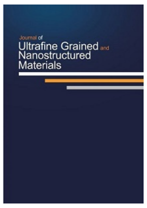

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Synthesis of Si/MgO/Mg_2SiO_4 Composite from Rice Husk-Originated Nano-Silica

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ABSTRACT

Silica exists in Rice husk, an agriculture waste, as a naturally occurring phase. In first step, acidic pre-treatment and calcination of the rice husk were performed to obtain nano-silica, in which various sizes of the nano-silica, totally with sizes under 80 nm, were achieved. Second, to reduce nano-silica to elemental Si and subsequently formation of the composite, Mg used as the reducing agent. In this work, the as-obtained composite mainly is the product of magnesiothermic reduction reaction of the nano-silica, which finally resulted in formation of elemental Si (silicon), MgO (magnesia) and Mg_2SiO_4 (magnesium silicate). The as-synthesized composite can be used as anode in lithium ion batteries. The products in each step were characterized using X-ray powder diffraction (XRD) and scanning electron microscopy (FESEM and HRSEM) techniques. X-ray powder diffraction patterns confirmed the formation of almost amorphous silica while the FE-SEM images were representing the spherical silica particles at various calcination temperatures. After the magnesiothermic reduction process, HRSEM micrographs indicated the formation of Si-MgO-Mg_2SiO_4 composite with particle sizes of 180-300 nm. The phase composition analysis was calculated by Rietveld method The electrical response of the Si/MgO/Mg_2SiO_4 composite was measured to be of $6\times10^8\,\Omega$.m resulted from I-V measurement.

Keywords: *Nano-silica; Silicon; Rice husk; Magnesiothermic reduction; Composite.*

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1. Introduction

Rice husk is a byproduct of rice cultivation farms, which is land-filled or used as aquatics feeding in most developing countries, nevertheless it can be counted as a new agro-based resource. A basic knowledge is of great importance for harnessing this added value, based on the clear understanding of its structure and properties. Chemical composition of rice husk (RH) might vary from sample to sample, because of factors such as climate and geographical conditions [1]. Chemical composition of RH obtained in different parts of the world generally consists of ash (silica and other impurities), organic constituents (i.e., cellulose, hemicellulose and lignin) and moisture.

Silica formed after burning in the atmosphere is eventually nanometric in size. So its achievable properties could be a benefit to advance applicability in many areas such as silicon chip manufacturing [2], producing silica gels, pharmaceutical products and ceramics [3]. Factors such as the calcination at various treatment temperatures and purification with different acids can yield different structures and purities. In spite of the approaches developed for synthesizing silica nano-particles such as using silica precursor [4] which are energy intensive and expensive and sometimes eco-hazardous [5], biogenic silica harvested from rice husk is cost-effective.

Silicon in various forms has attracted considerable interest in many applications, such as electronics, photovoltaic, biomedicine and innovatively as anodes in lithium ion batteries. Yanna NuLi et al investigated electrochemical intercalation of Mg^{2+} in magnesium manganese silicate with regard to its use as electro-active species in ion-transfer battery systems [6]. Magnesium as a coating material for silicon nanowires is proposed by Kohandehgan et al, they evaluate the effect of Mg-coating as a composite on performance of Li-ion battery anodes [7] thus it can be beneficial to compare between 'inactive–active' and 'active–active' composites.

In this work, we performed acidic pre-purification on rice husk before the calcining the material. After the calcination, the rice husk ash (RHA) consisting mainly of nano-silica was obtained. The effects of calcination temperatures and its duration on morphology and phase constitution were investigated. Magnesiothermic reduction process for preparing of Si-MgO-Mg_2SiO_4 composite was conducted and electrical property of final product was measured.

2. Experimental

RH was purchased from Babol, Iran (36° 32' 39" North, 52° 40' 44" East). Distilled water, solutions of hydrochloric acid (37%wt) (Merck) were used in the purification treatment process. An acid-leaching step employing hydrochloric acid solution was performed to remove metallic impurities, dust and alkaline and alkaline-earth oxides [8] from ground rice husk. Rice husk was refluxed into dilute hydrochloric acid (0.1 M) in a 1000 ml flask at 40°C for an hour under stirring. The residue was filtered and washed with distilled water and dried at 110°C for 24 hours prior to further processing. The acid-leached RH was calcined at 600-900 °C in air.

