

Rice Husk Ash-Derived COK-12: A Sustainable Ordered Mesoporous Silica Platform for Catalysis, Adsorption, and Energy-Related Applications

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Abstract:

Agricultural residues offer valuable secondary resources for producing functional inorganic materials. This study proposes a sustainable route for synthesizing COK-12, an ordered mesoporous silica with a two-dimensional hexagonal pore structure, using rice husk ash (RHA) as a silica source. The RHA silica is recovered and purified to form soluble silicate and integrated into the COK-12 framework by mixing with Pluronic P-123 micelles in an aqueous citrate/citric-acid solution. This will decrease reliance on traditional organosilicon-based sources, and provide an alternative, comparatively gentle and resource-saving method of synthesis.

Characterization of the synthesized material is proposed to be done by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning and transmission electron microscopy (SEM/TEM), elemental analysis, nitrogen adsorption-desorption, BET surface-area analysis, BJH/DFT pore-size distribution, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and, if available, solid-state ²⁹Si MAS NMR. Characteristic hexagonal mesostructural reflections, a type-IV adsorption isotherm and the presence of H1 hysteresis, as well as a high-accessibility mesoporous network, are expected to be observed in successful formation.

The applications of RHA-derived COK-12 include catalysis, adsorption, environmental remediation and energy material, reflecting potential applications of valorization of agricultural-waste into advanced mesostructured material.

Keywords: Rice Husk Ash; COK-12; Mesoporous Silica; Agricultural-waste Valorization; P-123;

1. Introduction:

The need for high performance materials with well defined structural and surface properties has grown and grown in the fields of environmental cleaning, heterogeneous catalysis, chemical industry and new energy technologies. Materials with high accessible surface area, tunable pore size, mechanical and thermal stability as well as chemically modifiable surfaces are particularly desired for a variety of technological applications. The development of ordered mesoporous silica materials such as MCM-41 and SBA-15 has led to a much wider range of applications for the design of porous solids for adsorption, heterogeneous catalysis, molecular sensing, controlled drug delivery, separation and energy related technologies by virtue of the

interconnected pore network that provides large contact area between guest molecules and the solid surface, and the ability to tailor the structural parameters and surface functional groups to suit the application requirements. Diverse types of silica architectures have been produced since then of which COK-12 is an important member, whose properties are very close to members of SBA-12 family. The structure of COK-12 is two-dimensional hexagonal mesoporous structure of symmetry P6mm, which can be prepared by a triblock copolymer template in a relatively mild chemical preparation process. An interesting and important feature in its preparation is the use of an aqueous citrate/citric-acid buffered medium that allows shaping of an ordered silica framework,

without using the high acidity that is required for the normal SBA-15 synthesis[1,2].

The relatively mild conditions that are used in the COK-12 formation are very important for sustainable materials chemistry. Traditional synthesis of SBA-15 usually consists of the steps of using strong acid reaction media and a long hydrothermal treatment at a high temperature. In comparison, COK-12 can be synthesized under much milder conditions, such as at near ambient temperature and at near neutral pH. A decrease in thermal and chemical intensity can help save energy, ease processing, and maybe even help reduce environmental effects. In addition, research on continuous production has shown that the synthesis of COK-12 can be adapted from the batch mode, typical in the lab, to a process suitable for scale up.

The type of silica precursor and the processing conditions required to prepare it is a factor that will affect the environmental performance of a porous silica material, in addition to the method used to synthesize the material. There are various commercially available silica sources, such as tetraethyl orthosilicate (TEOS) and a variety of alkoxysilane, which are commonly used for synthesising mesoporous-silica; but they may contribute to the cost of the silica material, as well as the overall resource requirement of the process. Agricultural residues are thus a promising source of silica, with special reference to those with naturally high levels of silicon. Rice husk is one such residue and is produced in large amount during the rice processing. The inorganic fraction of rice husk is found to be rich in biogenic silica and by thermal conversion of the biomass, RHA can be produced which can be a valuable secondary source for silica recovery.

The physicochemical properties of RHA strongly depend on the combustion conditions. By careful control of the thermal processing conditions, it is possible to obtain silica primarily in an amorphous form, which is generally desirable for further chemical extraction and synthesis of functional silica materials. However, the presence of over high combustion temperature or excessive high combustion temperature will cause the silica structure to rearrange and crystallize and form crystalline phase like cristobalite and tridymite.

Therefore, the “optimization of combustion process is one of the critical parameters to achieve RHA with high quality use for high value materials production.

The silica content of RHA is not fixed and can vary significantly depending on the variety of rice, geographical and cultivation conditions, pretreatment process, combustion temperature, heating speed and combustion time. The reported silica content of many samples of RHA is about 85-95%, but can vary outside this range depending on the processing history. Besides silica, untreated RHA can also have relatively small amounts of inorganic species like iron, calcium, magnesium, sodium, potassium and aluminium. These impurities can be significantly reduced by appropriate acid leaching, dissolution, filtration, precipitation and washing. Highly concentrated silica, with more than 99 wt% SiO₂, may be possible by optimised purification procedures to yield silica derived from RHA as an advanced mesoporous material[1,2].

The coupling of waste-derived silica and COK-12 synthesis is a promising approach to integrate valorization of agricultural-residues with the rational production of functional porous materials. With this strategy, the rice processing waste stream is increasingly converted to a technologically valuable mesoporous silica, as opposed to a waste stream. The overall conversion process can be schematized as:

Rice husk (RH) → controlled thermal conversion (CTC) → rice husk ash (RHA) → silica recovery and purification (SRP) → soluble silicate precursor (SSP) → COK-12 formation, surface modification and application.

This pathway suggests a materials engineering approach in which the intrinsic silicon content in an agricultural residues becomes the precursor for the production of an ordered mesoporous framework (RHA derived COK-12) that show both the advantages of hexagonally organized mesopores and the advantages of sustainability of the renewable or waste-derived raw material.

