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## COMMUNICATION

# Synthesis of High Strength Monolithic Alumina Aerogels at Ambient Pressure

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**Alumina aerogel has many fascinating properties, such as high temperature stability, high surface areas, which result in them having great potential applications. However, its mechanical property is very poor, which greatly limits its practical application and commercialization. In this communication we successfully synthesized monolithic alumina aerogels via ambient pressure drying by using attapulgite (ATP) as reinforcement. And the resulting attapulgite/alumina composite aerogel exhibits strong mechanical property. TEM/SEM analysis showed that alumina particles firmly adhered to the surface of rod shaped crystal of attapulgite and attapulgite played a supporting role as the skeleton in the structure of the composite aerogels.**

Aerogels are highly porous solid materials derived from gels formed when the gas substitutes the liquid component within the pores of the gel,<sup>1-3</sup> which make them possess many excellent properties, such as thermal super-insulators, adsorbents, catalyst carriers and sensors.<sup>4</sup> But now the application of the aerogels is greatly limited because of the lacking of the drying method and the poor mechanical properties of aerogels, especially inorganic oxide aerogels, which easily break into fragments even under slightly stress.<sup>5,6</sup> Therefore, improving the strength of the aerogels and applying new drying method become the main direction of the aerogel research. Parmenter et al.<sup>7</sup> synthesized the ceramic fiber/silica aerogels by supercritical ethanol drying, and reported that the monolithic composites have stronger mechanical properties than single silica aerogels. Yang et al.<sup>8</sup> prepared inorganic fiber-reinforced silica aerogel by supercritical drying, which showed high compressive strength as well as without sacrificing its thermal conductivities. Fu et al.<sup>9</sup> fabricated activated fiber/carbon aerogel (ACF/CA) composites by supercritical drying and found that fiber could fortify the structure of carbon aerogel. Our research group studied the

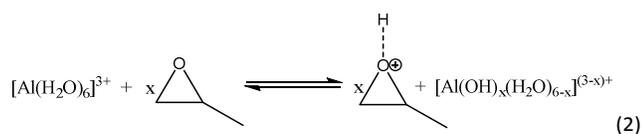
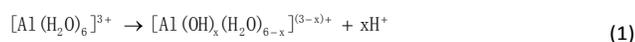
aerogel drying methods thoroughly and successfully prepared monolithic inorganic oxide aerogels through organic solvent sublimation drying method (OSSD).<sup>10</sup> Alumina aerogels possess better thermal and chemical stability besides the basis properties of aerogels, which make them have great potential applications, such as high temperature resistant materials and catalyst supports with high surface area.<sup>11</sup> Therefore, study on preparation of alumina aerogel has attracted increasing attention.<sup>12-14</sup> However, alumina aerogels are also friable and have poorly mechanical property<sup>4</sup>, which make their practical application greatly restricted.

Attapulgite (ATP) is a type of rare natural hydrated magnesium aluminum silicate clay mineral with layer-chain and fibrous crystal structure.<sup>15</sup> Owing to its intrinsic properties, such as special crystal structure and superficial character, ATP possesses many fine properties, such as adsorptive and adiabatic<sup>15</sup>. Recently, ATP is widely used as inorganic filler added into the polymer or rubber matrix, and brings great improvement to the properties of the composites, such as tensile strength,<sup>16, 17</sup> compressive strength.<sup>18</sup> This mainly attributed to the fibrous and layer-chain structure.<sup>19</sup> Additionally, the hydrophilic fibrous structure may be typically compatible with the hydrophilic polymer.

Therefore, in this communication we proposed to add ATP into the structure of alumina aerogel, so as to improve its strength through the support effect of the special structure of ATP.

