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Article

The Morphologically Controlled Synthesis and Application of Mesoporous Alumina Spheres

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Abstract: The control of alumina morphology is crucial yet challenging for its various applications. Unfortunately, traditional methods for preparing alumina particles suffer from several limitations such as irregular morphology, poor dispersibility, and restricted application areas. In this study, we develop a novel method for preparing spherical mesoporous alumina using chitin and Pluronic P123 as mixed templates. The effects of reaction temperature, time, and the addition of mixed templates on the phase structure, micromorphology, and optical absorption properties of the samples were investigated. The experimental results indicate that lower temperature and shorter reaction time facilitated the formation of spherical mesoporous alumina with excellent CO₂ adsorption capacity. The periodic density functional theory (DFT) calculations demonstrate that both (110) and (100) surfaces of γ -Al₂O₃ can strongly adsorb CO₂. The difference in the amount of CO₂ adsorbed by Al₂O₃ is mainly due to the different surface areas, which give different number of exposed active sites. This approach introduces a novel strategy for utilizing biological compounds to synthesize spherical alumina and greatly enhances mesoporous alumina's application efficiency in adsorption fields. Moreover, the study explored the electrochemical performance of the synthesized product using cyclic voltammetry and discovered improved loading of electrocatalysts and enhanced electrocatalytic activity.

Keywords: mesoporous alumina; chitin; P123; hydrothermal method

1. Introduction

In recent years, alumina has gained significant attention in high-value applications such as adsorbent [1–3], ceramic [4,5], catalyst and catalyst carrier [6–9], etc. The application of alumina is not only dependent on particle size but also on particle shape. Different shapes of alumina, such as rod-like [10], fibrous [11], plate-like [12], and spherical [13], have been widely used. Seyed [14] got massive γ -aluminum with particle sizes between 0.5 μ m and 0.9 μ m, but the morphology was irregular. Dabbagh, et al. and Feng, et al [15,16] prepared rod-like, fibrous, and spherical alumina, but the process was complex and hard to control, resulting in poor dispersibility. Lv et al. [17] synthesized spherical alumina with a highly spherical shape and uniform particle size by using the oil-ammonia drop method, but the particle size was large, which limited its application area. Using aluminum isopropoxide as precursor and Pluronic P123 (P123) as template, Wu et al. [18] used aluminum isopropoxide as a precursor and P123 as a template to synthesize organized mesoporous alumina

with a hierarchical structure. However, these methods suffer from limitations such as irregular morphology, poor dispersibility, and limited application areas.

Mesoporous materials are highly valued due to their higher specific surface area, organized pore structure, narrow pore size distribution, and continuous pore size, which make them important for adsorption and separation, as well as catalytic reactions [19]. Among various shapes of alumina, spherical alumina has high fluidity, making it less prone to gathering and producing channeling during catalytic processes, which significantly enhances catalyst activity. Therefore, the preparation of mesoporous alumina can greatly improve the application efficiency of mesoporous alumina spheres in adsorption, separation, and catalysis [20].

Chitin ($(C_8H_{13}O_5N)_n$) is a naturally occurring biopolymer that is highly organized and abundant in the exoskeletons of crustaceans and insects. The primary chitin fibrils' structural arrangement varies among arthropod species, with some having helical structures called the Bouligand structure, which enhances photonic and mechanical properties. This structure resembles cholesteric lyotropic liquid crystals. The hierarchical structure of chitin fibrils makes them an excellent natural template for developing new materials. The use of biomass as a porous material can be biodegradable, achieve biocompatibility, and achieve green and sustainable development [21–23]. Pluronic-P123 (P123) is a soft template with a symmetric triblock copolymer comprising poly (ethylene oxide) (PEO) alternating with poly (propylene oxide) (PPO), PEO-PPO-PEO. Its phases vary depending on the concentration and combination of solvents [24–27] and it is often used as a crystal structure modifier in the preparation of mesoporous materials [28].

In this study, mesoporous alumina spheres were successfully prepared using alumina hydrate ($Al(OH)_3$) as a precursor, $(NH_4)_2CO_3$ as a precipitant, as well as Chitin powder and P123. The preparation process, which involved evaporation induced self-assembly (EISA), was green, low cost, and pollution-free. This method significantly improved the catalyst loading firmness and service life of mesoporous alumina spheres. The effects of synthesis temperature, time, and the addition of mixed templates on the structure and morphology of the products were investigated. The CO_2 adsorption performance of spherical mesoporous alumina and the electrochemical performance of supported SnO_2 were also evaluated.

2. Experimental Section

2.1. Synthesis of Mesoporous Alumina Spheres

The typical synthesis process involves the following steps: Firstly, 6.6 g of hydrated alumina is added to ultrapure water with a resistivity of 18 MΩ·cm, and dissolved in a volumetric flask to prepare a 0.6 mol/L hydrated alumina solution. Subsequently, 3 g of Chitin and 1g of P123 are dissolved in 40 mL of isopropanol, followed by the addition of 2.4 g of urea, and stirring until fully dissolved. Next, 30 mL of the prepared hydrated alumina solution is added and vigorously stirred at room temperature. After 30 minutes, the solution is transferred into an autoclave with a PTFE liner, and reacted at 140 °C for 3 hours. Following this, the product is rapidly cooled to room temperature using a water bath. The synthesized samples were purified by repeated redispersion in ultrapure water followed by filtration to remove any unreacted reagents. The samples were washed with 500 mL of ultrapure water and 200 mL of absolute ethanol respectively for 3-5 times. The obtained material is then dried under vacuum at 80 °C, and finally calcined at 700 °C for 2 hours. The resulting product is a white spherical mesoporous alumina powder.

