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A novel strategy for synthesis of Al powder comprising of Al nanoflakes via ultrasonication of Al foil

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Abstract

Aluminum (Al) nanopowders have potential applications as hydrogen storage medium, energetic materials, pigments, and for production of metal matrix parts via powder metallurgy, to name a few. They are synthesized by methods which are either expensive or result in the product with impurities. A novel methodology based on ultrasonication of commercially available Al foil has been developed for synthesis of Al powders. Al foil was immersed in an organic medium and subjected to ultrasonication in a 160-watt bath ultrasonicator operated at 35 kHz frequency. Morphological, crystal structural, and dimensional characterization of ultrasonicated Al was carried out with the help of scanning electron microscopy (SEM), X-ray diffraction (XRD), and atomic forces microscopy (AFM) respectively. Characterization results revealed that Al foil was eroded laterally as well as axially, resulting in the formation of micro and nanosized flake-like pure Al powder.

Keywords: Aluminum; Powder Technology; Ultrasonic Energy; Nanosheets; SEM; XRD

1. Introduction

Aluminum (Al) metal has a high strength to weight ratio as compared to other structural materials, having density of 2.78 g/cm^3 [1] and is used in pure form only for applications that require moderate mechanical strength with decent capability to form in different shapes such as cans of soft drinks and roof panels of cars [2]. It is generally used in the form of alloys for large number of industrial applications [3]. Recent progress in powder metallurgy and additive manufacturing has placed higher demands on production of Al powder. It is commonly used as a propellent in solid rocket boosters [4], conductive contacts in electronics and photovoltaics [5], in thermal barrier coatings for aircrafts [6], for injection molded products [7], explosives [8] and as pigments in paints in order to make them conducting and reflecting [9]. Nanopowders of Al are used for hydrogen storage [10] and are added in explosives to increase the stored energy [11].

Al nanoparticles are currently synthesized by various techniques which include atomization, electrowinning, mechanical comminution, mechanochemical techniques, laser ablation techniques, exploding wire technology and by wet chemical processing. In atomization, molten metal is sprayed in the form of fine droplets which form metal powder upon solidification [12]. Atomization techniques generally result in the formation of metal powders with particles size in micrometers. Electrowinning process of Al uses an electrolytic cell to form Al powder by reducing Al ore by using electric current. The process for electrowinning suffers from high energy consumption, refractory lining instability, consumable electrodes, and hazardous emissions [13]. Mechanical comminution methods are used for synthesis of fine metal powders [14] but they are highly susceptible to contamination. Mechanochemical techniques utilize mechanical working along with a chemical reaction [11] but they also result in undesirable byproduct phases [15]. In laser ablation techniques, Al source is submerged in a fluid, laser melts the metal and form a plasma plume. Al nanoparticles are formed upon condensation of plasma plume in the fluid but high energy plasma plume may react with cooling fluid thereby adversely affecting purity of the developed powder [16]. Exploding wire method uses high current, strong magnetic field, and a dense fluid medium for the synthesis of metal nanopowders [17]. It has been used for synthesis of copper, iron, silver and Al nanoparticles; however, it is an expensive method due to the high cost of equipment, operation, maintenance, and need of skilled manpower. Al nanopowder has also been synthesized through wet chemical processing. Though the process is simple and time-sparing, but presence of impurities such as carbon, oxygen, and chlorine (depending primarily on the

type of precursor used) [18], has been reported. Aforementioned methods for synthesis of Al micro or nanoparticles are either complex or too expensive to be carried out for small batch productions or result in process-based impurities.

Ultrasonication is commonly used for cleaning of different materials such as glassware, wafers of semiconductors, and textiles [19]. Ultrasonication has recently been explored for development of magnetic nanoparticles ($Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO_3$) [20], photocatalyst nanomaterials (titania) [21], and nanostructures of layered materials (graphene, vermiculite nanosheets, BN nanosheets, etc.) [22] but it's potential for the development of pure metal powders by top down approach has not been explored yet. The present study aims at developing a very simple method for synthesis of Al nanopowder by the top-down approach. It is based on disintegration of commercial grade Al foil fragments by ultrasonication to achieve Al powder comprising of nanoflakes. The proposed technique for synthesis of Al powder is cleaner, economical, easier to adapt, and can also be widely applied for recycling of other soft foil materials.