To obtain Si/MgO/Mg_2SiO_4 composite, magnesium powders (0.06-0.3 mm, Merck) were premixed with nano-silica sample obtained after heat-treatment at 700°C for 3h using 10%wt excess magnesium and then vacuumed in a quartz glass cylinder. Then, the quartz glass cylinder was heat treated at 650°C for 3 hours in a protective argon (99.9% purity) atmosphere.

Si/MgO/Mg_2SiO_4 composite was mixed with PVB for preparing slurry for following pelletizing which was pressed for I-V curve measurement. The pellet was electrically conductive with a drop-casting of Ag dispersion on both surfaces of the pellet followed by drying and roll-pressing. Linear Polarization tests were harnessed in the voltage range of -3 V to +3 V with step height of 0.005 V in air under open circuit voltage (OCV) using a PARSRAT 2273 potentiostat. Sample resistance was calculated from the slope of the as-obtained I-V curve.

The calcined samples were obtained are hereafter referred to as RHA-T-d (T: Calcination temperature (600, 700, 800 or 900°C); d: duration of Calcination, respectively. Samples were analyzed using X-ray powder diffraction (XRD) using Rigaku Ultima IV diffractometer with CuK_α radiation (k= 1.5405 Å), The morphology of the samples was investigated by scanning electron microscopy (SEM; CAMSCAN MV2300), FE-SEM (TESCAN MIRA3) and Energy-dispersive X-ray spectroscopy (EDS, Bruker) measurement.

3. Results and discussion

Silica obtained from RH by pre-purification and subsequent calcination. XRD patterns generated from RH for all samples are shown in Fig 1. A large broad peak was observed around 22 degree clearly, representing the formation of silica. These data showed that the SiO_2 has an almost amorphous structure (Fig. 1).

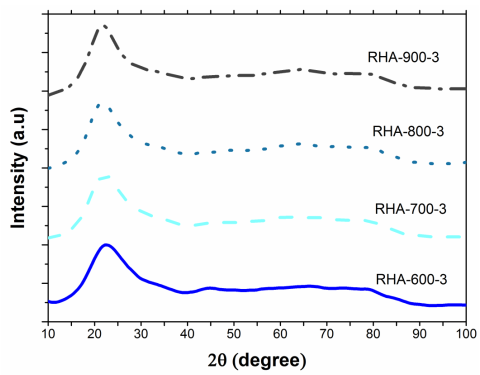

Fig. 1- XRD patterns of samples calcined at various temperatures.

Micro structural studies using FESEM were conducted on calcined RH (RHA) samples for all calcination temperatures (RHA-600-3, RHA-700-3, RHA-800-3, RHA-900-3) as shown in Fig 2(a-d)). Morphology of the samples is composed of uniform sized semi sphere-like nano-particles with average diameter of 23 nm for RHA-700-3 and 34 nm for RHA-800-3. FESEM images suggested that higher temperature and longer calcination times led to coarsening and diffusion of SiO_2 nano-particles.

Visual testing of RHA-600-3 product revealed black impurities which are carbonaceous residues from the incomplete burning of lignocellulose in RHs. As in previous studies, it is suggested that employing higher calcination temperatures improves purity. The RHA-700-3 sample was selected basically because of its relatively small particle size and also possessing a fully white appearance which is attributed to its high purity which is in agreement with works of other researchers [9]. Although the RHA-600-3 sample consisted of particles smaller than RHA-700-3, traces of unburnt carbon was detected.

After publication of the first report on magnesothermic reduction of silica into Si by $Mg_{(g)}$ via the reaction (1) by Bao et al [10], the process gained a special attention, because of the fact that Mg vapor (b_p=650°C) can access the whole surface of silica, So the magnesiothermic reduction performed on RHA-700-3 sample and as expected the products of reaction i.e. Mg_2SiO_4 and MgO, Si formed due to the equation of (1), (2):

$$SiO_2(s)+2Mg(g)=2MgO(s)+Si(s) \quad \Delta G^o_{298}=-282\ kJ/mol \quad (eq.\ 1)$$

$$SiO_2(s)+2MgO(s)=Mg_2SiO_4(s) \quad \Delta G^o_{298}=-62.233\ kJ/mol \quad (eq.\ 2)$$

The reflections of Si, MgO and, Mg_2SiO_4 phases are detected in the proceesed sample (Fig. 3). The particle size of the Si-contained composite was found to be mainly about 180-300 nm with a mean diameter of 208 nm and had a uniformly spherical shape (Fig 4 (a-c)). EDS is an elemental analysis method and conducted to ensure the presence of Si, Mg and O while Rietveld method is based on phase compositional analysis[11]. Hence, one may not expect the same results from these two techniques.