The hydrothermal reaction temperature is 120 °C, 140 °C, 160 °C, and 180 °C. The hydrothermal reaction time is 3 h, 9 h, and 15 h. The Chitin: P123 weight ratio is maintained in the range of 0-4. Table 1 is the process parameters for preparing alumina and spherical mesoporous alumina, respectively. The resultant samples were denoted as $R_mT_nH_s$ (m = Chitin:P123 weight ratio, n (reaction temperature)= 120, 140, 160 or 180 °C, respectively; s (reaction time)= 3, 9 or 15 h, respectively).

2.2. Physical characterization

The physical properties of the synthesized spherical mesoporous alumina materials were determined using various techniques. The X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert PRO diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) over the 2θ range of $10-80^\circ$. The N₂ adsorption-desorption isotherms were measured at -196°C using a Micromeritics Tristars 3000 analyzer. The CO₂ adsorption isotherms of the synthesized spherical mesoporous alumina materials were measured using a Micromeritics Tristars 3000 analyzer instrument at 25°C . Prior to the measurements, the samples were degassed at 180°C under vacuum for 6 hours to remove any moisture and adsorbed gases. The CO₂-adsorption isotherms were obtained at various pressures ranging from 0 to 1 bar. The CO₂ uptake capacity of the materials was calculated from the amount of gas adsorbed at equilibrium and the mass of the sample. The specific surface area (SSA) and pore volume were calculated using the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) analysis, respectively. The scanning electron microscopy (SEM) images were obtained using a KYKY-2800B microscope. Transmission electron microscopy (TEM) measurements were carried out on Tecnai G2 F20 operated at 200 kV.

2.3. Electrochemistry characterization

The electrochemical performance of the synthesized spherical mesoporous alumina materials was evaluated using a three-electrode system with a platinum wire as the counter electrode, a mercury/mercury oxide electrode as the reference electrode, and the synthesized material as the working electrode. The electrochemical tests were carried out using a CHI660D electrochemical workstation in a 5 mol/L KOH electrolyte solution. Cyclic voltammetry (CV) was carried out in the potential range of 0 to 0.7 V vs. Hg/HgO at a scan rate of 0.025 V/s-0.1 V/s to investigate the electrochemical stability of the synthesized materials.

3. Results and Discussion

Synthesis of Mesoporous Alumina Spheres The synthesis of spherical macroporous alumina materials has been achieved through the hydrothermal method, using hydrated alumina (AlOOH) as the precursor, along with Chitin and P123 as the templates, and urea as a precipitant, while adapting the evaporation induced self-assembly (EISA) method, as depicted in Figure 1. By systematically varying the reaction conditions, the impact of reaction temperature and time, as well as the Chitin:P123 weight ratio, on the morphology and properties of the resulting spherical mesoporous alumina materials was investigated. The Detailed process parameters are shown as following table. During the calcining process at 700°C , the organic components, including Chitin and P123, underwent decomposition and evaporation, creating voids within the alumina matrix. This decomposition and evaporation of organic materials resulted in the formation of well-defined mesopores within the macroporous alumina microspheres.

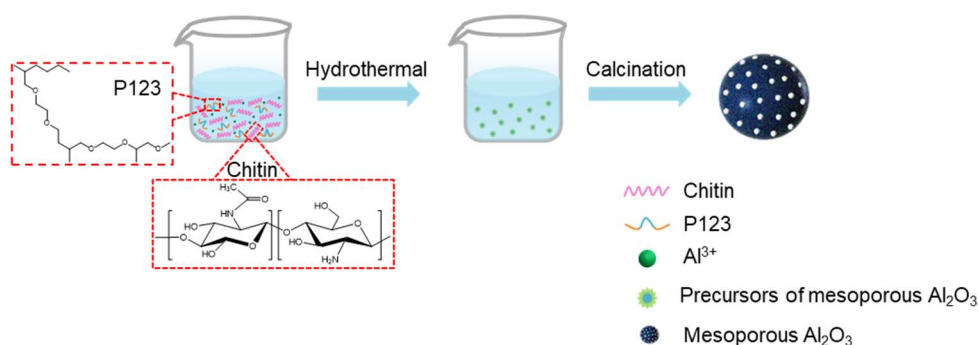


Figure 1. Schematic diagram of the preparation of spherical mesoporous alumina materials.

Table 1. Detailed process parameters for preparing spherical mesoporous alumina.

Sample	Weight ratio (Chitin:P123)	Reaction temperature (°C)	Reaction time (h)
R _{2:1} T ₁₂₀ H ₃	2:1	120	3
R _{0:1} T ₁₂₀ H ₉	0:1	120	9
R _{4:1} T ₁₂₀ H ₁₅	4:1	120	15
R _{1:2} T ₁₄₀ H ₃	1:2	140	3
R _{3:1} T ₁₄₀ H ₉	3:1	140	9
R _{1:1} T ₁₄₀ H ₁₅	1:1	140	15
R _{0:4} T ₁₆₀ H ₃	0:4	160	3
R _{2:3} T ₁₆₀ H ₉	2:3	160	9
R _{3:1} T ₁₆₀ H ₁₅	3:1	160	15
R _{3:1} T ₁₈₀ H ₃	3:1	180	3
R _{1:2} T ₁₈₀ H ₉	1:2	180	9
R _{0:4} T ₁₈₀ H ₁₅	0:4	180	15

