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Structural, Morphological and Physiochemical Analysis of $SiC_8H_{20}O_4/C_2H_5O/C_7H_{16}$ Modified Mesoporous Silica Aerogels

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Silica Aerogels are well recognized and have attracted a considerable attention due to their unique properties. Using rice husk ash as the main precursor and ambient pressure drying as method, we synthesized and compared the four different mesoporous silica aerogel variants independently modified with TEOS, Ethanol and n-Heptane. The variants were characterized by BET, SEM, EDX, and XRD. According to our results, the highest porosity percentage, surface area, pore volume, average pore size and the lowest volume shrinkage of 85%, 312 $m^2\ g^{-1}$, 0.76 $cm^3\ g^{-1}$, 9.6 nm, and 91.16% were observed in sample treated separately with TEOS, ethanol and n-heptane (SGTEH-Iso). However, the mentioned data for the sample treated with simultaneous solvent exchange/n-heptane aging (SGTEH-Sim) were 79.5%, 298 $m^2\ g^{-1}$, 0.75 $cm^3\ g^{-1}$, 9.2 nm, and 91.86%. Moreover, TEOS ($SiC_8H_{20}O_4$), ethanol (C_2H_5O) and n-heptane (C_7H_{16}) enhanced the silica purity, strengthened the gel network and suppressed the crack formation during ambient pressure drying. In conclusion, due to their high porosity, pore volume and average pore size, the SGTEH-Iso and SGTEH-Sim variants have potential application as adsorbents for the removal of heavy metals from wastewater.

Keywords: Silica aerogel, Sol-gel method, Rice husk ash, Ambient pressure drying, Mesoporous

INTRODUCTION

Silica aerogels have attracted the attention of researchers due to their unique properties and their potential application in a various technological areas such as catalysts, thermal insulation, drug release, and membranes. These compounds have high specific surface area, high porosity, low density, low dielectric constant, and excellent heat insulation properties [1]. Kistler created the first silica aerogels in 1931 [2]. Todays, various techniques are used to synthesize silica aerogel; however, the sol-gel method is the most common one. In this method, silicon alkoxides, such as Tetraethyl orthosilicate (TEOS), are used as the precursors. It has been reported that TEOS that is non-toxic and low cost precursor can strengthen the gel network and prevent the crack formation in silica aerogels [3,4].

Rice husk ash (RHA), a byproduct of burnt rice husk, contains high amount of silica. It has a potential for being used as a low-cost silica source. The low cost, low density and renewable nature has enabled rice husk ash to be used as fillers in plastic and rubber composites [5-7]. Rice husk has become an easy source for the silicon and its compounds such as silica, silicon carbide, and silicon nitride. A recent research studied the adsorptive tendency of RHA toward the dyes and metal ions such as Pb(II), Cu(II), Cd(II) and others in aqueous solution. Rice husk has also been used as a silicate source for the production of various zeolites. A simple conventional hydrothermal route was used to synthesize the nanozeolite, NaA, and NaY from RHA. RHA, as a pozzolanic material with a high amorphous SiO_2 content and a large surface area, can be

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used to make an ultra-high performance concrete [8].

Usually, different drying techniques are used to produce the silica gel. However, ambient pressure drying technique as a cost-effective method is used widely by researchers. This technique involves drying the gel at atmospheric pressure; however, it has its own limitations. This drying technique usually results in crack formation due to the capillary stress. Hence, strengthening of gel network, surface modification, and solvent exchange are necessary to suppress the capillary tension and shrinkage [9]. This has been achieved in the present study by using TEOS, ethanol, and n-heptane.

In the present study, RHA was used as a main precursor for synthesis of silica aerogels. The sol-gel method was used to produce four different variants of silica aerogels dried at ambient pressure. The choice of RHA and ambient pressure made the process easy, sustainable and inexpensive. Moreover, strengthening the gel network, suppression of capillary stress, and reduction of crack formation were achieved by using TEOS ($SiC_8H_{20}O_4$), ethanol (C_2H_5O) and n-heptane (C_7H_{16}). In addition, the four synthesized variants of silica aerogels were characterized and compared via BET, SEM, EDX, and XRD.