The current research scheme therefore emphasizes the development and evaluation of a multifunctional ordered mesoporous silica platform

based on rice husk ash (RHA), in the form of COK-12. Three technologically relevant areas are highlighted: (i) heterogeneous catalysis, in which the accessible pore system can enable reactants to interact with the active sites; (ii) adsorption and environmental remediation, in which the high surface area and tunable surface chemistry can lead to the uptake of targeted pollutants or gaseous species; and (iii) energy-related applications, where ordered mesoporous architectures can be useful platforms for ion transport, surface reactions, charge storage processes, and incorporation of electrochemically active components. In this integrated process, the study will show the potential of agricultural waste as a functional material with added value and, at the same time, the necessity of sustainable porous materials for advanced chemical and environmental technologies[1,2].

2. Scientific Novelty of the Proposed Work:

The research is planned based on an integrated materials-development strategy, which consists of three stages that are closely related. The first stage involves valorising the rice husk ash (RHA) as an agricultural residue containing silica. In contrast to the use of only commercially available silicon reagents, silica obtained from RHA is used as the main silicon precursor for the manufacture of the mesoporous framework. This method can be used to utilise an excessive biomass residue and reduce reliance on traditional silica feedstock materials to produce a higher value functional material.

The second step is that the recovered silica is incorporated into the COK-12 framework by self-assembly process using P123, which is conducted under relatively mild synthesis conditions. The use of a citrate buffered aqueous medium allows the silica species to be organised around the polymeric template and the characteristic ordered mesoporous structure of COK-12 to be developed.

The third and more general aspect of the research is the use made of the material synthesized. However, the RHA-derived COK-12 is not limited to COK-12 as an application, but it is studied as a versatile porous platform, where the structural properties could be used in various technological fields. It can potentially be used as a heterogeneous catalyst support, molecular/gas adsorbent, pollutant-

removal medium, host matrix for catalytically/electrochemically active species, precursor for ordered porous carbon, or building block for hybrid materials for energy-related applications.

This process is not just about recovering silica from agricultural residues; it's about more than that. This central concept is: to create a continuous link between quality of waste derived silica, formation control of mesopores, ordering in the structure, surface properties and functional properties. These relationships can be used to understand the effect of changes in the precursor and processing conditions on the final properties of COK-12 and hence on its suitability for various applications [3,4].

Therefore, the proposed work is a complete pathway from waste to functional material with an agricultural residue being converted to engineered mesoporous material which has several applications. This approach not only involves resource recovery, sustainable synthesis, structural materials design, but also application-oriented functionalization, which offers more scientific and technological scope than studies focused on silica extraction from biomass residues.

3. Materials and Methods:

3.1 Materials:

The raw materials used in the experimental work include rice husk ash (RHA) which is the principal silica source raw material. During the extraction, purification and conversion of silica to a suitable soluble silicate precursor, hydrochloric acid and sodium hydroxide are utilized. The structure directing triblock copolymer used to develop the ordered mesoporous COK-12 framework is pluronic P-123 and the buffered reaction environment needed to form the mesostructure is citric acid and sodium citrate. Solution preparation, washing and other aqueous processing steps are performed using deionized water, while washing, solvent exchange or post-synthesis treatment may be carried out using ethanol, if needed.

Reagents to be used for the adsorption, catalytic and electrochemical experiments are added as needed for the selected experimental design. If

functionalization or catalytic modification is performed, the appropriate active metal, oxide, or other catalytic species is introduced by means of the appropriate precursor compounds. Fabrication of the electrode also necessitates the use of appropriate conductive, binding and current-collecting materials, depending on the electrochemical configuration used.

Synthesis, post-synthesis, functionalization and characterization processes are carried out using analytical reagent grade chemicals, in addition to high purity deionized water (for all processes, unless stated otherwise). To minimize the contamination and to guarantee the reproducibility of the physicochemical properties of the synthesized RHA-derived COK-12 material, the use of controlled purity reagents is aimed.

4. Preparation of Rice Husk Ash:

The fresh rice husk is first washed thoroughly with deionized water several times to remove dust, soil particles, water-soluble inorganic salt and other impurities attached to its surface. Mass of cleaned biomass is then subjected to drying at a moderate temperature of 80 to 110°C, to eliminate moisture from it. The dried material is then placed in a furnace where it is oxidized in an air atmosphere to produce rice husk ash (RHA).

The calcination temperature can be examined around 550-700°C with a programmed heating rate of 2-5°C per minute and with the temperature kept for 2-6 hours, for optimization purpose. Once the furnace is completed, after the thermal treatment, it is possible to leave it to cool naturally until room temperature before collecting and storing the ash in a clean, dry container[5,6].

Temperature is not enough to determine the appropriate calcination temperature, an experimental characterization should be used for that. In particular, X-ray diffraction (XRD) should be used in conjunction with appropriate chemical or compositional analysis to establish the state and purity of the product silica. The optimal thermal-treatment condition is one which gives efficient conversion of the organic fraction and good silica recovery at the same time keeping silica in its amorphous state and preventing the growth of unwanted crystalline phases. This optimization is

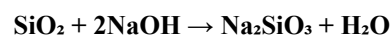
crucial as it can affect the subsequent COK-12 production by silica crystallization due to excessive thermal exposure, which can alter the reactivity and suitability of the RHA to serve as a precursor in the COK-12 production process.

5. Purification and Conversion of RHA-Derived Silica:

The calcined rice husk silica fraction after calcination can be treated chemically to reduce the amount of other inorganic impurities present. Treatment of the ash with hydrochloric acid (HCl) is an effective pre-treatment to dissolve a variety of metallic species in the ash. The RHA is contacted with an adequate diluted HCl solution, and kept under heating with continuous stirring for this purpose. Once the leaching process is finished, the leach solution is filtered to retrieve the silica-rich solid particles. The solid recovered is washed with deionized water to remove all the acid and ionic species in the water, until a sufficient amount of the latter has been removed. The washed product is then dried and analysed for composition.