The effect of synthesis temperature and time on the morphology of spherical mesoporous alumina. Figure 2a displays the X-ray diffraction (XRD) map of the precursor synthesized under various temperatures and durations. The precursors of R_{2:1}T₁₂₀H₃ and R_{0:1}T₁₂₀H₉ are primarily amorphous products. However, as the synthesis temperature increases to 160 °C and 180 °C, The precursors of R_{0:4}T₁₆₀H₃ and R_{3:1}T₁₈₀H₃ start to crystallize and become AlOOH (JCPDS 01-072-0359). This finding suggests that the synthesis temperature has a significant impact on the crystallization of the precursor. At lower hydrothermal temperatures, the system energy is insufficient to facilitate the formation and transformation of crystals, leading to the amorphous state of the samples. In contrast, when the hydrothermal temperature increases, individual diffraction peaks emerge, and their intensity and width grow, indicating the increased crystallinity of the particles. The precursors of R_{3:1}T₁₄₀H₉ and R_{1:1}T₁₄₀H₁₅ are synthesized at 140 °C for 9 h and 15 h, respectively, providing sufficient energy for crystallization. Nevertheless, the diffraction peak intensity and width of precursors R_{3:1}T₁₄₀H₉ and R_{1:1}T₁₄₀H₁₅ are smaller compared to those of precursors R_{0:4}T₁₆₀H₃ and R_{3:1}T₁₈₀H₃ synthesized at higher temperatures. This difference implies that the crystallinity of particles in precursors of R_{3:1}T₁₄₀H₉ and R_{1:1}T₁₄₀H₁₅ is weaker than that in precursors R_{0:4}T₁₆₀H₃ and R_{3:1}T₁₈₀H₃. By controlling the growth rate of crystal faces, the crystal orientation can be influenced, enabling control over the morphology and crystal structure of products.

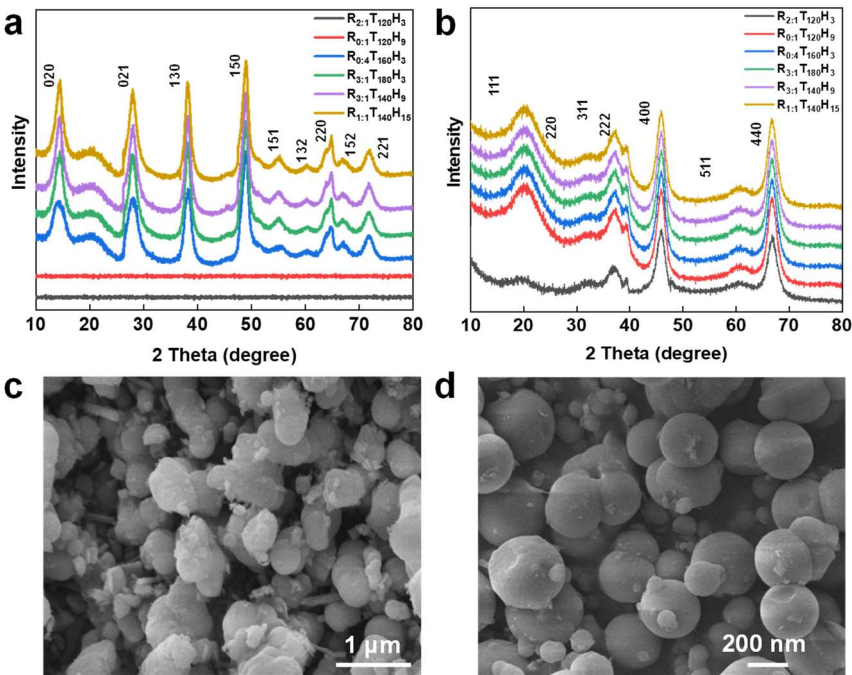


Figure 2. The X-ray diffraction (XRD) patterns of (a) the precursor and (b) mesoporous alumina XRD image under different synthesis conditions. The SEM images of mesoporous alumina under different synthesis conditions. (c) 120 °C, (d) 140 °C.

Figure 2b shows the mesoporous alumina XRD image after calcination at 600 °C. The amorphous precursor of $R_{2:1}T_{120}H_3$ and $R_{0:1}T_{120}H_9$ prepared at a lower synthesis temperature transforms into γ - Al_2O_3 under calcination at 700 °C; sample $R_{0:4}T_{160}H_3$, $R_{3:1}T_{180}H_3$, $R_{3:1}T_{140}H_9$ and $R_{1:1}T_{140}H_{15}$ are γ - Al_2O_3 (JCDPS 10-0425). With the increase of hydrothermal temperature, the position of each diffraction peak remains the same. However, the intensity and width of the diffraction peak grow larger, indicating an increase in the crystallinity of particles.