During preparation, we chose  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  as precursor. Acidic conditions favor hydrolysis, so we used hydrochloric acid (1M) as acid catalyst. The propylene oxide (PO) was used as gelation inducing agent. It can consume the protons from the hydrated metal species and drive the sol-gel polymerization reaction.<sup>20, 21</sup> The sol-gel mechanism could be described as follows:

## (1) Hydrolysis:



## (2) Condensation:

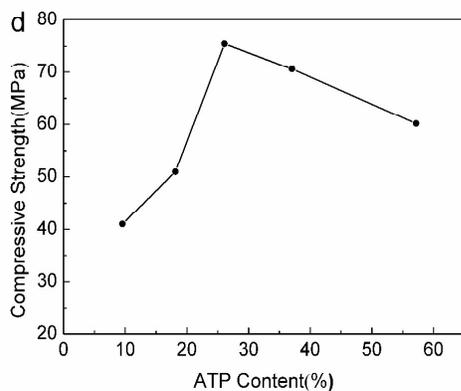
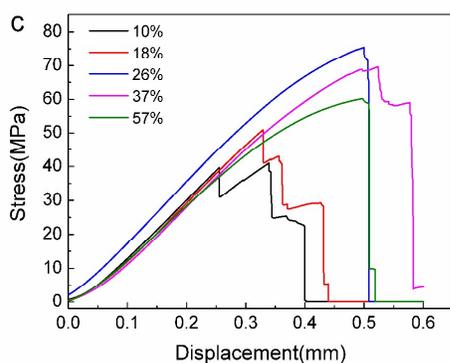
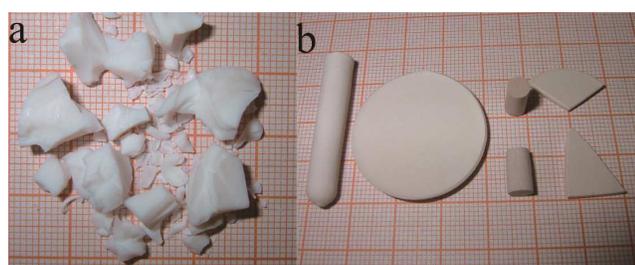
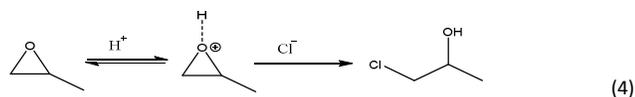
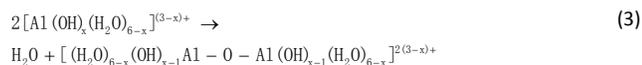


Figure 1. Pictures of pure alumina aerogel (a) and ATP/Al<sub>2</sub>O<sub>3</sub> composite aerogels (b) prepared by ambient pressure drying. Compressive stress-displacement curves (c) and compressive strength-atpulgite content curves (d) of ATP/Al<sub>2</sub>O<sub>3</sub> aerogel composites with different atpulgite weight ratios.

Monolithic alumina aerogel cannot be obtained (Figure 1a) via ambient pressure drying because of large capillary force.<sup>22</sup> While it could be easily prepared when a little ATP was added. We prepared various shapes of ATP/Alumina aerogel composites according to different demands (Figure 1b), and they all kept intact surface. In order to further investigate the effect of ATP, ATP/Alumina aerogel composites with different ATP weight ratios were synthesized by ambient pressure drying method. Because the monolithic pure alumina aerogel was not obtained via ambient pressure drying, its compression test cannot be carried out. Figure 1c shows the compressive stress-displacement curves of ATP/Al<sub>2</sub>O<sub>3</sub> aerogel composites with different atpulgite weight ratios. Figure 1d shows that the compressive strength significantly increased when a little ATP was added. With the ATP content increasing from 10% to 26%, the compressive strength increases from 40.99MPa to 75.44MPa. While as the ATP content continued increasing, the compressive strength began to decrease slightly, and crack-free ATP/alumina aerogel composites cannot be obtained when the content of ATP increased to 66wt%. The fragility of inorganic oxide aerogel is a well-recognized defect for its practical application. Our research shows that no matter how much the ATP content is, the compressive strength of ATP/Al<sub>2</sub>O<sub>3</sub> aerogel composites is far higher than that of pure alumina aerogels.

Figure 2 shows the TEM and SEM images of ATP, Al<sub>2</sub>O<sub>3</sub>, and ATP/Al<sub>2</sub>O<sub>3</sub> respectively. From figure 2 we can see that ATP exists as bundles of rod shaped crystal, the skeleton of Al<sub>2</sub>O<sub>3</sub> aerogels is formed by the random accumulation of colloidal particles (ranging from a few tens to a few hundred nanometers), and the skeleton of ATP/Al<sub>2</sub>O<sub>3</sub> aerogels is formed by the random assemble of rod unit (growing by alumina particles adhering to rod ATP). The rod-like crystal structure of ATP favored the formation of supporting framework, which can effectively improve the mechanical properties of alumina aerogels. That is to say the ATP offers a supporting framework as an initiate skeleton, and the alumina particles can firmly adhere to it and gradually grow up to 3D network (see Figure 2f), then the total structure of alumina aerogel composites are fortified.