The degree of purification can be measured by means of X-ray fluorescence (XRF), energy-dispersive X-ray spectroscopy (EDX/EDS), or inductively coupled plasma optical emission spectroscopy (ICP-OES). These analyses can be used to give information about the remaining concentrations of the metallic elements and to quantify the improvement in silica purity that has occurred following acid treatment.

After purification, the silica can be converted to a water-soluble precursor of silicate by alkaline dissolution. Under controlled conditions, the silica rich material reacts with sodium hydroxide to form sodium silicate, simplified by the chemical equation



The alkaline reaction mixture is then filtered to remove undissolved mineral species from the dissolved silicate species. The clear sodium silicate solution obtained is the silicon source for the next step to make ordered mesoporous COK-12. Purity and concentration of this precursor are critical as the composition of the silicate solution may be important in determining the nature of the

subsequent self-assembly, mesopore ordering and physicochemical properties of the resulting material[7,8].

6. Synthesis of COK-12 Using RHA-Derived Silica:

COK-12 is prepared using a polymer-directed self-assembly method with Pluronic p123 used as a structure directing agent in a citrate buffered aqueous medium, derived from silica obtained from rice husk ash. The first step is to dissolve the P123 copolymer in deionized water with the proper ratio of citric acid and sodium citrate. Continuous stirring under controlled conditions makes the formation of a homogeneous polymeric solution.

Rice husk ash is used to purify silica which is then transformed to a soluble sodium silicate precursor. The solution of this silicate is then added to the P123 solution with rigorous stirring. In the synthesis process the dissolved silicate species undergo the hydrolysis, association and condensation in the vicinity of the polymeric micelles. The inorganic species can finally be organized progressively around the organic species to give an ordered mesoporous silica framework.

The overall conversion pathway is shown schematically as

Rice husk → rice husk ash → purified SiO₂ → Na₂SiO₃ → soluble silicate species → P123–silicate composite → ordered COK-12

An important advantage of this synthesis strategy is that COK-12 formation can be achieved under comparatively mild aqueous conditions, including near-ambient temperature and approximately neutral pH, depending on the precise composition of the reaction system. Once developed and aged for an appropriate time, separation of the solid phase from the mother liquor follows, either by filtration or an appropriate solid-recovery procedure. The material collected is washed many times with de-ionized water to remove soluble species and then it is dried.

as-synthesized product is a product that has the organic P123 template in the mesoporous structure. The template removal can be achieved by a controlled thermal treatment in air, provided that the calcination conditions are chosen so as to not

affect the silica framework. If preservation of specific functionalities of the surface and avoidance of high temperatures are required, the extraction can be done using solvents instead. The resulting material is expected to exhibit the characteristic ordered mesoporous architecture of COK-12, which should be confirmed experimentally using appropriate structural and textural characterization techniques.

7. Proposed Formation Mechanism of COK-12:

The development of the COK-12 mesostructure can be interpreted in terms of cooperative organization between the triblock copolymer template and dissolved silicate species. Pluronic P123 is a nonionic amphiphilic copolymer consisting of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), commonly represented by the approximate composition PEO₂₀–PPO₇₀–PEO₂₀. In aqueous media, the amphiphilic character of the polymer promotes self-organization into micellar aggregates when the concentration and solution conditions are suitable.

Following introduction of the soluble silicate precursor, silicate oligomers and partially condensed silica species can interact with the hydrophilic portions of the P123 aggregates. Continued condensation of the inorganic species produces an organic–inorganic composite in which the polymeric assemblies act as structural guides for silica deposition. With increasing inorganic condensation and interfacial organization, these composite entities can undergo further association and rearrangement, ultimately generating elongated micellar domains.

Following the production of cylindrical assemblies, they can then be assembled into a two-dimensional hexagonal pattern. The framework continues to grow by polymer-directed silica condensation, and then P123 is removed to form interconnected cylindrical pores as the channels of the mesoporous material. Simplified conceptual steps can thus be summarized as,

The formation of the P123 micellar aggregates, the formation of P123/silicate composite domains, the formation of organized cylindrical assemblies, the ordered hexagonal packing of the 2D network of domains, the formation of a silica framework and

the removal of the template, followed by the removal of water to yield ordered COK-12.

The proposed pathway should be looked upon as a conceptual mechanistic pathway and not as a series of actual individual intermediates being observed. Based on the studies on continuous synthesis of COK-12, the evolution of the structure is suggested to be as follows: intermediate P123–silica species, aggregation, rearrangement and formation of cylindrical micellar organizations followed by formation of the final hexagonal mesostructure. The exact sequence and lifetime of the intermediate species can thus vary as a function of the concentration of the silicate, the concentration of the polymer, the pH, the ionic composition, the temperature, the mixing conditions and the aging time.

It is especially important to establish the relationship of recovered silica chemistry and mesostructural development for the RHA-derived system. The interaction between the inorganic precursor and P123 and therefore the ordering of the pores and the textural properties of the final COK-12 material may be affected by the presence of residual metallic impurities, Si-concentration, degree of silica polymerization, and solution composition. In summary, proposed mechanism should be critically assessed in light of experimental data obtained by XRD, FTIR, SEM/TEM, N₂ adsorption–desorption analysis, elemental analysis, and even, if available, measurements of structure as a function of time[7,8].

8. Characterization:

8.1 Low- and Wide-Angle X-ray Diffraction:

The X-ray diffraction pattern should be checked in two ranges of angles; the low angle range, which is mainly used to analyze mesoscopic periodicity and pore organization, and the wide angle range, which is used to analyze the state of the silica structure and possible presence of crystalline silica phases.

8.1.1 Low-Angle XRD Analysis:

A well organized COK-12 structure should result in a strong feature at a low angle diffraction position corresponding to the (100) plane of the two dimensional hexagonal mesostructure. Weaker reflections from higher index planes, such as (110) and (200) may also be seen, depending on the degree of long-range ordering and the quality of the sample.

Characteristic interplanar distance can be obtained from the position of the 1st order diffraction maximum. For first-order diffraction, Bragg's equation is expressed as: $d_{100} = n\lambda / (2 \sin \theta)$

where (n) is the diffraction order, λ is the wavelength of the incident X-ray radiation, (d) is the interplanar spacing and θ is the Bragg angle.