Figure 2c, d illustrates the SEM images of the mesoporous alumina samples prepared under different synthesis conditions. The images reveal that the temperature significantly influences the sample morphology, and 140 °C promotes the formation of spherical particles. When synthesized at 120 °C, the sample particles are massive and spherical (Figure 2c), while at 140 °C, the particles are regularly spherical with a smooth surface and particle sizes ranging between 50 nm and 200 nm (Figure 2d). As the synthesis temperature increases, more particles begin to crystallize and form crystalline solids. While these solids can completely transform into γ - Al_2O_3 at 700 °C, the amorphous precursor requires more energy to undergo phase transformation at this temperature. Thus, crystallization is relatively slow, which favors the preparation of spherical mesoporous alumina (Figure 2a, b). However, at higher synthesis temperatures, the Chitin powder used as a template tends to carbonize and lose some of its templating function. As a result, the sample transforms into irregular and flocculent particles that agglomerate (Figure S1a-d). Moreover, longer synthesis times are also not conducive to the development of spherical alumina particles (Figure S1c, d). Such conditions promote the development of flocculent, strip, and irregular particles, which hinder the normal growth of spherical particles.

The Effect of Chitin:P123 Weight Ratio on Spherical Morphology. During the synthesis process, the amount of additive used has a significant impact on the morphology and structure of the final product.[29–31] Table 1 displays the test results of spherical mesoporous alumina prepared using different Chitin:P123 weight ratios (Chitin quality:P123 quality).

When Chitin/P123 weight ratio is 0 ($R=0:4$), the predominant types of pores observed in the samples are ink-bottle type pores with a large opening and small diameter, as well as uneven crack-like pores, as shown in Figure 3a. The nitrogen adsorption isotherm (see Figure 3f) exhibits a type IV curve with a hysteresis loop between H2 and H3 in the middle to high voltage range of 0.5 p/p^0 to 0.9 p/p^0 . The adsorption amount in this range is limited to only 0.4 to 1 mmol/g. This is primarily due to the irregular stacking of the strip-shaped samples, which results in a low number of mesoporous structures being distributed. As shown in Figure 3g, the pore sizes are mainly distributed in the range of approximately 7 nm.

As the weight ratio increases to 3, 4 ($R=3:1, 4:1$), the particle size of the sample becomes larger and the spherical shape becomes more regular (see Figure 3d,e). The nitrogen adsorption isotherms show that in the middle-high pressure area, nitrogen adsorption capacity has further increased to about 7-8 mmol/g, as shown in Figure 3f,g. The pore size has further increased to about 9.4 nm and the pore volume has increased to 0.7 cm^3/g . The type IV curve of nitrogen adsorption isotherms shows a hysteresis loop between type H1 and H2. The formation of inkbottle pores becomes more prominent, and the mesoporous structure becomes more developed. However, with the further increase of weight ratio, the nitrogen adsorption capacity gradually decreases, indicating that excessive chitin may hinder the formation of the mesoporous structure. Therefore, the optimal weight ratio of Chitin/P123 is 3, 4 ($R=3:1, 4:1$).

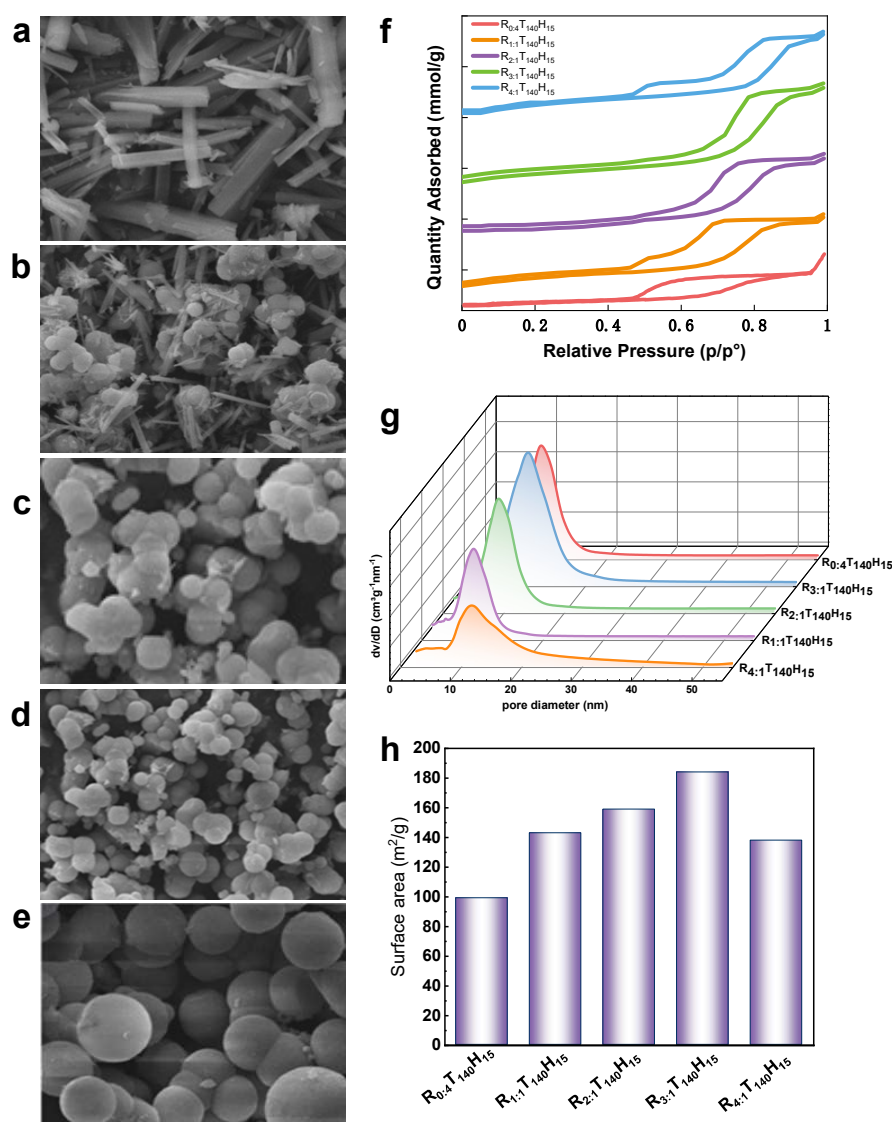


Figure 3. Nitrogen sorption isotherms (a-e: sample number R0.4:T140H15, R1.1:T140H15, R2.1:T140H15, R3.1:T140H15, R4.1:T140H15, respectively.), inset are corresponding pore size distributions (above), and corresponding SEM images (below) of the spherical.