MATERIALS AND METHODS

Initial Washing and Leaching of Rice Husk

1 kg of rice husk was initially washed several times with distilled water to remove the adhering dirt and impurities. The washed rice husk was first sun dried for 5 h followed by drying in a drying oven at 110 °C for 24 h. The dried rice husk was leached with 1 M HCl for one hour under continuous stirring to remove metallic impurities [10-12]. In every 25 g of rice husk, 500 ml of acidic molar solution was added in the beaker. After leaching, the solution was disposed and the rice husk was washed several times with distilled water until pH 7.

Calcination of Rice Husk

To produce rice husk ash, the leached rice husk was calcined in the muffle furnace at 600 °C for 4 h. Previous studies have shown that 600 °C for 4 h produces amorphous rice husk ash with high silica purity [13-16]. The silica content in the samples was determined by using element to stoichiometric conversion ratio. This was done by multiplying the silicon weight percentage found through EDX with conversion factor number of 2.1392. This number varies for each element.

Sol-gel Method

Rice husk ash was divided into 4 samples, each weighing 25 g. To extract silica, the RHA samples were refluxed with 1 M NaOH solution for 1 hour under constant stirring (500 ml of 1 M NaOH for every 25 g of RHA). After one hour, the solution was filtered through filter paper (Whatman 40) [10]. The filtrate, sodium silicate solution, was titrated with 1 M HCl solution until pH 7. The initial pH of the sodium silicate solution was 12.5, which was reduced to 7 by dropwise titration and hand stirring. After every few drops of 1 M NaOH solution, the hydrosol was continuously stirred with hand, and the next few drops were added at least after one minute. The pH was being recorded after every minute until it reached 7. As pH 7 was reached, the solution turned from yellow to white hydrosol, indicating gelation. Before solvent exchange and modification, the hydrosol was dried at room temperature for 24 h, forming into hydrogel [1].

Silica Aerogel Variants

The sodium silicate solution was used to synthesize the four different silica aerogel variants. Figure 1 shows the

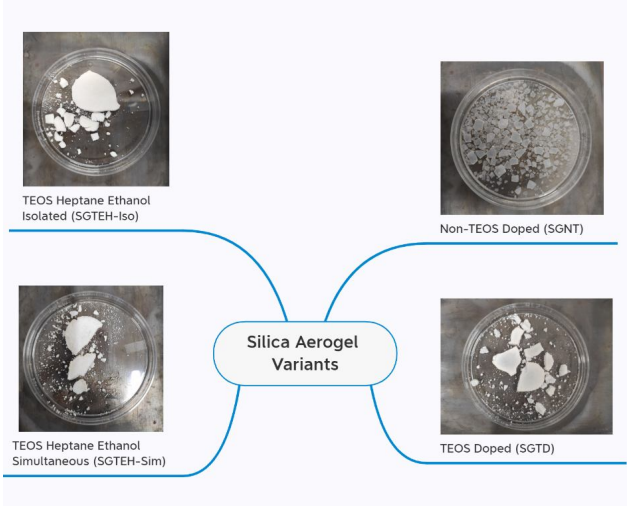

Fig. 1. Synthesized silica aerogel variants.

synthesized variants. The Synthesis procedure of the variants has been explained in the following sections.

Non-TEOS doped silica aerogel (SGNT). To synthesize this variant, ambient temperature dried hydrogel was soaked in an ethanol solution with 80 vol% ethanol/water for 24 h. After solvent exchange, the ethanol solution was disposed off and the alcogel was washed with de-ionized water 3 times, each time kept in deionized water for 4 h. This was done to remove sodium sulfate formed as a result of hydrosol neutralization. The washed alcogel was dried for 10 h at 40 ℃, followed 120 °C until constant weight at ambient pressure (Fig. 1) [17,18].

TEOS doped silica aerogel (SGTD). To synthesize this variant, the neutralized hydrosol and TEOS by volume ratio 1:10 relative to hydrosol were added. This was followed by aging of hydrosol at ambient temperature for 24 h. After 24 h, the hydrogel was soaked in De-ionized water 3 times, each time for 4 h to remove the sulfates. Then the hydrogel was aged inside Ethanol 80% Ethanol/Water solution for 24 h. After aging, ethanol solution was discarded and the alcogel was dried at ambient pressure for 10 h at 50 °C followed by 120 °C until constant weight (Fig. 1) [17].

