tube operating at 40 kV/40 mA and the “PROPORTIONAL Xe FILLED” detector. The data were collected in the range of 20–90°with a step size of 0.040 °and counting time of 0.8 s. The XRD patterns were evaluated using the Joint Committee Powder Diffraction Standards (JCPDS) for the phase determination. The patterns were analyzed with “High score plus” program.

FTIR studies were recorded using “PerkinElmer-Frontier FT-IR”, to specify extract bio-components involved in synthesis of nanoparticles and AL-O structure. The morphology and size of nanoparticles were investigated with scanning electron microscopy (SEM, Philips XL30) operating at 25 KV. In a complementary study; finest powder was also studied via transmission electron microscopy (TEM, Zeiss - EM10C - 80 KV). Morphology and shape of nanoparticles were also studied by ARA AFM model No.0101/A with non-contact mode of imaging.

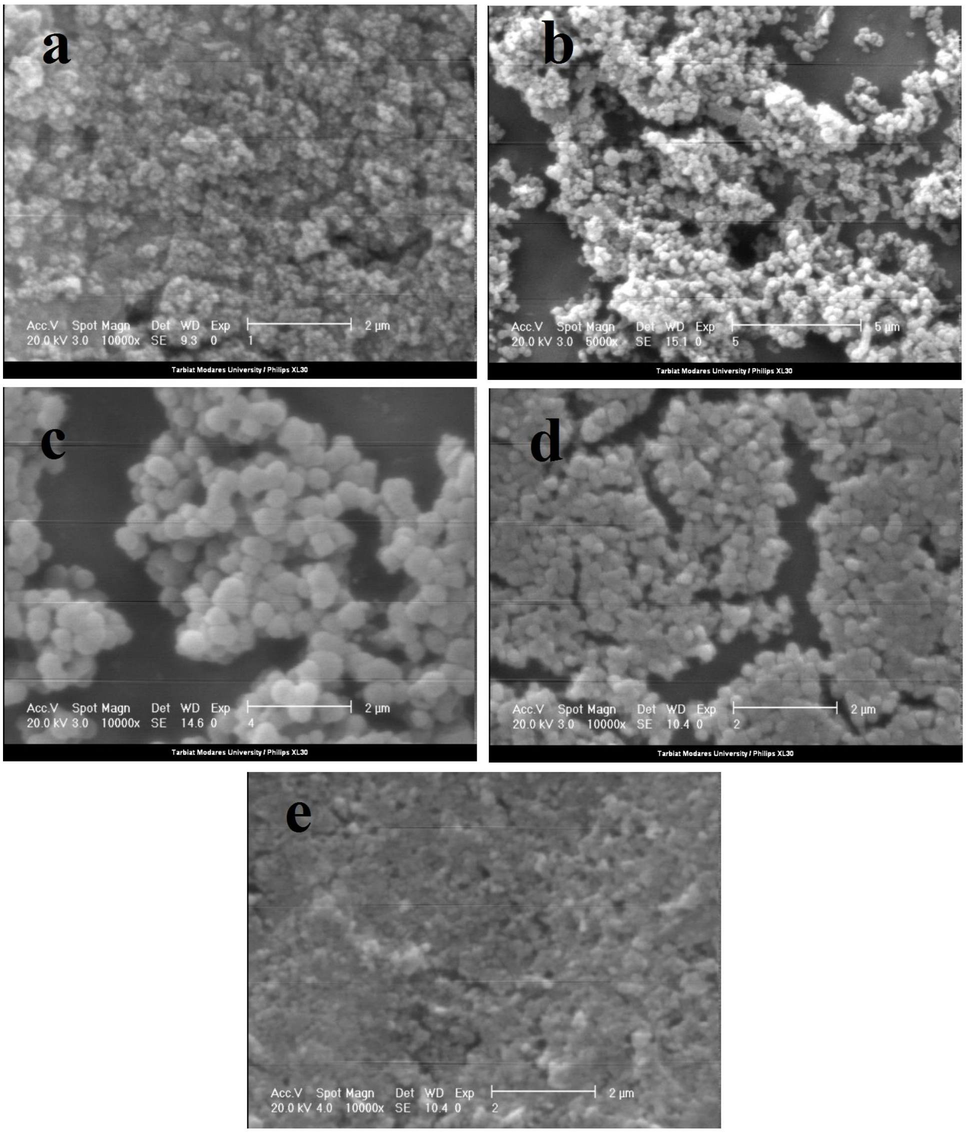

Fig 1. SEM image of a) ALNP-1 b) ALNP-2 c) ALNP-3 d) ALNP-4 e) ALNP-5

RESULTS AND DISCUSSION

Fig. 1 shows SEM images of synthesized nanoparticles. All synthesized nanoparticles seem to have near spherical form. Nanoparticle clusters were between 60-300 nm. To investigate the size and morphology of nanoparticles more precisely, AFM and TEM analysis were applied. TEM image of ALNP-1 as an example (Fig. 2) revealed that nanoparticles are nearly spherical with 3-5 nm diameter, which was verified by the measured size of nanoparticles in AFM image (Fig. 3). Summarized measurement of size of all synthesized nanoparticles, using AFM analysis, is presented in table 2. It is obvious that nanoparticles are significantly smaller than the estimated dimensions from SEM images, which may have roots in agglomeration of nanoparticles.