As shown in Figure 3d, at a weight ratio of 3, the sample formed regular, uniform, and monodisperse microspheres and the predominant pore structure is a regular cylindrical shape with uniform size and shape. The nitrogen adsorption isotherms for this sample show a steep type IV curve and an H1 hysteresis loop (see Figure 3f), indicating that the sample has a uniform meso-porous structure. and pore sizes are mainly distributed between 7 nm and 9 nm. Notably, the pore size has increased by 8.6 nm compared to the previous weight ratio, and the pore volume has also increased by 0.3 cm³/g.

In summary, the Chitin/P123 weight ratio has a significant effect on the morphology and structure of the mesoporous alumina sample. When the weight ratio is 0 (R= 0:4), the sample has irregular strips with few mesoporous structures. As the weight ratio increases to 3(R= 3:1), the sample forms regular and uniform microspheres with a uniform mesoporous structure, which leads to an increase in pore size, pore volume, and BET surface area. However, when the weight ratio is further increased to 4 (R= 4:1), the sample exhibits adhesion and aggregation, and the pore size, pore volume, and BET surface area decrease. This is due to the increase in viscosity of the solution, which affects the template space steric effect and weakens homogeneous nucleation.

Using the method, the experiment successfully prepared spherical mesoporous alumina with uniform pore size, good dispersion, and identical morphology, with a Chitin/P123 weight ratio of 3 (R= 3:1). The amorphous precursor was prepared at a lower temperature of 140 °C and for a shorter time of 3 hours. Upon calcination at 600 °C, inorganic Al^{3+} interacted slowly with and connected to the organic micelle interface via electrostatic interaction. This process allowed the aluminum ions to cover the entire particle surface and achieve consistent growth rates for all surfaces, ultimately resulting in the formation of spherical particles via homogeneous nucleation. The particle surface also formed a uniform mesoporous layer, resulting in the complete transformation of the precursor into spherical mesoporous Al_2O_3 , as shown in Figure S2.

Figure S2 displays TEM images of spherical mesoporous alumina materials. The images clearly show that the alumina has a uniform and regular spherical form, as well as good dispersion. A 10 nm mesoporous layer uniformly covers the surface of the alumina particles, and the mesopore size is consistent throughout. The nitrogen sorption isotherms and corresponding pore size distributions of the spherical mesoporous alumina materials are also presented in Figure S2.

CO₂ adsorption on spherical mesoporous alumina. Figure 4a displays the CO₂ gas adsorption isotherm curves of spherical mesoporous alumina, which was synthesized with varying mass ratios of Chitin to P123 at a temperature of 273 K. With its large specific surface area and pore volume, spherical mesoporous alumina exhibits a high potential for gas adsorption. In this study, we investigated the adsorption capacity of spherical mesoporous alumina, synthesized with different ratios of template agents (Chitin:P123), for carbon dioxide at 273 K.

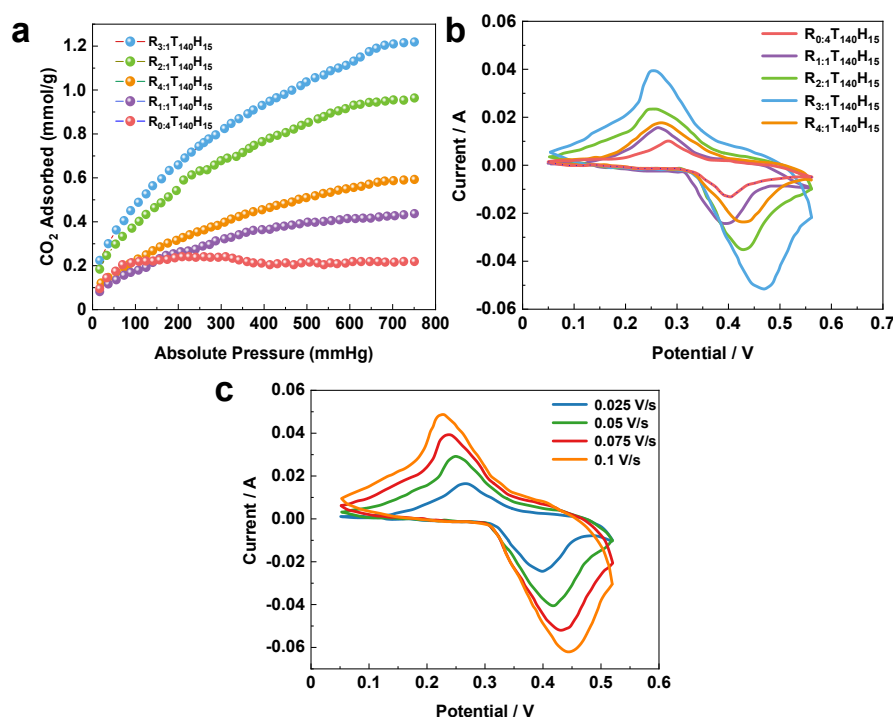


Figure 4. (a) CO₂-adsorption isotherms of mesoporous alumina sphere synthesized with different templating agent ratios. Cyclic voltammograms of (b) different templating agent ratios and (c) different scan rates.