Figure 3 shows the pore size distribution and N<sub>2</sub> adsorption-desorption isotherms for alumina aerogel (a) and ATP/Al<sub>2</sub>O<sub>3</sub> aerogel composite (b, w<sub>ATP</sub>=26%). The isotherms are type IV with H<sub>2</sub> hysteresis loops characteristic of mesoporous materials. The most probable pore size (BJH) and specific surface areas (BET) of the pure alumina and ATP/alumina aerogel (w<sub>ATP</sub>=26%) were 12.12nm and 13.89nm, 295.18m<sup>2</sup>·g<sup>-1</sup> and 242.86m<sup>2</sup>·g<sup>-1</sup>, respectively. The parameters of the two kinds of aerogels are similar, but ATP/Al<sub>2</sub>O<sub>3</sub> aerogel exhibits as a crack-free monolith. It indicates that the structure of alumina aerogel is strengthened and can withstand the tensile forces of liquid after adding a little ATP. The SEM and TEM images of Al<sub>2</sub>O<sub>3</sub>, and ATP/Al<sub>2</sub>O<sub>3</sub> reveal the distinct textures and indicate that the main channels of ATP/Al<sub>2</sub>O<sub>3</sub> (ranging from a few tens to a few hundred nanometers) are effected by the random accumulation of rod unit (see Figure 2d, f).

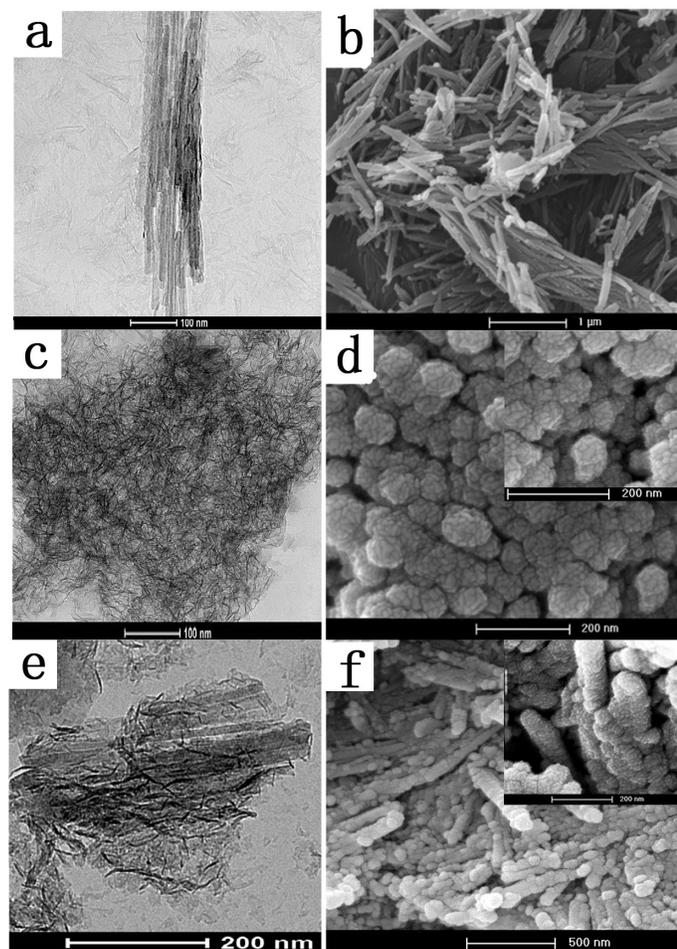


Figure 2. TEM (a, c, e) and SEM (b, d, f) images of attapulgite,  $\text{Al}_2\text{O}_3$  aerogel and ATP/ $\text{Al}_2\text{O}_3$  aerogel prepared by ambient pressure drying; a,b) ATP; c,d)  $\text{Al}_2\text{O}_3$ ; e,f) ATP/ $\text{Al}_2\text{O}_3$  ( $w_{\text{ATP}}=26\%$ ).