TEOS/ethanol/heptane simultaneous (SGTEH-Sim). For this variant, the neutralized hydrosol was aged at room temperature for 24 h. After aging, the hydrogel was soaked in De-ionized water 3 times, each time for 4 h to remove the sulfates. Soaking was followed by aging the hydrogel simultaneously in a mixture of TEOS/ethanol/heptane (1:1:1) for 24 h, which was a novel technique for simultaneous solvent exchange and gel strengthening used in the present work. After 24 h, the mixture was disposed and the gel was dried at atmospheric pressure for 10 h at 50 °C, followed by 120 °C until constant weight (Fig. 1) [17,19].

TEOS/ethanol/heptane isolated (SGTEH-Iso). This variant was synthesized by the addition of TEOS to the neutralized hydrosol using ambient temperature drying for 24 h, as explained previously. Unlike SGTEH-Sim, the prepared hydrogel was soaked separately in ethanol and n-heptane solutions. The hydrogel was first soaked in 80 vol% ethanol/water solution for 24 h. The soaked alcogel was washed with distilled water to remove ethanol. The washed gel was then soaked in n-heptane solution for 24 h. Finally, the gel was dried at ambient pressure for 10 h at 40 °C, followed by the oven drying at 120 ℃ for an hour (Fig. 1) [17,19].

Characterization of Silica Aerogel Variants

The prepared silica aerogel variants were characterized using SEM, EDX, and XRD to observe their morphological and chemical compositions. The surface morphology was determined using Scanning Electron Microscopy FESEM JSM 6701F (JOEL) operated at 15 kV and 20 kV. The chemical composition of the samples was determined using Energy Dispersive X-Ray (Model, JEOL JSM-7400F). To confirm the amorphous nature of the samples, XRD (Model Dw-Y3000) was used.

1- RESULTS AND DISCUSSION

Physical Properties of Silica Aerogel Variants

Table 1 shows the physical properties of the synthesized silica aerogel variants. Samples SGTEH-Iso and SGTEH-Sim showed the lowest volume shrinkage with white color, whereas samples SGTD and SGNT were white-transparent and semi-transparent, respectively. The lowest volume shrinkage was found in SGNT sample, which is due to the absence of TEOS. TOES enhanced the silica purity as well as reduced the volume shrinkage by strengthening the gel network. The highest porosity of 85% was found for the sample SGTEH-Iso, followed by 79.5% for the sample SGTEH-Sim. The Non-TEOS (SGNT) sample showed the lowest porosity. Enhanced porosity in the samples SGTEH-Iso and SGTEH-Sim can be attributed to the ethanol and n-heptane.

Table 1. Physical Properties of Silica Aerogels

Sample	Color	Volume shrinkage (%)	Porosity (%)
SGNT	Semi-transparent	94.75	69.8
SGTD	Warm white	93.23	74.9
SGTEH-Sim	Ivory white	91.86	79.5
SGTEH-Iso	Pure white	91.16	85

BET Analysis

Figures 2 and 3 show the pore size distribution and N_2 adsorption/desorption isotherms of the respective aerogel variants. As shown in Table 2, the isolated and simultaneous solvent exchange/n-heptane aging caused the samples to acquire higher pore size (9.6 and 9.2) and surface area (312 and 298 $m^2 g^{-1}$), respectively. On the other hand, the sample with TEOS doping showed significantly higher surface area, average pore size and pore volume than the Non-TEOS doped sample. This is an explicit result of adding TEOS to the hydrosol before ambient temperature and pressure drying. Moreover, ethanol and n-heptane resulted in stronger gel network against crack formation during ambient pressure drying, bigger average pore size and higher surface area. Aging in the n-heptane reduced the crack formation and capillary stresses due to its low surface tension. Furthermore, Fig. 2 shows that the pore diameters of silica aerogel variants are within mesoscale dimension. Also, the isotherms obtained for all variants were Type IV, confirming the mesoporous structure.