2. Experimental procedures

Commercially available Al foil (*Diamond Aluminum Foil*) having thickness of 20µm was cut in square fragments of 5mm×5mm with help of a pre-cleaned paper cutter and was immersed in WD-40 oil (obtained from *WD-40 Company Limited, UK*) and in distilled water, separately. Glass vials containing Al fragments immersed in WD-40 oil/water were then placed in ultrasonic bath (*Sonorex Super RK 510H*) which was operated at 2.5A, 160-watt and 35 kHz frequency. Ultrasonication may lead to increase in the temperature of the ultrasonic bath and formation of gasses in the glass vials. Temperature of the bath was monitored with the help of a thermometer, which remained under 70°C during experimentation. Gasses released due to increase in temperature of bath were vented by opening cap of the vial after every hour. Suspension obtained after 36 hours of sonication was carefully separated from Al powder sediment in a separate glass vial. Suspension of Al nanoflakes in WD-40 was then cleaned with n-hexane in the centrifuge (*Centurion Scientific C2 Series* operated at 4000 RPM) in order to separate Al nanoflakes from the organic medium (WD-40). Suspension of n-hexane and Al was then dried in a vacuum oven at 80 °C and -0.09MPa pressure. Morphological, crystal structural and dimensional characterization of obtained Al powder was carried out with the help of SEM (*JEOL JSM 6490LA and TESCAN VEGA3 LMU*) operated at 20 kV of

accelerating voltage, XRD (*Bruker D8 Advanced* equipment operated at 40 kV and 30mA) and AFM (*Nanosurf-3000* operated in tapping mode) respectively.

3. Results and discussion

Al foil was initially immersed in water and ultrasonicated for different intervals of time. Condition of Al foil as a function of ultrasonication time is shown in the **Fig. 1 (a)**. Color of the water, during ultrasonication, changed to milky white pointing out possibility of reaction between Al and water during the process. XRD pattern of the powder, achieved after 36 hours of ultrasonication in water, is shown in the Fig. 1 (b). Presence of only aluminum hydroxide peaks in the XRD pattern confirmed reaction of Al with water to form $Al(OH)_3$. It is proposed that increase in surface area of Al due to the formation of micron and nanosize particles during ultrasonication increased its activity and it reacted with water to form aluminum hydroxide. This mechanism has been named as '*erosion assisted oxidation*'. Al has also been previously reported to react with water according to the following chemical reaction [23].

$$Al + 3H_2O \rightarrow Al(OH)_3 + {}^{3}/_{2}H_2\uparrow \quad -----(1)$$

SEM images of aluminum hydroxide formed as a result of reaction of Al with water during ultrasonication are shown in the **Fig. 1 (c)** which revealed irregular morphology of the developed powder.