X-ray diffraction pattern of synthesized nanoparticles are presented in fig. 4. XRD of nanoparticles synthesized with Syzygium aromaticum extract is slightly different from others nanoparticles, which indicates poor crystalline structure [24]. According to Fig. 4, XRD pattern of

Table 2. Height of alumina nanoparticles measured with AFM analysis

Sample number	Average size (nm)
ALNP-1	8
ALNP-2	3
ALNP-3	5
ALNP-4	2
ALNP-5	9

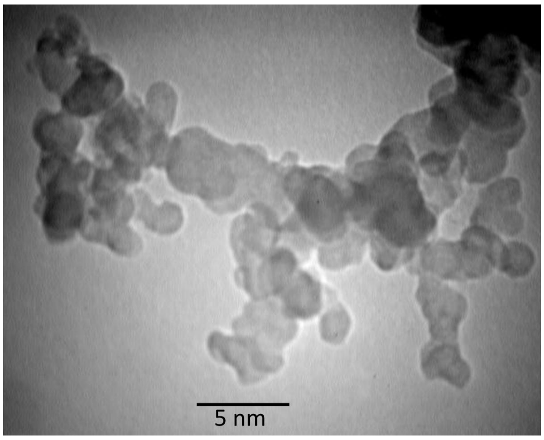

Fig 2. TEM image of ALNP-1

ALNP-1 has 3 characteristic peaks may be related with hexagonal corundum phase according to JCPDS card 96-900-9672. These significant peaks were detected at 2θ=40.99, 50.72, 67.80, correspond to (104), (113), (214) respectively. Broaden peaks are indicative of very small crystalline size [25]. Crystalline size calculated according to Debye–Scherer formula[26], d=0.89λ/βcosθ, where'd' is the crystallite size and 0.89, Scherrer's constant, λ, the wavelength of X-rays. Θ is the Bragg diffraction angle, and β, the full width at half-maximum (FWHM) of the diffraction peak. Using the Debye–Scherrer's formula, crystalline size of nanopowders evaluated to be about 3-9 nm. XRD pattern of ALNP-3 might be assigned to cubic Al_2O_3 with JCPDS card 01-075-0278. XRD pattern of other nanoparticles show no significant characteristic peak (Fig. 4). It may originate from being amorphous phase [27] or ultra-small particles of less than 5 nm [27, 28]. Moreover, It should be noted that distinguishing of amorphous and nanocrystalline structure is also dependent on line resolution which is determined by wavelength of X-ray radiation [29].