The adsorption capacity of CO₂ is highest (1.21 mmol/g) when the ratio of template agents is 3, resulting in the preparation of spherical mesoporous alumina with excellent dispersion and uniform pore size. Notably, the different mass ratios of template agents used in the synthesis produced alumina with distinct shapes, which significantly impacted their adsorption capacities.

Electrochemical performance of porous alumina supported SnO₂. The electrochemical performance of porous alumina supported SnO₂ was studied using spherical mesoporous alumina-supported SnO₂ particle electrodes. The electrodes were prepared by a dip-calcination method, with

a loading amount of 4%. Cyclic voltammetry tests were carried out using a three-electrode system with 5 mol/L KOH solution as the electrolyte, a mercury/mercury oxide electrode as the reference electrode, and a platinum electrode as the auxiliary electrode. The prepared electrode sheet was used as the working electrode.

The CV curves of spherical mesoporous alumina-supported SnO₂ prepared with different ratios of template agents (Chitin:P123) at a scan rate of 0.075 V/s were shown in Figure 4b. The redox peak in the Figure 6a indicates the pseudocapacitive properties of the material. It was observed that when the ratio of template agent increases, the area of the cyclic voltammetry curve increases, and the specific capacitance increases significantly, indicating that the spherical mesoporous alumina has a better energy storage performance. However, when the ratio of template agent is too large (R= 4), the viscosity of the solution increases significantly. This increase in viscosity can affect the steric effect of the template space and weaken the homogeneous nucleation, which can lead to poor dispersion of particles. Poor particle dispersion can result in a poor carrier effect, which can negatively impact the electrochemical performance of the material.

The CV curves at different scan rates when the ratio of template agent (Chitin:P123) is 3 and the loading of SnO₂ is 4% were shown in Figure 4c. The CV curves were observed to be different with different scan rates, and with the increase of the test scan rate, the area of the closed graph also increased. This can be attributed to the high surface area and porous structure of the alumina support, which provides a large number of active sites for SnO₂ deposition and enhances the catalytic activity of SnO₂. Mesoporous alumina sphere can be an excellent electrocatalyst support due to its special mesoporous structure.

Periodic density functional theory (DFT). To gain deep insight on CO₂ adsorption, we performed periodic density functional theory (DFT) calculations (see Supplemental Information for computational details). The (110) and (100) surfaces of γ -Al₂O₃ were selected, as these two surfaces are predominant in γ -Al₂O₃, proved by XRD in Figure 2b.^[1] The optimized structures of Al₂O₃(110) and Al₂O₃(100) surfaces are shown in Figure S3. The bare Al₂O₃(110) surface is terminated with two-coordinated O_(II), three-coordinated O_(III) and four-coordinated Al_(IV), while Al₂O₃(100) surface is exposed with three-coordinated O_(III) and five-coordinated Al_(V). Our results indicate that the surface energy of Al₂O₃(110) is lower than that of Al₂O₃(100) (1.41 J·m⁻² vs 2.45 J·m⁻²), indicating that the Al₂O₃(110) surface is more stable.

The adsorption energies and optimized structures of CO₂ on Al₂O₃(110) and Al₂O₃(100) surfaces are shown in Figure 5 and Figure S4. DFT calculated results show that the formation of carbonate species is the most stable adsorption model, where CO₂ binds in abidentate configuration across the O-Al bridge sites with an adsorption energy of -0.93 eV and -0.75 eV on Al₂O₃(110) and Al₂O₃(100), respectively. To obtain the insight into the nature of molecular adsorption behavior, the differences of charge density ($\Delta\rho$) of the most stable adsorption CO₂ on Al₂O₃ surfaces are calculated. The results are clearly plotted in Figure 5. It is evident that charges accumulate and deplete around the O and C of CO₂ on both surfaces, respectively. The net result is the transfer of electrons from Al₂O₃ surfaces to the adsorbed CO₂. The Bader charge analyses proved that the electronic charges transferred from the Al₂O₃(110) and Al₂O₃(100) surfaces to CO₂ are 0.28 a.u. and 0.29 a.u., respectively. These two surfaces achieve the purpose of CO₂ activation by transferring their electrons to the antibonding molecular orbital of CO₂. The former is more stable, mainly because there are more electrons near the Fermi level on the atoms of surface active site Al_(IV)-O_(II) on Al₂O₃(110) than that of Al_(V)-O_(III) on Al₂O₃(100) (see projected density of states in Figure S5). The above results demonstrate that both surfaces can strongly adsorb CO₂, which explains the experimental results. The difference in the amount of CO₂ adsorbed by Al₂O₃ synthesized under different conditions is mainly due to the different surface areas, which give different number of exposed active sites. The higher the crystallinity, the higher the surface content of Al₂O₃(110) [32].