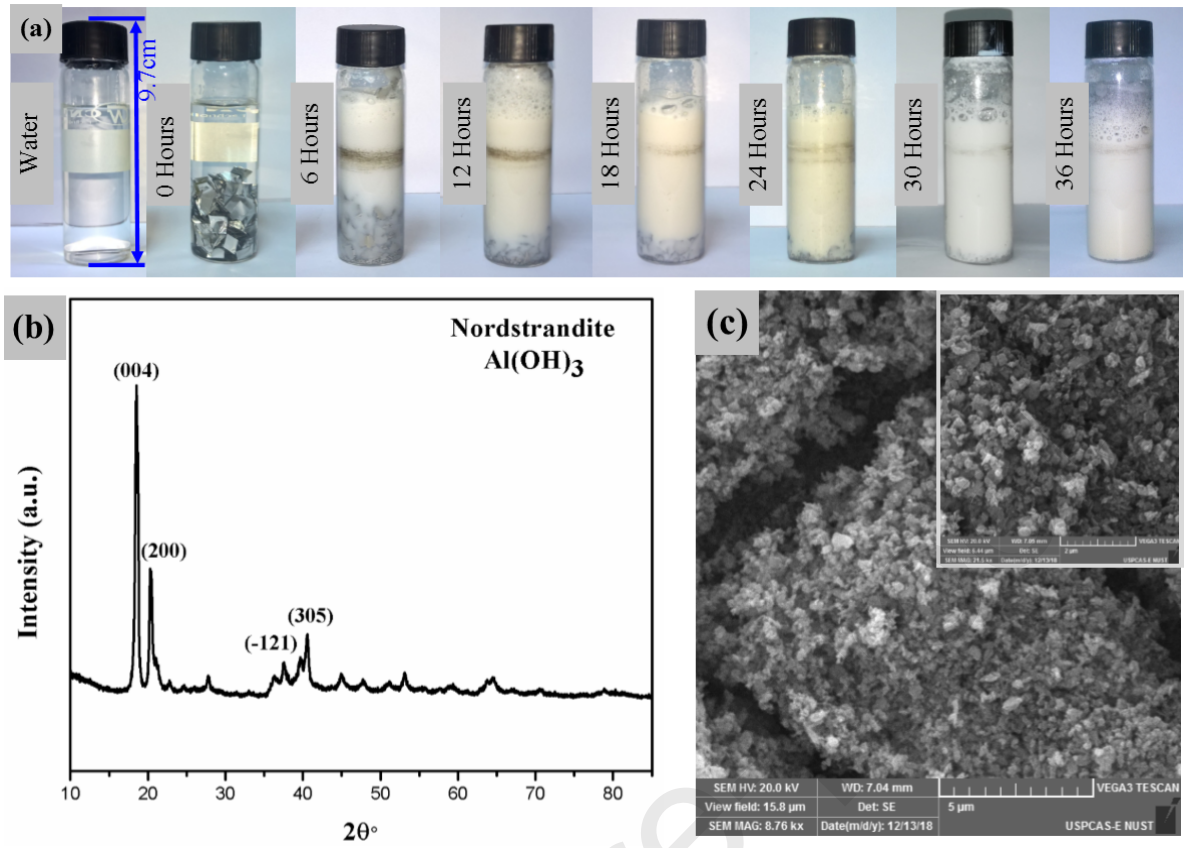

Fig.1. Al foil transformation in water as a function of ultrasonicating time **(a),** X-ray diffraction pattern of aluminum hydroxide **(b)**, and scanning electron micrographs of aluminum hydroxide **(c)**.

To avoid formation of aluminum hydroxide, water was replaced an organic medium (WD-40 oil) and ultrasonication was carried out for 36 hours. Effect of ultrasonication time when WD-40 oil was used as ultrasonication medium is shown in the **Fig.2 (a)**. No change in the color of the organic medium indicated absence of any chemical reaction between Al foil and WD-40. Suspension obtained after 36 hours of ultrasonication was carefully separated from Al powder sediment in a separate glass vial and cleaned with n-hexane in centrifuge, operated at 4000 rpm. After centrifugation, suspension of n-hexane and Al nanoflakes was dried in a vacuum oven at 80 °C and -0.09 MPa pressure and analyzed with the help of SEM, XRD, and AFM.