The EDS spectrum of the obtained products

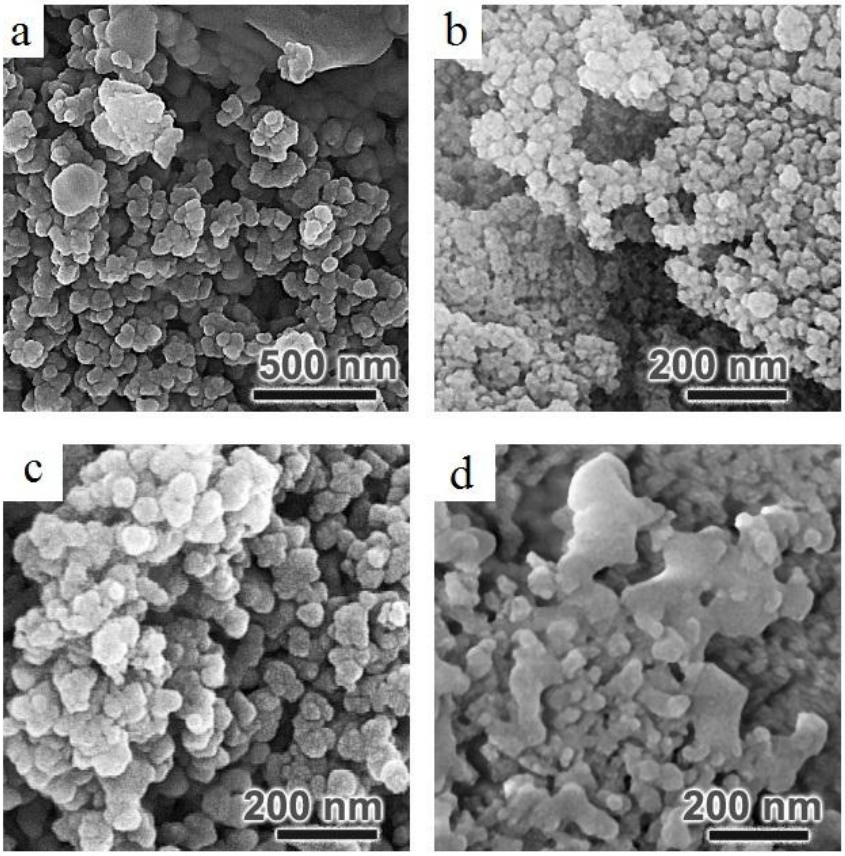

Fig. 2- FE-SEM images of processed samples: RHA-600-3(a), RHA-700-3(b), RHA-800-2(c), and RHA-900-8 (d).

revealed the presence of Si beside Mg and O as well, as shown in Fig 4 (d). After magnesiothermic reduction, mixture was composed of 16.47 % Si, 25.14 % Mg_2SiO_4 and 58.39 % MgO deduced by Rietveld method.

Electrical property of the synthesized composite was measured by I-V measurements (Fig 5). The electrical response of a pellet of the composite was tested, and it showed ohmic I-V characteristics. The relatively high resistivity of 6×10^8 Ω·m could be due to the magnesium oxide and magnesium silicate, which lessens the interparticle conductivity compared to highly pure nanostructured silicon (333.33 Ω·m) [12]. Low electrical conductivity is

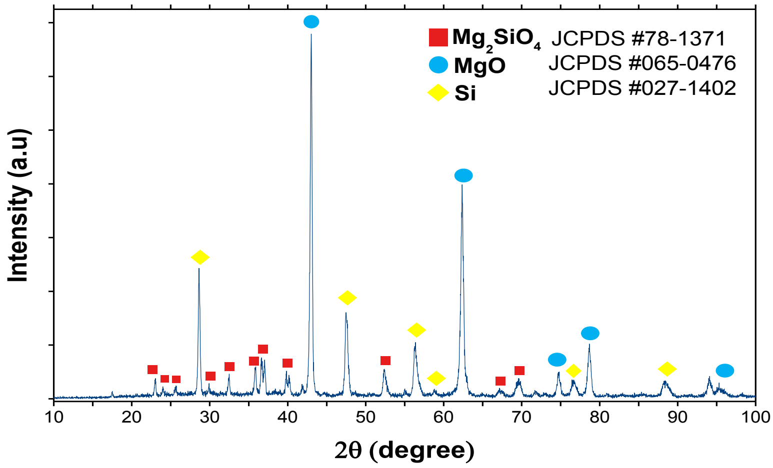

Fig. 3- X-ray powder diffraction pattern of synthesized composite.