Based on the micro-morphology of alumina particles and ATP unit, we propose the following mechanism to explain the improvement for mechanical property of the alumina aerogel by adding ATP (Figure 4). The rod ATP in the sol allows the alumina particles condensing onto it. As condensation proceeds, alumina particles are growing up to secondary particles and the skeleton of ATP/ $\text{Al}_2\text{O}_3$  aerogels is forming by the random assemble of rod unit (growing by alumina particles adhering to rod ATP). The alumina colloidal particles firmly adhere to rod ATP and gradually grow up to 3D network, and then the total structure gets fortified. Due to the formation of reinforced framework, the wet gel can withstand the destructive capillary pressure during ambient pressure drying. The structure of the ATP/ $\text{Al}_2\text{O}_3$  aerogel remains intact and crack-free during the entire drying process.

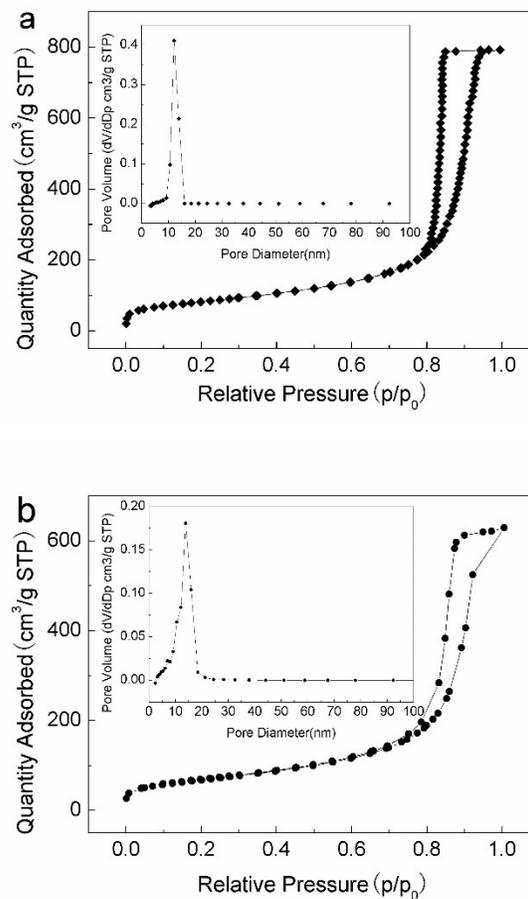


Figure 3. Nitrogen sorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution of pure alumina aerogel (a) and ATP/alumina aerogel composite ( $w_{\text{ATP}}=26\%$ ) (b).

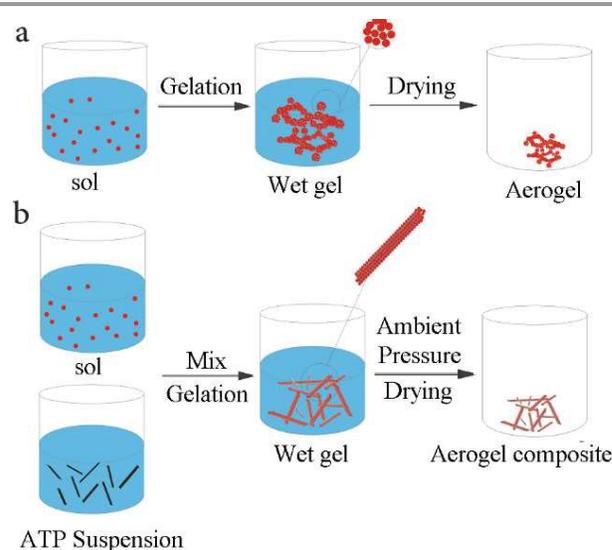


Figure 4. Schematic of the formation of alumina aerogel (a) and ATP/alumina aerogel composites (b) at ambient pressure condition.