EDX Analysis

EDX was conducted to determine the chemical composition of the silica aerogel variants. As shown in Fig. 4, the variants contained negligible amount of metallic impurities. This indicates that leaching with 1 M HCl solution removed 99% of the impurities. Moreover, the metallic impurities being removed paved the way for the silica extraction, hence enhancing the silica purity (Fig. 5). Among all the samples (Fig. 4), the highest silica purity was observed in SGTEH-Iso and SGTEH-Sim samples, as indicated by Fig. 5. This can be attributed to the addition of TEOS, which is a well-known precursor as well as well co-precursor for the synthesis of silica gel. An increase in silica purity can be observed clearly among the samples SGNT and SGTD, which is due to the TEOS addition. On average, addition of TEOS enhanced the silica purity by 1.84% compared to the purity of the Non-TEOS SGNT sample.

XRD Analysis

X-Ray Diffraction is a non-destructive technique used to determine the structure of a material. The structure is

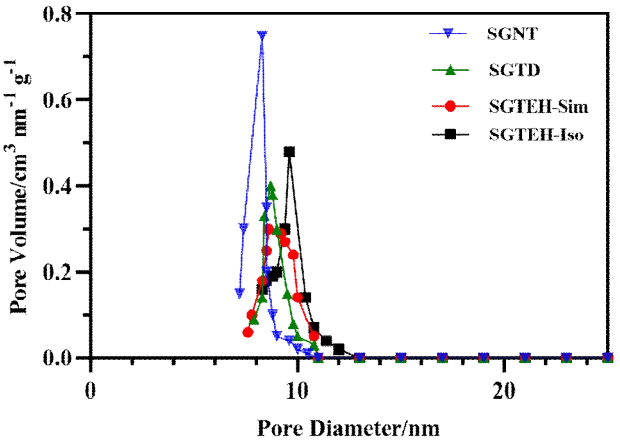

Fig. 2. BET pore size distribution of silica aerogel variants.

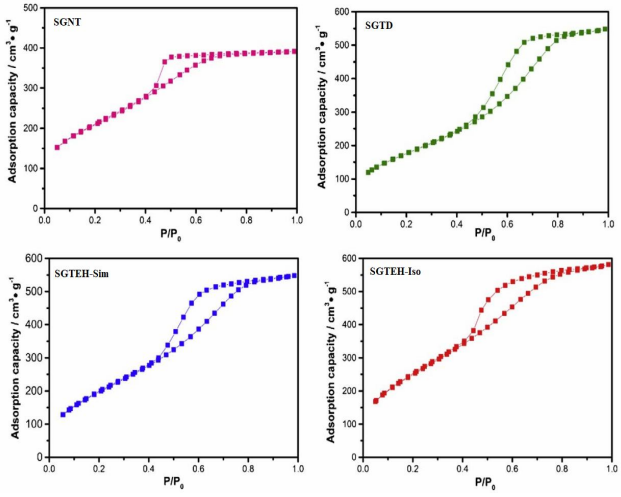

Fig. 3. N_2 Adsorption/desorption isotherm of synthesized silica aerogel variants.

Table 2. Properties of Silica Aerogel Variants

Sample	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Average pore size (nm)
SGTEH-Iso	312	0.76	9.6
SGTEH-Sim	298	0.75	9.2
SGTD	264	0.56	8.7
SGNT	220	0.48	8.3

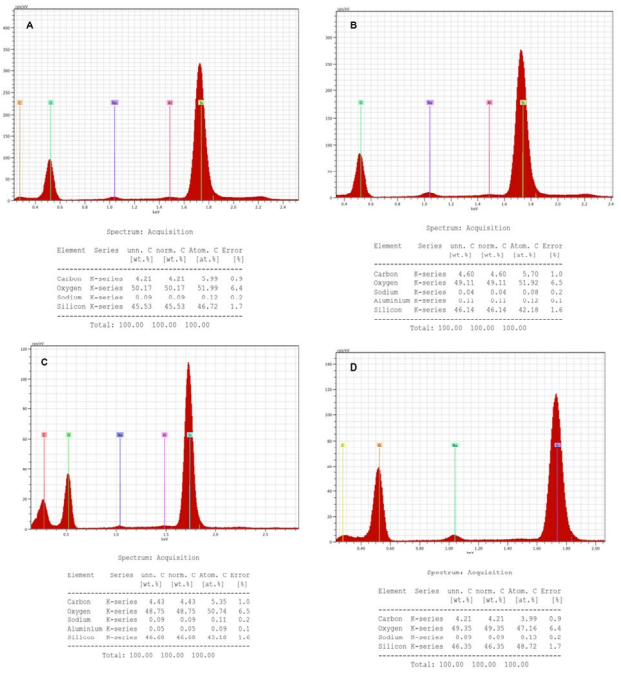

Fig. 4. EDX Results (A) SGNT (B) SGTD (C) SGTEH-iso (D) SGTEH-Sim.