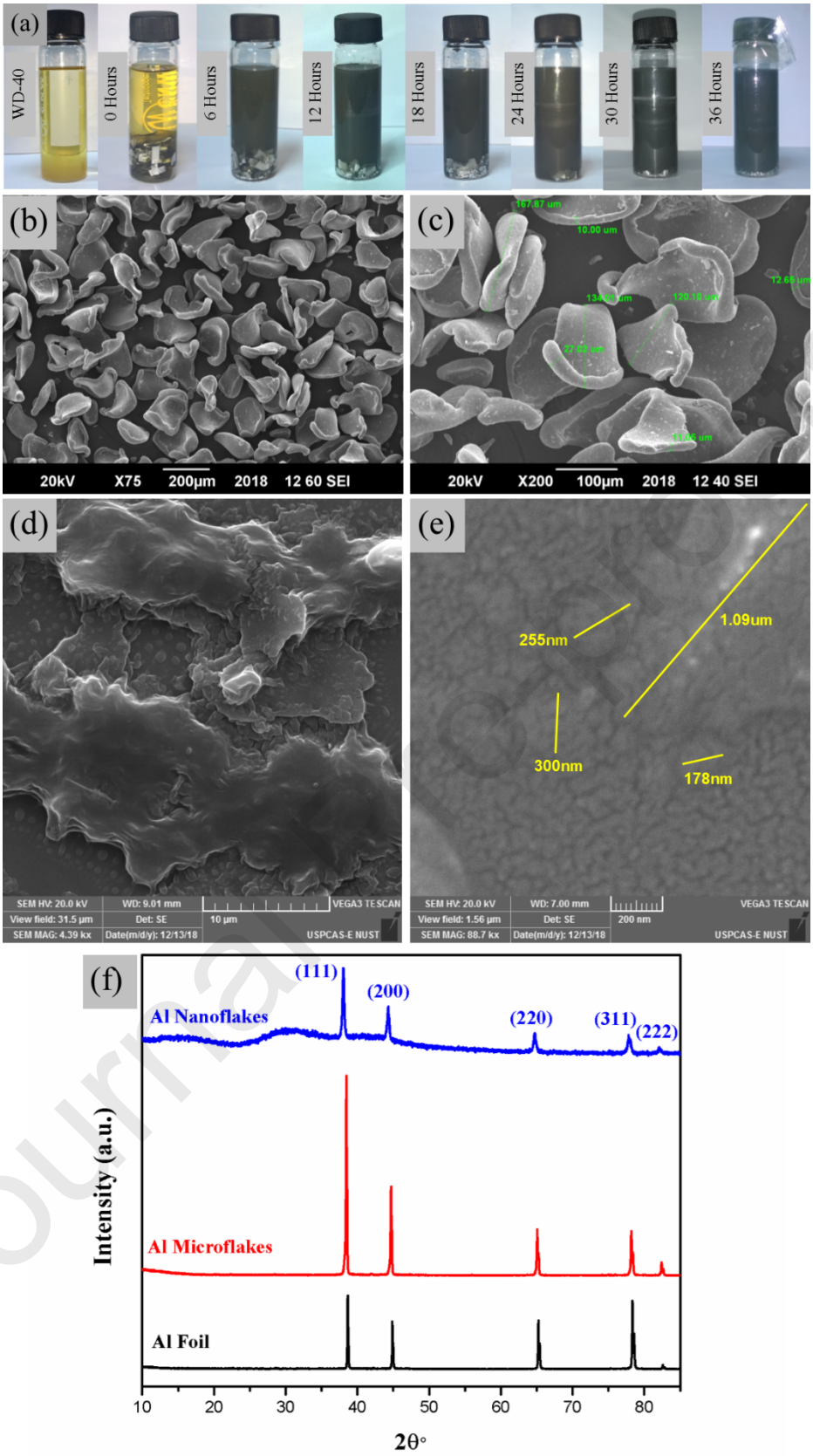

Fig.2. Al foil transformation in WD-40 as a function of ultrasonicating time **(a),** SEM images of Al powder obtained from the sediment **(b,c)**, SEM images of Al powder obtained from the sediment **(d, e)** and XRD patterns of Al foil, Al microflakes (obtained from sediment) and Al nanoflakes (obtained from suspension) (f).