FTIR analysis was done to investigate Al-O bond and structural properties. Fig 5a illustrates FTIR spectroscopy of ALNP-1 nanoparticles. Alumina peaks are revealed from 467 to 922cm^{-1}. The band at 467cm^{-1}is assigned to AlO_6 bending mode[5] and 580 cm^{-1} is ascribed to asymmetric stretch of AlO_6 [30]. Broad band at 638 cm^{-1}, indicates AlO_6 structure [7], and 759cm^{-1} peak is assigned to AlO_4 symmetric stretching [30, 31]. 834 and 922 cm^{-1} are possibly related to complex AlO_4, and AlO_6 interactive vibration [32]. Other peaks are located between 1000 and 1750 cm^{-1}, related to bio-functional groups originated from extract [15]. These groups are assumed to be flavonoids, tannins and terpenoids [19] attached to the nanoparticles and play an important role in synthesis and stabilization of nanoparticles [9, 15]. 1073cm^{-1} peak is related to C-N stretching frequency[9]. Peak located at 1200cm^{-1}, is possibly due to stretching vibration of Polyol [33]. 1376 cm^{-1} peak is due to presence of geminal methyl group [9, 19]. 1590 cm^{-1} peak could be assigned to adsorption of water [34, 35]. Peak located at 1446 cm^{-1} is supposed to be originated from C–O–H in-plane bend of the hydroxyl groups[33]. Small band located at 1697 cm^{-1} is possibly related to C=C aromatic ring [20]. FTIR of ALNP-2 is presented in Fig. 5b. Only one peak is related to alumina nanoparticles that is located at 609cm^{-1}and it is indicative of octahedron AlO_6 only formation [5]. 1104 cm^{-1} peak, is due to C-O-C stretching frequency and 1487 cm^{-1} band is originated from Methylene group CH_2 bending [36, 37] and finally, 1614 cm-1