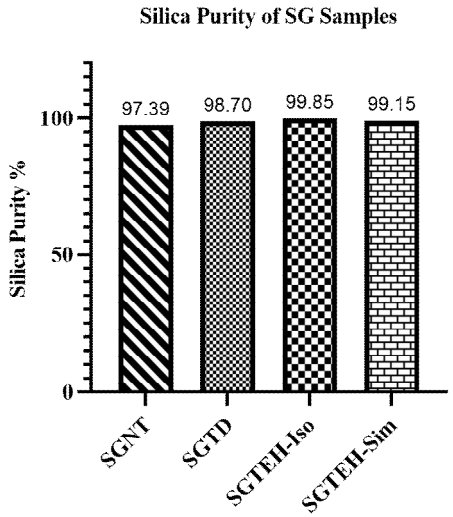

Fig. 5. Silica purity of silica aerogel variants based on EDX.

indicated by the angles generated. The amorphous structure of the material is indicated when the peaks lie between 21° and 22°. As revealed by the results in Fig. 6, all the silica

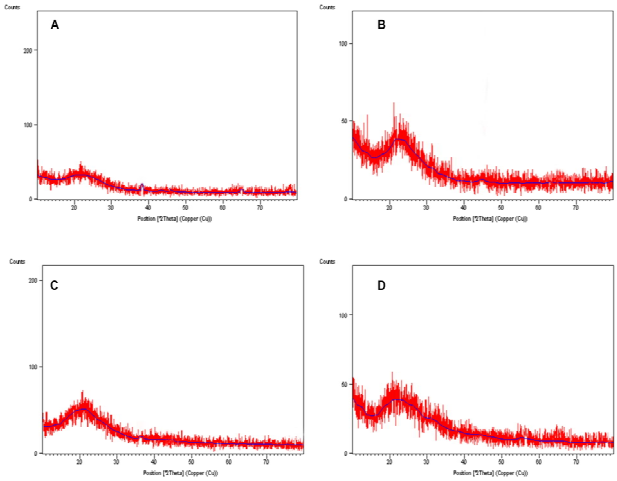

Fig. 6. XRD Results: (A) SGNT (B) SGTD (C) SGTEH-iso (D) SGTEH-Sim.

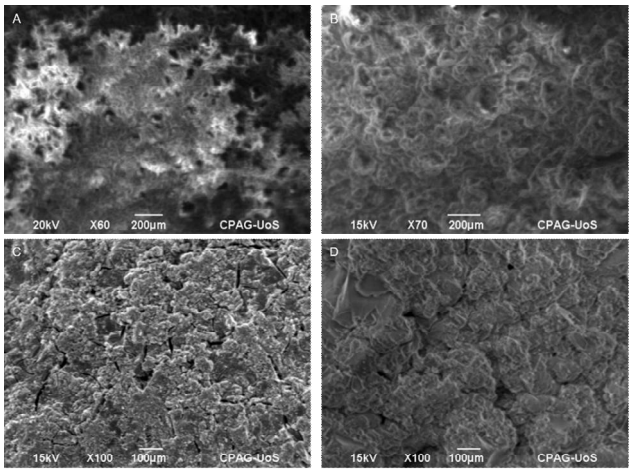

Fig. 7. SEM Images (A) SGNT (B) SGTD (C) SGTEH-Iso (D) SGTEH-Sim.

aerogel variants showed the peaks lying between 21 and 22°, hence indicating their amorphous structure. This can be attributed to the number of factors such as leaching of rice husk with HCl, calcination of rice husk at 600 °C for 4 h, and modification of variants through TEOS/Ethanol/n-Heptane.