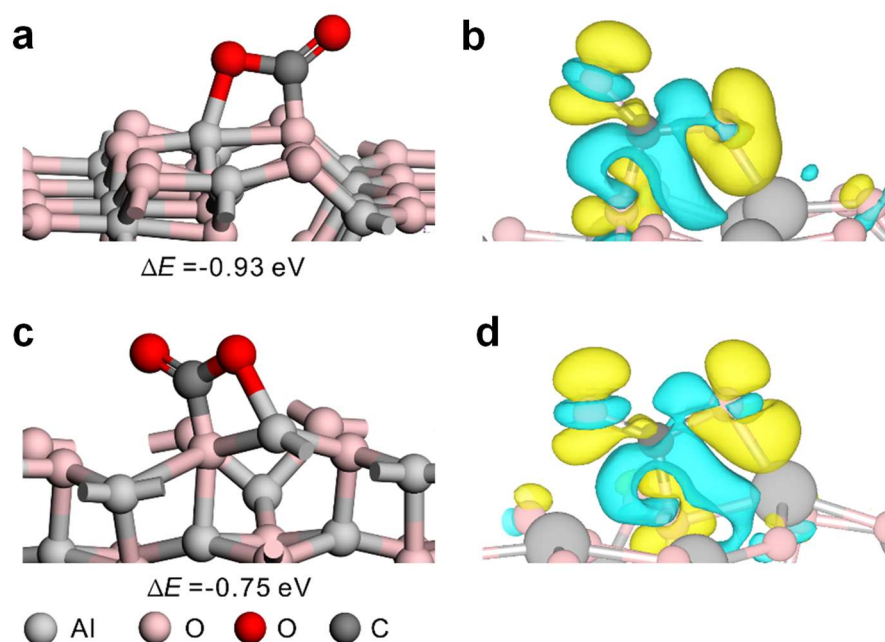


Figure 5. The adsorption energies and optimized structures of CO₂ on (a) Al₂O₃(110) and (c) Al₂O₃(100) surfaces. (b) and (d) are the charge difference of CO₂ adsorption on Al₂O₃(110) and Al₂O₃(100) surfaces, respectively. The values of the isosurfaces are ± 0.003 e/Å³. Yellow and light cyan isosurfaces indicate the accumulation and depletion of charge density.

4. Conclusions

In summary, using P123 as soft templates, mesoporous alumina sphere with high specific surface area, larger pore size, and pore volume was synthesized. The synthesis conditions, such as temperature, time, and weight ratio of additives, have a significant impact on the morphology and properties of the material. By optimizing these conditions, monodisperse spherical shape and uniform mesoporous structure can be elicited, leading to better CO₂ adsorption capacity and improved electrocatalytic effect. This method provides a new method to control pore size and structure, and the material has potential applications in various fields. The periodic density functional theory (DFT) calculations results demonstrate that both (110) and (100) surfaces of γ -Al₂O₃ can strongly adsorb CO₂, which explains the experimental results. The difference in the amount of CO₂ adsorbed by Al₂O₃ synthesized under different conditions is mainly due to the different surface areas, which give different number of exposed active sites. The higher the crystallinity, the higher the surface content of Al₂O₃(110). The research contributes to the development of mesoporous materials and enriches the diversity in solution phase synthetic chemistry.