SEM analysis of the powder obtained from the sediment and from the suspension are shown in the **Fig. 2 (b,c)**, and **Fig. 2 (d, e)** respectively. As can be seen from the Fig.2, powder obtained from the sediment and from the suspension comprised of Al microflakes and Al nanoflakes respectively. Thickness of the synthesized Al microflakes, as shown in the **Fig. 2 (c)**, is around 10μm whereas initial thickness of the Al foil used was 20μm. It can be safely concluded that ultrasonication not only broke down the structure laterally but also led to the exfoliation and erosion of Al layers axially. Uniformity in size of synthesized flakes can also be observed. SEM images of Al nanoflakes, obtained from the suspension, are shown in the **Fig. 2 (d,e)**. Granular background in the SEM images corresponds to the sputtered gold islands formed on polished silicon substrate. X-ray diffraction patterns of starting material as well as of Al microflakes and nanoflakes powders obtained after 36 hours of ultrasonication in WD-40 are shown in the **Fig. 2 (f)**. XRD measurements of developed powders confirmed presence of peaks corresponding to the pure Al. Absence of any extra peaks in the XRD pattern of the developed powders confirmed that no chemical reaction took place between Al and WD-40 during ultrasonication. Absence of Al_2O_3 peaks in the XRD pattern of developed powder indicated no or very small oxidation took place as developed powders were kept under n-hexane atmosphere and were dried in vacuum oven just before XRD analysis. Hump observed in the diffraction pattern at low angles corresponds to the amorphous polymeric sample holder used for XRD measurements. Height of Al nanoparticles was determined with the help of atomic forces microscopy. Suspension containing the Al nanoparticles was drop casted on a polished silicon substrate and analyzed under a *Nanosurf* AFM equipment. Height of Al particles shown in the **Fig. 3 (b)** was determined with the help of AFM software which is indicated in the **Table 1**.

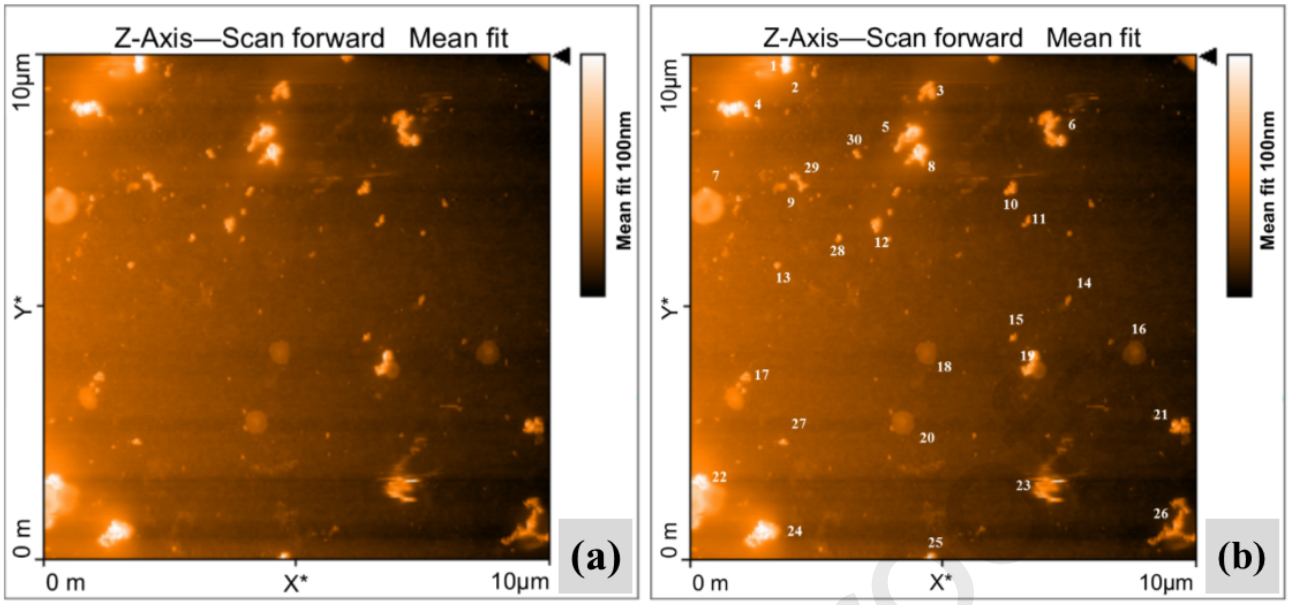

Fig.3. AFM images for 10µm × 10µm area on a polished silicon substrate **(a)**, numbers are assigned to particles for defining height of particles in Table 1 **(b)**.