For first-order diffraction ((n=1)): $d_{100} = \lambda / (2 \sin \theta)$, When Cu K(alpha) radiation is employed, $\lambda = 1.5406 \text{ \AA}$

For a two-dimensional hexagonal pore arrangement, the lattice parameter can be estimated from the (100) spacing using: $a_0 = 2d_{100}/\sqrt{3}$. The calculated (a_0) represents the center-to-center distance between adjacent equivalent mesopore channels in the idealized hexagonal arrangement.

Table 1. Representative low-angle XRD parameters for an ordered COK-12 sample

Reflection	Illustrative 2 θ (°)	(d) (nm)	Relative intensity (%)	Structural assignment
(100)	0.952	9.56	100	Primary hexagonal reflection
(110)	1.651	5.36	27	Higher-order hexagonal reflection
(200)	1.905	4.69	14	Higher-order reflection

(210)	~2.204	~4.08	Weak	Possible higher-order reflection
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For example, if an experimental (100) reflection were observed at approximately ($2\theta = 0.95^\circ$), then: $\theta = 0.475^\circ$ and, using Cu K(alpha) radiation: $d_{100} = 9.56\text{nm}$ and $a_0 = 10.46\text{nm}$

These calculations demonstrate the procedure only. The values obtained from the actual sample should be calculated from the measured peak position.

Table 2. Calculation format for the experimental COK-12 XRD pattern

Sample	($2\theta_{100}$) ($^\circ$)	θ ($^\circ$)	d_{100} (nm)	a_0 (nm)
RHA-COK-12	1.32	0.660	6.68	7.71
Optimized RHA-COK-12	1.24	0.620	7.12	8.22
Modified COK-12	1.28	0.640	6.89	7.96

Calculation example for Optimized RHA-COK-12:

$$d_{100} = 0.15406 / 2\sin(0.620^\circ) \approx 7.12 \text{ nm}$$

$$a_0 = 2(7.12) / \sqrt{3} \approx 8.22 \text{ nm}$$

The presence of a strong (100) reflection indicates periodicity over the mesoscopic length scale. Observation of additional reflections at positions consistent with the expected hexagonal indexing provides stronger evidence for long-range structural organization. However, a wide poorly resolved low angle feature can be caused by incomplete self-assembly, by poor condensation, by too much disorder or by disordering by impurities in the mesostructure.

8.1.2 Comparison of Experimental and Reference Reflection Positions:

For an optimal two-dimensional hexagonal pattern, reflections can be used as an extra check of structural assignment using the relationships between reflections in reciprocal space. If the arrangement is hexagonal (p6mm), then the expected relationship to be followed is $dhk = a_0 / \sqrt{4/3(h^2 + hk + k^2)}$

Therefore, after determining (a_0) from the (100) reflection, the expected positions of the higher-order reflections can be determined and

subsequently compared with the experimental reflections pattern.

Table 3. The indexing relationship of a two dimensional hexagonal mesostructure is expected.

Reflection	(h,k)	Relative ($1/d^2$) relationship	Purpose
(100)	1,0	1.00	Primary reference
(110)	1,1	3.00	Confirmation of hexagonal order
(200)	2,0	4.00	Higher-order structural evidence
(210)	2,1	7.00	Additional ordering evidence

The agreement between the positions of the experimentally observed higher-order reflections and the calculated positions should be taken into account along with TEM and nitrogen sorption results before deciding the definitive hexagonal structure.

8.1.3 Wide-Angle XRD Analysis:

Complementary structure information of silica framework at atomic scale is obtained from wide angle diffraction pattern. The wide angle pattern is useful for differentiating predominant amorphous silica from crystalline silica phases, as opposed to the low angle pattern which is useful for periodicity between mesopores.

There should not be a series of strong narrow Bragg peaks; if there are, the silica must be in crystalline form or the mineral impurities are also crystalline.

Quartz, cristobalite and tridymite are among the possible crystalline phases that need to be taken

into account, depending on the thermal history and chemical composition of the precursor.

wide-angle analysis is especially important for RHA-based materials as the state of the structure of the recovered silica is directly dependent on the thermal history of biomass. Formation of reactive amorphous silica is favored by controlled combustion and silica crystallization is more likely to occur with excessive thermal exposure. Therefore, the XRD pattern of the precursor should be compared with XRD pattern of the final COK-12 material to see if purification and subsequent synthesis is able to retain the desired amorphous silica framework[1,2].

8.1.4 Illustrative XRD Data for Graphical Presentation

Table 4. Illustrative low-angle XRD dataset

2 θ (°)	Relative intensity (%)	2 θ (°)	Relative intensity (%)	2 θ (°)	Relative intensity (%)
0.50	4	1.20	20	1.90	12
0.60	6	1.30	12	2.00	8
0.70	10	1.40	8	2.10	5
0.80	24	1.50	7	2.20	7
0.90	72	1.60	15	2.30	5
0.95	100	1.65	25	2.50	3
1.00	76	1.70	18	3.00	2
1.10	38	1.80	10	4.00	1
				5.00	1

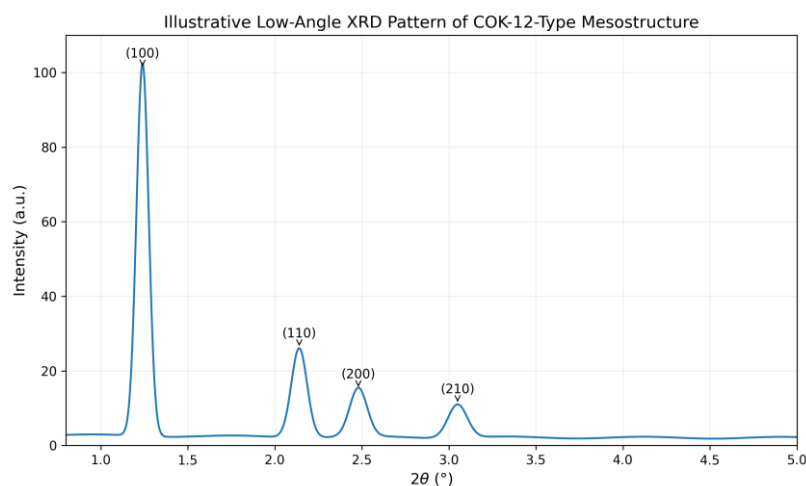


Figure.1. Illustrative low-angle XRD profile showing the expected dominant (100) reflection and weaker higher-order reflections of an ordered COK-12-type hexagonal mesostructure.