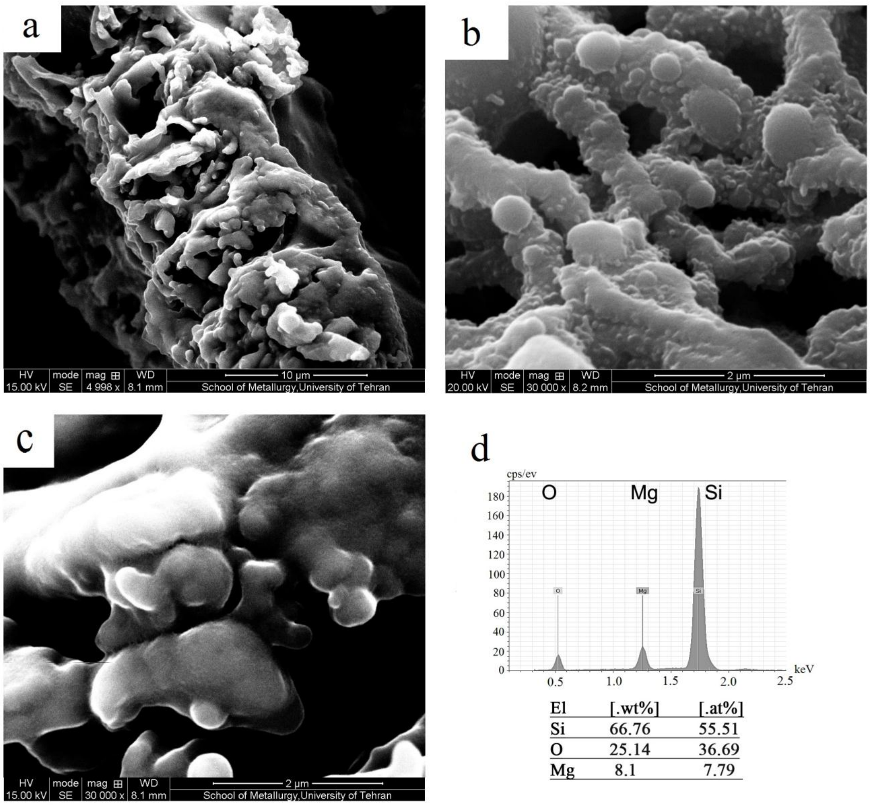

Fig. 4- HRSEM images of Si-MgO-Mg_2SiO_4 particles prepared by magnesiothermic reduction process (a, b,c) and corresponding EDS spectrum (d).

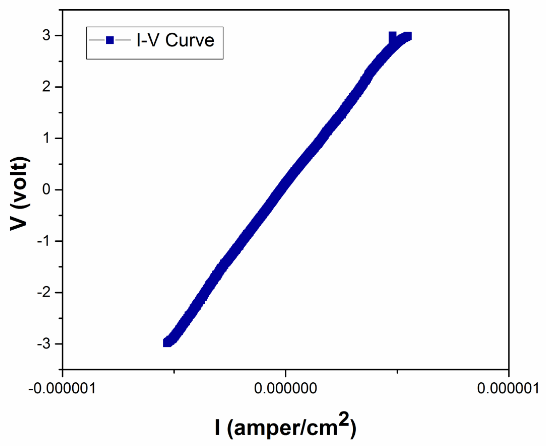

Fig. 5- I-V measurement of obtained composite.

one of the major concerns of Si-based electronic components. But Si-based materials come with the advantage of high gravimetric and volumetric capacity. Conductive additives such as carbon black are added to enhance conductivity in fixed ratios [13, 14]. So this composite may serve as a suitable candidate for anodes in Li-ion batteries despite its low electrical conductivity.

4. Conclusion

Rice husk can be a source for many silicon-based materials if treated thermally under controlled conditions. The silica thus produced is X-ray amorphous, white amorphous silica of high chemical purity can be obtained from rice husk at temperatures higher than 600°C in 3h period of time. 3 hours of calcination at 700°C appeared to be ideal to produce silica nano-particles with a diameter of ca. 20–30 nm from HCl-treated RHs. The new way for the production of Si-MgO-Mg_2SiO_4 composite was introduced in this work which is based on a magnesiothermic reduction reaction. The SEM and XRD results showed the nanometric silica could successfully converted into a crystalline Si-contained composite with MgO and Mg_2SiO_4. The electrical response of the Si-contained composite was measured to be of 6×10^8 Ω·m.

Acknowledgements

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