Table.1. Height of particles of Al nanoflakes determined with the help of AFM

Particle Number*	**Height (nm) ± (0.92nm)**	**Particle Number***	**Height (nm) ± (0.92nm)**	**Particle Number***	**Height (nm) ± (0.92nm)**
1.	90	**11.**	35.7	**21.**	59.3
2.	48	**12.**	61.6	**22.**	92
3.	60	**13.**	45.7	**23.**	52
4.	90	**14.**	25.4	**24.**	92.6
5.	58	**15.**	46.1	**25.**	53.4
6.	58	**16.**	26.1	**26.**	55
7.	66.3	**17.**	50.9	**27.**	46
8.	89.7	**18.**	15.4	**28.**	54.6
9.	28.5	**19.**	54.7	**29.**	46.9
10.	44.7	**20.**	19.7	**30.**	51.3
Average height of Al nanoflakes					**53.9nm ± 0.92nm**
Standard deviation in height of Al nanoflakes					**20.61nm**

*: Particle numbers refer to the particles shown in the Fig. 3 (b).

The proposed methodology is based on acoustic cavitation effect which caused erosion and disintegration of Al foil laterally as well as axially, resulting in the formation of Al micro and nanoflakes. XRD measurements confirmed purity of the exfoliated powder whereas morphological and dimensional characterization confirmed development of Al nanopowder with an average particle height of $53.9 \pm 0.92nm$. Increase in surface area of the starting material due to exfoliation and increase in energy of the ultrasonication medium due to ultrasonic shock waves, may facilitate a chemical reaction. Careful selection of ultrasonication medium is therefore required for successful development of pure metal powder. As the proposed methodology, unlike conventional comminution methods, does not suffer from process-based impurities and requires only inexpensive starting materials (Al foil) and equipment (ultrasonication bath), it can serve as an economical alternative for development of nanosize powder of Al and other soft metals.

Conclusions

A novel methodology, based on the acoustic cavitation effect, has been successfully developed for synthesis of nanosized Al powder from commercially available Al foil. X- ray diffraction analysis confirmed absence of any chemical reaction during ultrasonication when organic medium was used. Morphological characterization of developed powder carried out with the help of SEM, which confirmed lateral as well as axial erosion of Al foil resulting in formation of micro and nanosize flake-like Al powder. Average height Al nanoflakes was found to be 53.9 ± 0.92nm with a standard deviation of 20.61nm by AFM.

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Figure Captions

Fig.1. Aluminum hydroxide, **(a)** Extent of Al foil transformation into powder in result of ultrasonication at regular time intervals in water, **(b)** X-ray diffraction pattern of aluminum hydroxide, and **(c)** scanning electron micrographs of aluminum hydroxide.

Fig.2. Al powder, **(a)** Extent of Al foil transformation into powder in result of ultrasonication at regular time intervals in WD-40, **(b) and (c)** Sediment Al microflakes, **(d) and (e)** Al nanoflakes from suspension and **(f)** X-ray diffraction patterns of Al foil and synthesized materials.

Fig.3. AFM images of Al powder comprising nanoflakes, **(a)** AFM image for 10μm × 10μm area on a polished silicon substrate, and **(b)** same as image represented in **Fig. 3 (a)**, numbers are assigned to particles for defining height of particles in **Table 1**.

Table Captions

Table 1. Height of particles of Al powder comprising nanoflakes, particles numbers refer to **Fig. 3 (b)**.

Highlights

- Aluminum (Al) micro and nanoflakes were synthesized by ultrasonicating Al foil in organic medium
- WD-40 (organic medium) was found to be more beneficial as compared to water for synthesis of Al powders
- Only Al peaks were observed in XRD diffraction pattern of Al powder synthesized in WD-40
- Height of Al nanoflakes was found to be $53.9 \pm 0.92\ nm$ as measured by AFM