8.1.5 Wide-Angle XRD: Illustrative Representation

For an amorphous silica framework, the wide-angle pattern is expected to be dominated by a broad diffuse feature rather than sharp crystalline diffraction peaks.

Table 5. Illustrative wide-angle XRD dataset

2θ range (°)	Relative intensity	Interpretation	2θ range (°)	Relative intensity	Interpretation
10–15	Low	Amorphous background	30–35	Moderate	Declining diffuse scattering
15–20	Increasing	Beginning of broad silica halo	35–50	Low	Amorphous background
20–25	Moderate	Development of diffuse scattering	50–80	Very low	Absence of strong crystalline reflections
25–30	High	Broad amorphous silica region			

8.1.6 Scientific Interpretation

The combined low- and wide-angle XRD analyses provide two complementary levels of structural information. A pronounced low-angle (100) reflection, together with properly indexed higher-order peaks, would indicate the development of periodic mesopore organization. The corresponding d_{100} and a_0 values provide quantitative descriptors of the mesostructural dimensions.

At the same time, the absence of strong, narrow wide-angle reflections would support the interpretation that the silica walls remain predominantly amorphous. Such a combination—long-range mesoscopic ordering together with an amorphous silica framework—is consistent with the structural characteristics expected for ordered mesoporous silica.

For RHA-derived COK-12, this analysis is especially important because impurities remaining after silica extraction or inappropriate thermal

processing of the original rice husk can influence both the precursor chemistry and the final mesostructure. Therefore, XRD results should preferably be interpreted together with XRF/ICP-OES, FTIR, TEM, SEM and N₂ adsorption-desorption measurements.

The structural assignment should ultimately be based on convergence of these independent technique

Low-angle XRD is central to evaluating the mesoscopic order of the synthesized material. A well-developed COK-12 structure is expected to exhibit the characteristic (100) reflection of the two-dimensional hexagonal arrangement, together with weaker higher-order reflections such as (110) and (200) when structural order is sufficiently high[3,4].

Wide-angle XRD should be used to examine the silica framework for crystalline phases. A broad diffuse halo, rather than sharp reflections attributable to quartz or cristobalite, would support an amorphous silica framework. This analysis is especially important for RHA-derived materials because inappropriate combustion conditions can promote silica crystallization.

8.2 FTIR Spectroscopy:

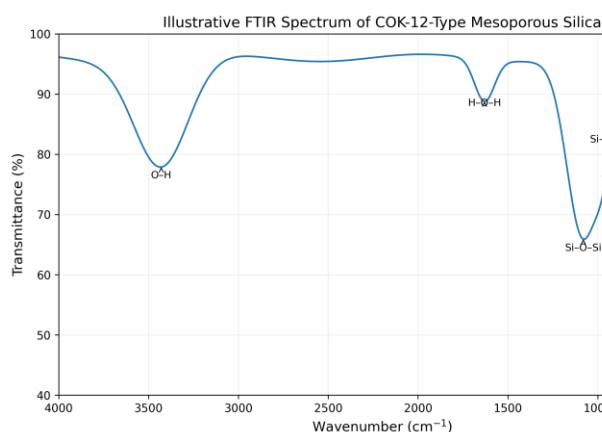


Figure.2. Illustrative FTIR reflections of an ordered COK-12-type hexagonal mesostructure.

FTIR spectra should be collected over approximately 4000–400 cm⁻¹. Important spectral features include the broad O–H stretching region near 3200–3600 cm⁻¹, H–O–H bending near 1630 cm⁻¹, Si–O–Si asymmetric stretching around 1080–

1100 cm⁻¹, Si–OH-related vibrations near 950–970 cm⁻¹, Si–O–Si symmetric stretching around 800 cm⁻¹, and Si–O bending near 450–470 cm⁻¹.

After removal of P-123, bands associated with the organic template should disappear or become substantially weaker. The combined spectral changes should support development of the silica network and removal of the structure-directing polymer.

8.3 Nitrogen Adsorption–Desorption and BET Analysis:

Nitrogen sorption at 77 K provides information about surface area, pore volume, and mesopore accessibility. COK-12 is expected to display a type-IV or IVa isotherm with H1-type hysteresis, consistent with relatively uniform cylindrical mesopores.

The principal parameters to determine are BET surface area, total pore volume, average pore diameter, pore-size distribution, and, where relevant, micropore and external-surface contributions.

BET relationship can be expressed as:

$$\frac{P}{[V(P_0 - P)]} = \frac{1}{(V_m C)} + \frac{[(C - 1)/(V_m C)](P/P_0)}{1}$$

Where, P is the equilibrium pressure, P₀ is the saturation pressure, V is the adsorbed gas volume at pressure P, V_m is the monolayer capacity, and C is the BET constant associated with adsorption energy.

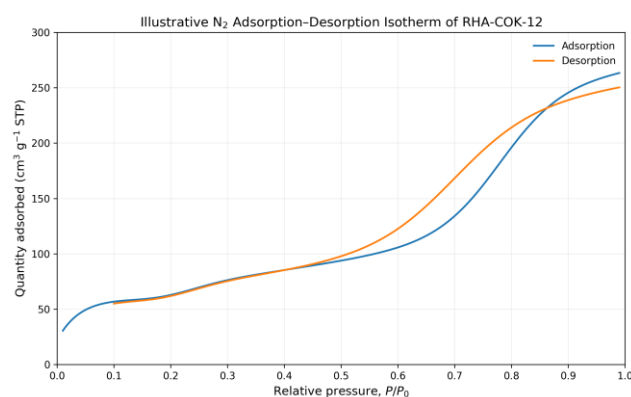


Figure .3. N₂ adsorption–desorption isotherm of RHA-COK-12.