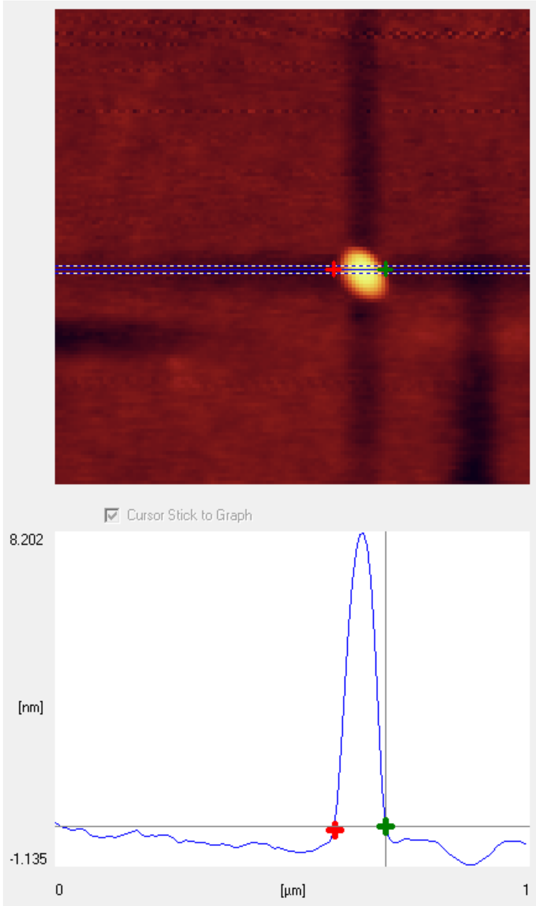

Fig 3. AFM image of ALNP-1

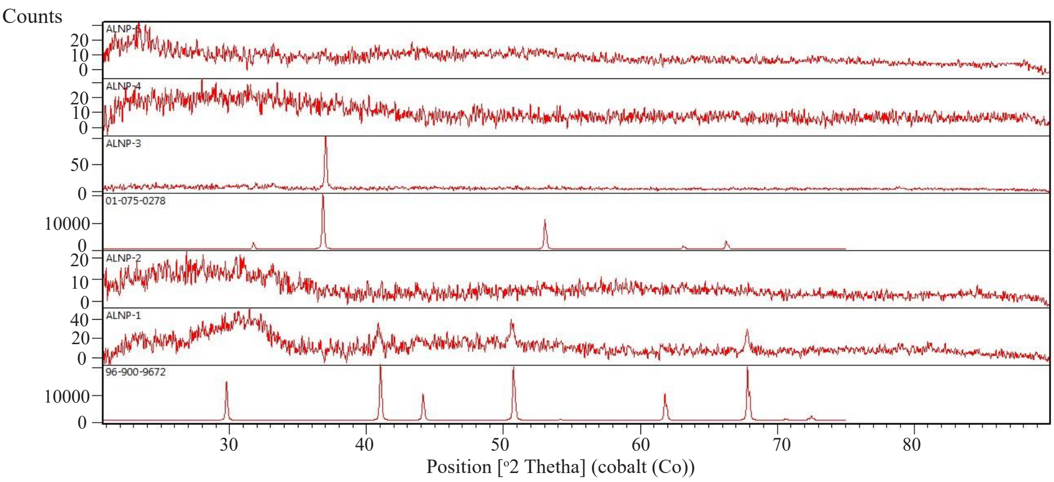

Fig 4. XRD pattern of Alumina nanoparticles

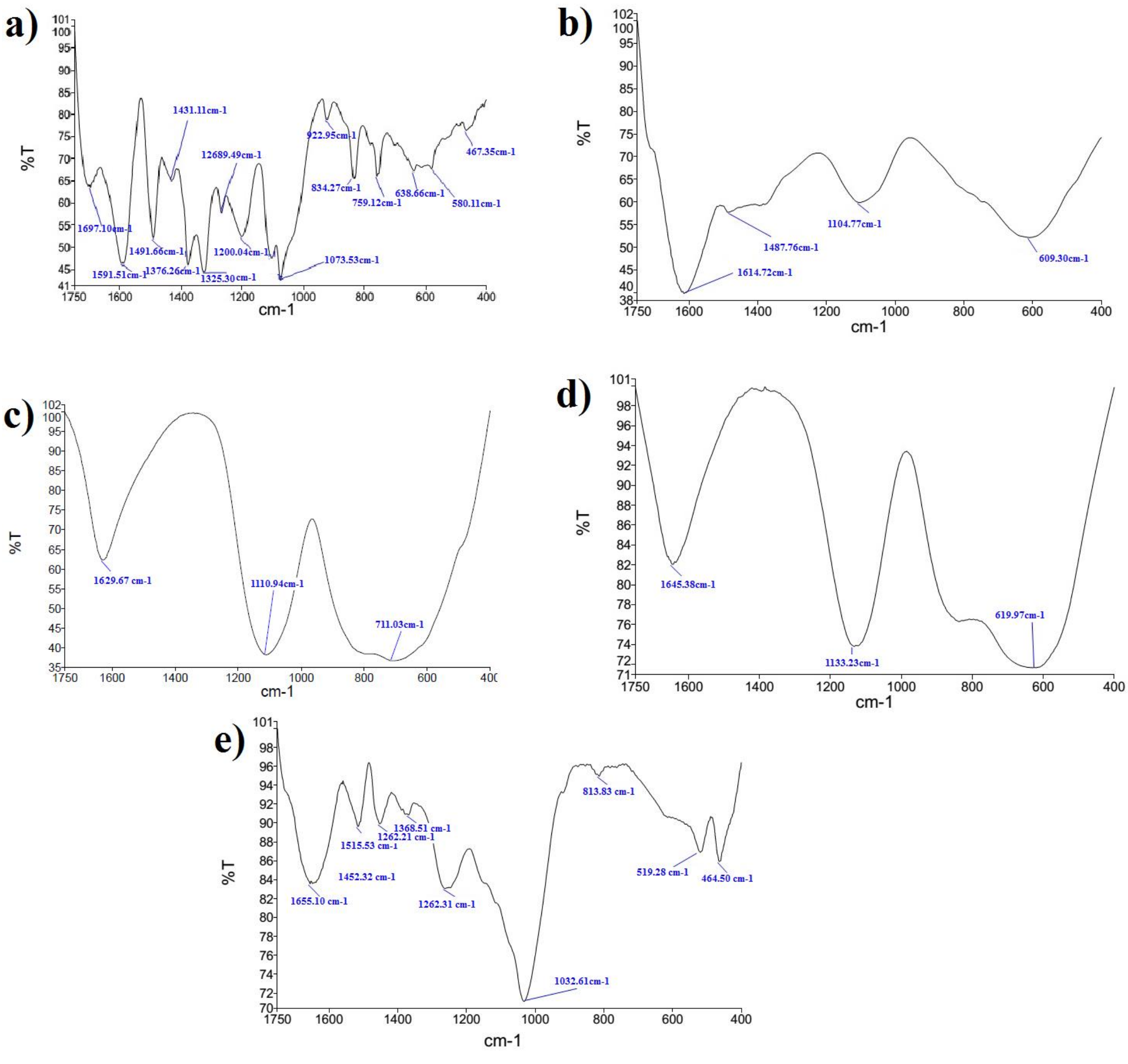

Fig 5. FTIR analysis of a) ALNP-1b) ALNP-2c) ALNP-3d) ALNP-4e) ALNP-5

suggests C=C aromatic bending [20]. Characteristic band of 711 cm^{-1}in FTIR of ALNP-3 represents Al-O band (see Fig 5c). Origanum majorana extract contains Tannins, Flavonoids, Phenol compounds and Triterpenes[38]. Characteristic band of 1110 and 1629 may represent C-O stretch and aromatic ring respectively [22]. These peaks confirm presence of flavonones as adsorbed functional groups. FTIR of ALNP-4 is shown in Fig 5d, showing a broad band at 619cm^{-1} that is indicative of symmetric stretching of AlO_6 [32]. The bands observed at 1133 and 1645 cm^{-1} may be assigned to C-H or C-O stretch and C=C aromatic ring respectively [22]. Fig. 5e presents FTIR of ALNP-5. 464, 519 and 813cm^{-1} peaks are related to alumina nanoparticles. It can be suggested that both AlO_4 and AlO_6 were synthesized[39].There are also broad and small bands around 1000 to 1750 cm^{-1} which is indicative of bio-functional groups attached to the nanoparticles. Peaks located at 1032 cm^{-1} may represent C-N band [9]and 1262 cm^{-1}peak is ascribed to C-O band [22]. 1368 and 1452cm-1 peaks may represent methyl and hydroxyl groups respectively [33]. There is a small band at 1515 cm^{-1}, related to possible adsorption of water to surface [34, 35]and finally, 1655cm^{-1} broad band is indicative of aromatic ring [22].

CONCLUSION

Syzygium aromaticum, Origanum vulgare, Origanum majorana, Theobroma cacao and Cichorium intybus were used as green routes for microwave assisted synthesis of alumina nanoparticles.

XRD pattern of particles synthesized with Syzygium aromaticum showed semi-crystalline structure while others showed no significant peak that might be assigned to nano dimension of particles or their amorphous structure.

FTIR studies of nanoparticles showed peaks in range of 450-1000 cm^{-1}, assigned to AlO_4 and AlO_6 bonds, and some peaks in range of 1000-1750 cm^{-1}: assigned to bio-functional groups responsible for particles synthesis.

SEM analysis of nanoparticles showed clusters of nanoparticles in 60-300 nm range. TEM and AFM analysis revealed that individual nanoparticles have less than 10 nm size.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publicaton of this manuscript.

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