SEM Analysis

The SEM was used to determine the apparent morphological changes in the silica aerogel variants. As can be seen from Fig. 7, all the silica aerogel variants were

porous in their structure. There can be seen the white and black parts as bulges and pores. The black parts indicate the pores of the material. Moreover, the apparent porosity in the SGTD, SGTEH-Iso and SGTEH-Sim variants was higher compared to that in SGNT. This can be attributed to the modification/aging with TEOS, ethanol and n-heptane.

Synthesis Time for Silica Aerogel Variants

Synthesis and modification of silica aerogels is a time-consuming process. Time consumed in synthesis of each variant is shown in Fig. 8. As it is clear, the highest time was consumed by the SGTEH-Iso variant, whereas the lowest time was consumed by the SGNT and SGTD. The SGTEH-Sim sample was shown to consume much lower time than the SGTEH-Iso sample and a slightly higher time than the SGNT and SGTD samples.

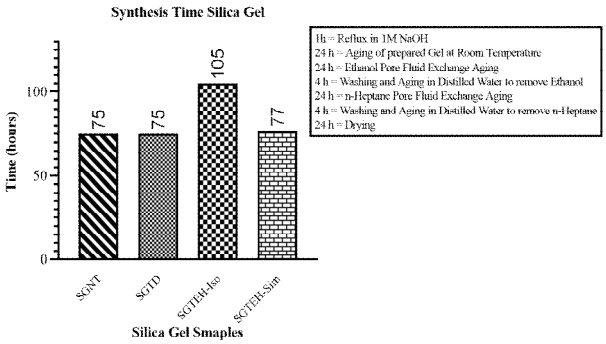

Fig. 8. Synthesis time of silica aerogel variants.

Volume Shrinkage

Volume shrinkage of the synthesized variants was determined using the following formula (Eq. (1)), where I.V. refers to the initial volume of the hydrosol and F.V. refers to the final volume of the Silica Aerogel after drying.

$$\frac{I.V. - F.V.}{I.V.} \times 100 \quad (1)$$

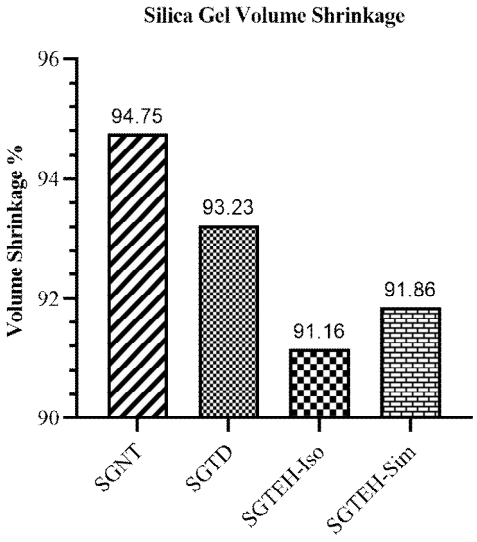

Fig. 9. Volume shrinkage of silica aerogel variants.

As reflected in Fig. 9, the highest volume shrinkages were observed in SGNT and SGTD samples, whereas the lowest shrinkages were related to SGTEH-Iso and SGTEH-Sim, respectively. The lower volume shrinkage indicates the stronger gel network and lesser crack formation. Hence, the solvent exchange and n-heptane in SGTEH-iso and SGTEH-Sim samples resulted in stronger gel network and lesser crack formation, thereby reduced volume shrinkages during ambient pressure drying.

CONCLUSIONS

Silica aerogel has attracted a widespread attention due to its unique properties. Due to its high specific surface area, high porosity, and high adsorption capacity, it has been used in applications such as adsorption of heavy metals from wastewater. In the present work, four different silica aerogel variants were synthesized using sol-gel method. RHA was used as a main precursor, and the ambient pressure drying was used as the drying technique. Generally, the use of sol-gel technique, RHA and APD made this procedure easy, sustainable and inexpensive. Furthermore, the synthesized samples were characterized and compared using BET, SEM, EDX, and XRD. According to our results, TEOS could enhance the silica purity in the samples, whereas ethanol and n-heptane enhanced the pore size, gel network and suppressed crack formation during drying. The study outcomes show that the SGTEH-Iso and SGTEH-Sim samples are promising adsorbents for the adsorption of different heavy metals from wastewater.

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