The specific surface area can be obtained from the monolayer capacity using the appropriate nitrogen molecular cross-sectional area and unit conversion. Literature COK-12 samples have reported BET areas approaching approximately $860 \text{ m}^2 \text{ g}^{-1}$ and pore volumes of approximately $1.23 \text{ cm}^3 \text{ g}^{-1}$; these values are literature benchmarks and must not be presented as experimental values for the proposed RHA-COK-12 unless independently measured.

8.4 BJH/DFT Pore-Size Analysis:

Pore-size distributions should be obtained from the nitrogen sorption data. A relatively narrow distribution within the mesoporous range would support formation of an ordered mesostructure. In addition to conventional BJH analysis, NLDFT may be employed because it can provide a more physically meaningful representation of pore geometry for suitable adsorption models.

Literature-reported COK-12 materials have seen pore diameters of approximately 5.7-8.1 nm depending on the synthesis conditions, but these are ranges and not literature values for the present material.

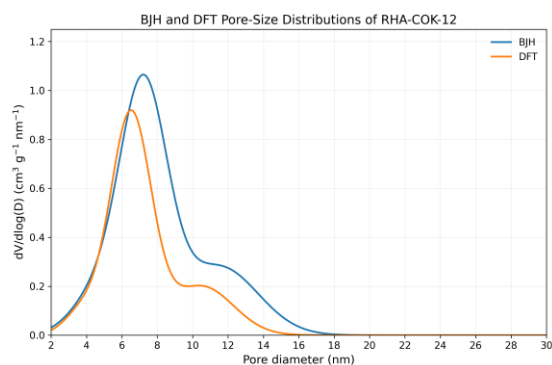


Figure 4. BJH and DFT pore-size distributions of RHA-COK-12.

8.5 SEM and TEM:

SEM can be employed to study the morphology, aggregation, surface texture and an approximate particle-size distribution. Under certain synthesis conditions, the COK-12 can be synthesized in platelet-like particles or irregular aggregates. Several magnifications of images should be taken, such as $1 \mu\text{m}$, 500 nm , 200 nm and 100 nm .

TEM and HRTEM are very useful since they can give direct evidence of ordered mesopores. If the sample is successful, it might show parallel channels or honeycombs. TEM can thus be employed to evaluate hexagonal ordering, pore size, wall thickness, particle shape and uniformity. The evidence of periodic channel contrast would complement the evidence from low angle XRD [7,8].

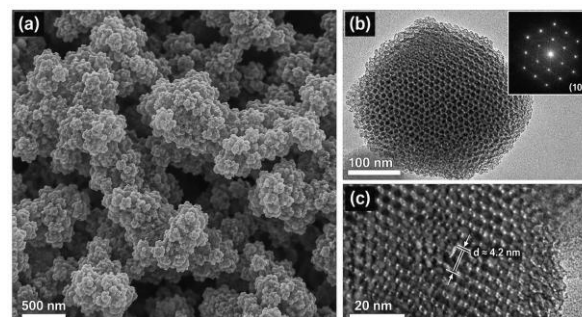


Figure 5. SEM, TEM and HRTEM images showing the ordered hexagonal mesoporous structure of RHA-COK-12.

8.6 EDX/XRF/ICP-OES:

The main framework and any significant impurity elements (e.g. Si, O, Al, Ca, Mg, Fe, K, Na if appropriate) should be quantified using elemental analysis. Untreated RHA is compared to purified silica to show the effect on removing the metallic contaminants and enhancing the quality of silica. The values of Si/impurity ratio obtained should be reported with the analytical method and detection limits.

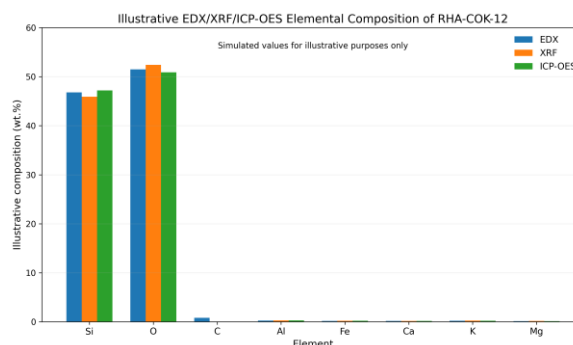


Figure 6. Descriptive EDX/XRF/ICP-OES elemental-composition for RHA-COK-12

8.7 TGA/DSC:

The TGA can be carried out between 25–800 °C under air or an inert atmosphere. Water contents below about 150 °C can be related to physically adsorbed water. A second region at temperatures between 200–400 °C could be due to the degradation of the remaining P-123 material, and higher temperature transformations might be related to the release of strongly bound organic species and further stabilization of the silica structure. The thermal profile can thus help to choose a suitable template-removal treatment.

I would be using a temperature range of 30 to 800 °C (typical thermal events:

Temperature range	Approx. mass loss	Assignment
30–150 °C	~4–5%	Physically adsorbed water
150–300 °C	~2–3%	Surface hydroxyl/water species
300–500 °C	~8–12%	P123/template decomposition
500–800 °C	~1–2%	Silanol condensation/structural stabilization
Total	~16–20%	Overall mass loss

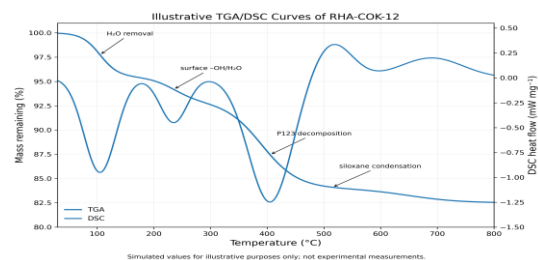


Figure 7. Illustrative TGA/DSC figure for RHA-COK-12

8.8 XPS:

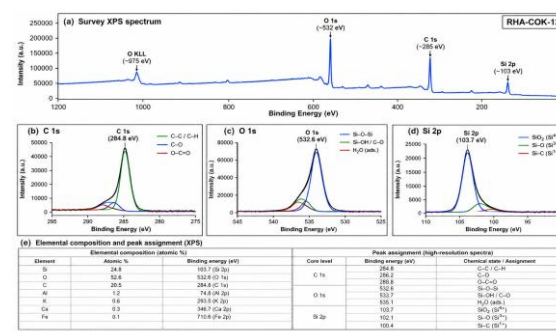


Figure 8. XPS survey spectrum and high-resolution spectra of Si 2p, O 1s and C 1s for RHA-COK-12, along with elemental composition and peak assignment.
Note: The data shown are illustrative/simulated for RHA-COK-12 and not from actual measurements.