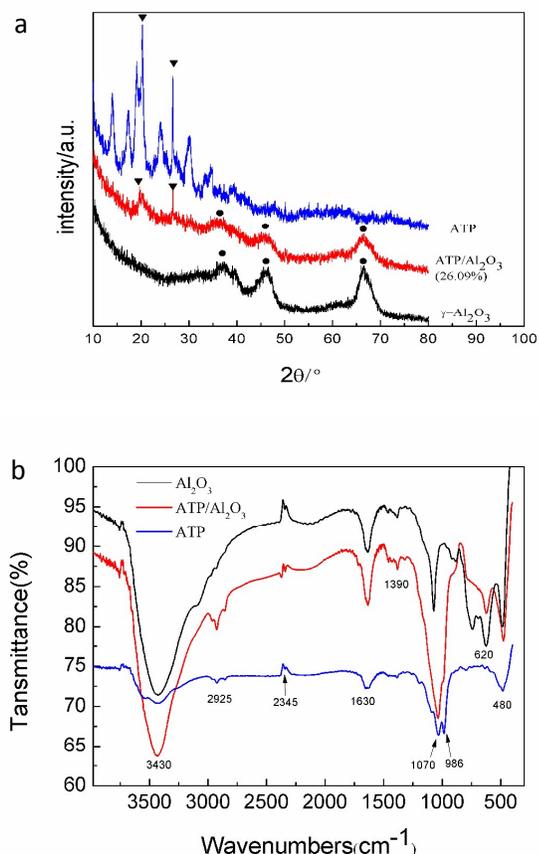


Figure 5. The XRD patterns (a) and FTIR spectra (b) of  $\text{Al}_2\text{O}_3$  aerogel (black line),  $\text{ATP}/\text{Al}_2\text{O}_3$  aerogel (red line) and ATP (blue line).

Figure 5 shows the XRD patterns and FTIR spectra of  $\text{Al}_2\text{O}_3$  aerogel,  $\text{ATP}/\text{Al}_2\text{O}_3$  aerogel and ATP. Combined with the IR spectra and XRD patterns, the new characteristic bands and peaks are not found in all the IR spectra and XRD patterns for the  $\text{ATP}/\text{Al}_2\text{O}_3$  aerogel composite material. This reveals that there is no new form generated when ATP adds into  $\text{Al}_2\text{O}_3$ , that is to say the addition of ATP will not change the origin nature of alumina aerogel (see Table S1, Figure S1, S2). In addition, low content and evenly dispersed of each component lead some characteristic peaks to shrink or disappear. Compared with traditional supercritical drying, ambient pressure drying is extremely convenient and cost-saving by adding ATP into alumina aerogel.

## Conclusions

In summary, the monolithic reinforced  $\text{ATP}/\text{Al}_2\text{O}_3$  aerogel composite was successfully synthesized under ambient pressure by adding ATP into alumina aerogel matrix. The compressive tests show that compressive strength of  $\text{ATP}/\text{alumina}$  aerogel ( $W_{\text{ATP}}=26\%$ ) can reach up to 75.44MPa. Owing to its fortified structure,  $\text{ATP}/\text{Al}_2\text{O}_3$  wet gel can be dried directly by ambient condition without time-consuming and costly solvent substitution. It is of vital significance for the preparation and application of

alumina aerogel, and this approach may also be used for the preparation of other inorganic oxide aerogels.

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## Notes and references

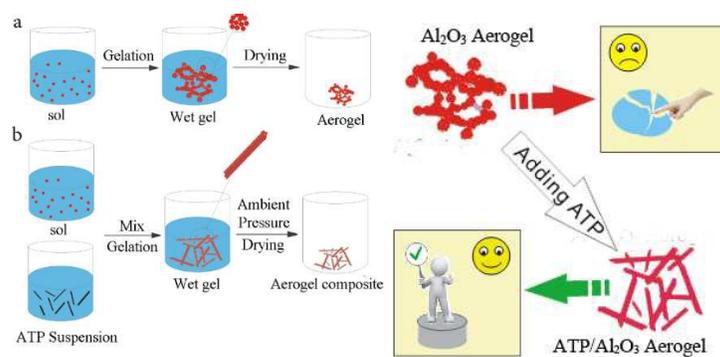
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## Table of contents entry



**Mechanically strong monolithic alumina aerogels** were obtained via ambient pressure drying by incorporating attapulgite (ATP) and alumina sol.