Author Contributions: Y.X. and X.T. conceived the project. Y.X., B.Y., Y.H., and X.T. supervised the project. Y.X., L.G., and M.X. carried out the material growth experiment and performed the Electrochemical and CO₂ adsorption measurements. Y.X., L.G., M.X., and B.Y. conducted SEM, TEM, Nitrogen sorption and XRD characterizations. All authors contributed to the scientific discussion and writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data sharing not applicable. No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhang H Y, Shan G B, Liu H Z, et al. Preparation of (Ni/W)-gamma-Al₂O₃ microspheres and their application in adsorption desulfurization for model gasoline. *Chemical Engineering Communications*, 2007, 194 (7): 938-945.
2. Al-Ghouti M A, Khan M, Malik A, et al. Development of novel nano-γ-Al₂O₃ adsorbent from waste aluminum foil for the removal of boron and bromide from aqueous solution. *Journal of Water Process Engineering*, 2022, 50: 103312.
3. Shen X, Yan F, Li C, et al. Biogas upgrading via cyclic CO₂ adsorption: application of highly regenerable PEI@ nano-Al₂O₃ adsorbents with anti-urea properties. *Environmental Science and Technology*, 2021, 55 (8): 5236-5247.
4. Bartsch M, Saruhan B, et al. Novel low-temperature processing route of dense mullite ceramics by reaction sintering of amorphous SiO₂-coated gamma-Al₂O₃ particle nanocomposites. *Journal of the American Ceramic Society*, 2004, 82 (6): 1388-1392.
5. Liu X, Zou B, Xing H, et al. The preparation of ZrO₂-Al₂O₃ composite ceramic by SLA-3D printing and sintering processing. *Ceramics International*, 2020, 46(1): 937-944.
6. Lietti L, Forzatti P, Nova I, et al. NO_x storage reduction over Pt-Ba/gamma-Al₂O₃ catalyst . *Journal of catalysis*, 2001, 204: 175-191.
7. Shumilov V, Kirilin A, Tokarev A, et al. Preparation of γ-Al₂O₃/α-Al₂O₃ ceramic foams as catalyst carriers via the replica technique. *Catalysis Today*, 2022, 383: 64-73.
8. Zhao J, Zhang G, Liu H, et al. Improved charge transfer and morphology on Ti-modified Cu/γ-Al₂O₃/Al catalyst enhance the activity for methanol steam reforming. *International Journal of Hydrogen Energy*, 2022, 47(42): 18294-18304.
9. Wang C , Zhang Q , Yan B ,et al. Facet Engineering of Advanced Electrocatalysts Toward Hydrogen/Oxygen Evolution Reactions. *Nano-Micro Letters*, 2023, 15(1):52.
10. Fereja S L , Li P , Zhang Z ,et al. W-doping induced abundant active sites in a 3D NiS₂/MoO₂ heterostructure as an efficient electrocatalyst for urea oxidation and hydrogen evolution reaction. *Chemical Engineering Journal*, 2022, 432:134274-134280.
11. Du C , Li P , Zhuang Z ,et al. Highly porous nanostructures: Rational fabrication and promising application in energy electrocatalysis. *Coordination chemistry reviews*, 2022(9):466.
12. Changshui W, Bing Y, Zhenzhao C, et al. Recent advances in carbon substrate supported nonprecious nanoarrays for electrocatalytic oxygen evolution. *Journal of Materials Chemistry A* 2021, 9 (46), 25773-25795.
13. Kim K T, Dao T D, Han M J, et al. Graphene coated with alumina and its utilization as a thermal conductivity enhancer for alumina sphere/thermoplastic polyurethane composite. *Materials Chemistry and Physics*, 2015, 153: 291-300.
14. Seyed Ali Hosseini, Aligholi Niaei, Dariush Salari. Production of γ-Al₂O₃ from Kaolin. *Open Journal of Physical Chemistry*, 2015, 01(2):23-27.
15. Dabbagh H A, Shahraki M. Mesoporous nano rod-like γ-alumina synthesis using phenol-formaldehyde resin as a template. *Microporous and Mesoporous Materials*, 2013, 175:8-15.
16. Feng J T, Lin Y J, Feng L, et al. Preparation, structure and properties of micro-spherical alumina with magnetic spinel ferrite cores. *Applied Catalysis A General*, 2007, 329(10):112-119.
17. Lv Y, Li D, Tang P, et al. A simple and promoter free way to synthesize spherical γ-alumina with high hydrothermal stability. *Materials Letters*, 2015, 155:75-77.
18. Wu Q, Zhang F, Yang J, et al. Synthesis of ordered mesoporous alumina with large pore sizes and hierarchical structure. *Microporous and Mesoporous Materials*, 2011, 143(2-3):406-412.
19. Tanaka K, Imai T, Murakami Y, et al. Microporous structure of alumina prepared by a salt catalytic sol-gel process. *Chemistry letters*, 2002, (1): 110-111.
20. Dahlan, Marsih I N, Makertihartha I, et al. γ-Alumina Nanotubes Prepared by Hydrothermal Method as Support of Iron, Cobalt and Nickel for Fischer-Tropsch Catalysts. *Chemistry and Materials Research*, 2012, 2(3): 31-38.
21. Saeb M R, Rabiee N, Seidi F, et al. Green CoNi₂S₄/porphyrin decorated carbon-based nanocomposites for genetic materials detection. *Journal of Bioresources and Bioproducts*, 2021, 6(3): 215-222.
22. Deeksha B, Sadanand V, Hariram N, et al. Preparation and properties of cellulose nanocomposite fabrics with in situ generated silver nanoparticles by bioreduction method. *Journal of Bioresources and Bioproducts*, 2021, 6(1): 75-81.
23. He M, Wang X, Wang Z, et al. Biocompatible and biodegradable bioplastics constructed from chitin via a “green” pathway for bone repair. *ACS Sustainable Chemistry & Engineering*, 2017, 5(10): 9126-9135.

24. Soni S S, Brotons G, Bellour M, et al. Quantitative SAXS analysis of the P123/water/ethanol ternary phase diagram. *The journal of physical chemistry B*, 2006, 110(31): 15157-15165.
25. Elma M, Wang D K, Yacou C, et al. Interlayer-free P123 carbonised template silica membranes for desalination with reduced salt concentration polarisation. *Journal of Membrane Science*, 2015, 475: 376-383.
26. Jia C, Zhang Y, Kong Q, et al. Soft-template synthesis of mesoporous NiFe_2O_4 for highly sensitive acetone detection. *Journal of Materials Science: Materials in Electronics*, 2020, 31: 6000-6007.
27. Biriaei R, Nohair B, Kaliaguine S. A facile route to synthesize mesoporous ZSM-5 with hexagonal arrays using P123 triblock copolymer. *Microporous and Mesoporous Materials*, 2020, 298: 110067.
28. Saúl C, El H J, Jaime A, et al. Surfactant-Assisted Synthesis of Mesoporous Alumina Showing Continuously Adjustable Pore Sizes. *Advanced Materials*, 1999, 11(5):379-381.
29. Mohan Y M, Vimala K, Thomas V, et al. Controlling of silver nanoparticles structure by hydrogel networks. *Journal of Colloid and Interface Science*, 2010, 342(1):73-82.
30. Li Q, Jiang R, Dou Y, et al. Synthesis of mesoporous carbon spheres with a hierarchical pore structure for the electrochemical double-layer capacitor. *Carbon*, 2011, 49(4):1248-1257.
31. Xin Y, Jiang P, Yu M, et al. A universal route to fabricate hierarchically ordered macro/mesoporous oxides with enhanced intrinsic activity. *Journal of Materials Chemistry A*, 2014, 2(18):6419-6425.
32. M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, Use of DFT to achieve a rational understanding of acid–basic properties of γ -alumina surfaces, *J. Catal.* 226 (1) (2004) 54-68.

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