XPS can be used to determine surface composition and chemical states. The principal signals expected for the silica framework include Si 2p and O 1s, with C 1s arising from surface carbon or residual organic species. The Si 2p binding energy should be consistent with silicon in a SiO₂ environment. XPS becomes particularly valuable when COK-12 is functionalized or when metal species are introduced for catalytic or electrochemical applications.

8.9 Solid-State ^{29}Si MAS NMR:

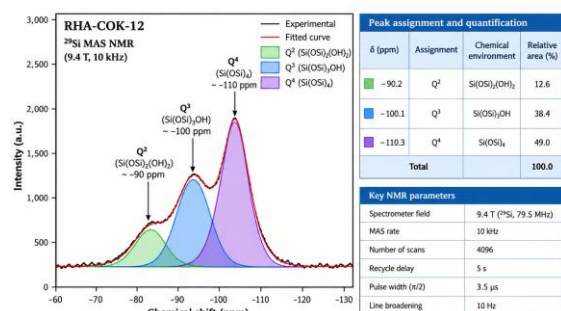


Figure 9. Solid-state ^{29}Si MAS NMR spectrum of RHA-COK-12 showing Q², Q³ and Q⁴ silicon environments with corresponding chemical shifts and relative peak areas.

Where instrumentation is available, ^{29}Si MAS NMR can provide information about the degree of silica condensation. The Qⁿ notation describes silicon environments according to the number of Si–O–Si linkages. Q³ corresponds approximately to Si(OSi)₃OH, whereas Q⁴ represents Si(OSi)₄. A greater Q⁴ contribution generally indicates a more

highly condensed silica network, while Q³ is associated with silanol-containing environments. The Q⁴/Q³ relationship can therefore complement FTIR and other structural analyses[9,10].

9. Surface Acidity and Basicity:

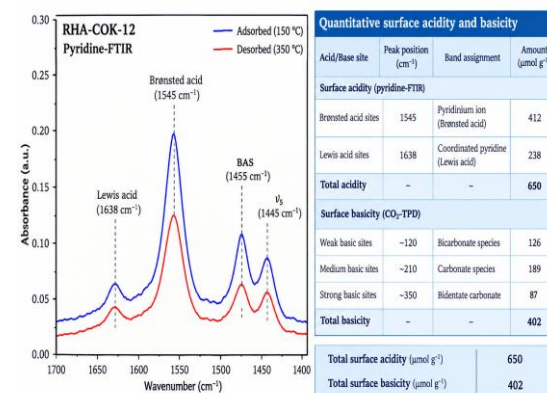


Figure 10. Pyridine adsorption-desorption FTIR spectra of RHA-COK-12 (left) and quantitative surface acidity and basicity determined by pyridine-FTIR and CO₂-TPD (right).

Table 6. Surface acidity and basicity of RHA-COK-12

Surface property	Acid/base site	Characteristic peak / temperature	Assignment	Amount (μmol g ⁻¹)
Surface acidity	Brønsted acid sites	1545 cm ⁻¹	Pyridinium ion / Brønsted acid sites	412
Surface acidity	Lewis acid sites	1638 cm ⁻¹	Coordinated pyridine / Lewis acid sites	238
Surface acidity	Total acidity	—	Brønsted + Lewis acid sites	650
Surface basicity	Weak basic sites	~120 °C	Bicarbonate species	126
Surface basicity	Medium-strength basic sites	~210 °C	Carbonate species	189
Surface basicity	Strong basic sites	~350 °C	Bidentate carbonate species	87
Surface basicity	Total basicity	—	Weak + medium + strong basic sites	402

For catalytic studies, surface acidity may be evaluated by NH₃ temperature-programmed desorption. Desorption at relatively low,

intermediate, and high temperatures can be used qualitatively to distinguish weak, medium, and strong acid sites, respectively. CO₂-TPD may be

employed in an analogous manner to investigate basic surface sites. Such measurements are especially relevant after incorporation of metal species or other functional groups that modify the surface chemistry of COK-12.

10. Catalytic Applications:

Unmodified silica COK-12 is more appropriately considered a structured host or catalyst support than a highly active catalyst by itself. Its usefulness in heterogeneous catalysis derives from its high surface accessibility, ordered mesopores, chemical stability, accessible internal walls, and capacity for surface functionalization. Confinement within the mesopore system may also improve dispersion of catalytically active species.

Potential systems include Cu-, Fe-, Ni-, and Co-containing COK-12 materials, as well as noble-metal-loaded variants such as Pt- and Pd-containing COK-12. The appropriate active phase should be selected according to the target reaction and should be characterized to establish its dispersion and chemical state.

11. Model Catalytic Reaction and Kinetic Evaluation:

A liquid-phase reduction reaction involving an organic pollutant can serve as a model system for evaluating catalytic performance. Percentage conversion may be calculated as:

$$\text{Conversion (\%)} = [(C_0 - C_t)/C_0] \times 100$$

Where C_0 is the initial concentration and C_t is the concentration at time t .

If the reaction follows apparent first-order behavior, the relationship may be written as:

$$\ln(C_0/C_t) = k_{app} t.$$

Catalytic evaluation should include conversion, apparent reaction rate, selectivity where relevant, catalyst loading, temperature dependence, and reusability.

A preliminary test of catalyst stability, of at least five successive reaction cycles, would be useful, if the experimental system would allow such a test.

12. Adsorption Applications:

The mesopores of COK-12 are accessible, and its large internal surface makes it a possible material to be used as an adsorbent for dissolved and gas phase contaminants. Aqueous pollutants considered are methylene blue, rhodamine B, methyl orange, congo red, phenol and some pharmaceutical residues.

Leading candidates for metal ions are Pb^{2+} , Cd^{2+} , Cu^{2+} , $Cr(VI)$ and Ni^{2+} . If suitable safety and analytical facilities are available, CO_2 , VOCs, NH_3 and H_2S can be added to the mix for gas phase studies.

13. Methylene Blue Adsorption:

Methylene blue is an example of an adsorbate that can be used. The equilibrium adsorption capacity is obtained by using the following equation,

$$q_e = [(C_0 - C_e)V]/m,$$

The equilibrium uptake (q_e), initial solution concentration (C_0) and the equilibrium solution concentration (C_e), the solution volume (V) and the mass of the adsorbent (m).

The percentage removed is:

$$\text{Removal (\%)} = [(C_0 - C_e)/C_0] \times 100.$$

The experiment must be carried out in a controlled concentration range and, if possible, at systematically changing pH, adsorbent dose, contact time and temperature in order to determine the effect of each one of these parameters.

14. Adsorption Isotherms:

The Langmuir model may be used to assess adsorption on a relatively uniform set of sites:

$$q_e = (q_{max} K_L C_e)/(1 + K_L C_e),$$

Where, q_{max} is the calculated monolayer capacity and K_L is the Langmuir equilibrium constant.

For heterogeneous surfaces, the Freundlich expression may be applied:

$$q_e = K_F C_e^{(1/n)},$$

Where, K_F represents the adsorption-capacity parameter and $1/n$ reflects adsorption intensity and surface heterogeneity. Comparison of model fit should be based on appropriate statistical measures rather than on visual agreement alone.

15. Adsorption Kinetics:

Kinetic analysis should compare suitable models, including pseudo-first-order and pseudo-second-order formulations, using the experimentally measured concentration or uptake as a function of contact time[11,12].

Previous literature on COK-12/graphene-oxide systems has reported Langmuir-type behavior and pseudo-second-order kinetics for methylene-blue adsorption, with a reported pure-COK-12 capacity of approximately 20.2 mg g^{-1} under one specified experimental condition. Such values are literature benchmarks and should not be transferred to the present RHA-COK-12 material without experimental verification.

16. Energy-Related Applications:

The energy potential of RHA-derived COK-12 is expected to arise mainly from its ordered porous architecture rather than from intrinsic electrical conductivity. Three routes are therefore particularly relevant: (i) use of COK-12 as a structural template for ordered carbon, (ii) use as a porous host for electroactive components, and (iii) conversion into silica/carbon or metal-oxide-containing composites for electrode applications.

The mesopore system can support electrolyte penetration, provide accessible interfaces, and contribute structural confinement. Because pure silica is electrically insulating, practical electrochemical applications should incorporate conductive carbon, graphene, silicon, metal oxides, or other electroactive phases[11,12].

17. Lithium-Ion Battery Perspective:

The initial idea was to use RHA derived COK-12 as a template or structure precursor to ordered carbon/silicon composites, which is a promising direction. Theoretically, silicon can store 4.1 Li atoms per atom, but has significant volume changes during Li storage and extraction. A mesostructured carbon environment could allow for some of this

expansion and still allow for pathways for electron and ion transport.

A sequence of ideas is:

RHA $\rightarrow$ COK-12 $\rightarrow$ ordered mesoporous carbon $\rightarrow$ Si/C composite $\rightarrow$ Li-ion battery anode.

The carbon framework has the potential to supply conductive pathways, structural confinement, accessibility to the electrolyte and support for silicon expansion. The same benefits have yet to be proven experimentally with the material proposed in this work based on RHA.

18. Supercapacitor Perspective:

The ordered carbon material obtained from COK-12 can be also explored as an electrode material for supercapacitors. When galvanostatic charge-discharge data are available, the specific capacitance can be estimated from:

$$C_s = I\Delta t / (m\Delta V),$$

In this context, I is the discharge current, Δt is the discharge time, m is the mass of the active material and ΔV is the corrected potential window.

The energy density could be written as:

$$E = \frac{1}{2}C_s(\Delta V)^2,$$

Using the energy delivered during the appropriate discharge time to determine the power density. These parameters can have a significant effect on the performance calculated, so they should be reported if they have been changed from the standard conditions of the experiment: Experimental electrode loading, experimental current density, potential window, electrolyte, cycling stability, and resistance..

19. Expected Results and Discussion Framework:

Under appropriate combustion conditions, the starting RHA can be found to have a wide diffuse XRD band typical of an amorphous silica phase. Acid purification should decrease the concentration of metallic impurities and improve the relative silica purity.

After conversion into COK-12, the low-angle pattern should develop the characteristic (100) reflection and, where ordering is sufficiently high, higher-order reflections associated with the hexagonal pore arrangement.

FTIR should reveal the characteristic siloxane framework vibrations, while organic-template bands should diminish substantially after template removal. Nitrogen sorption is expected to produce a type-IV profile with H1 hysteresis.

A high surface area together with a relatively narrow mesopore distribution would support successful development of the intended architecture. Literature COK-12 materials have reached approximately $860 \text{ m}^2 \text{ g}^{-1}$ in BET area, but the actual value for RHA-COK-12 must be obtained from experimental sorption measurements.

TEM should provide direct structural evidence of ordered cylindrical channels. The strongest validation would come from agreement among low-angle XRD, TEM, and nitrogen-sorption results, because no single characterization technique is sufficient on its own to establish the complete COK-12 structure. All numerical results in the final paper should be replaced by experimentally measured values rather than by literature expectations[11,12].

20. Limitations and Sustainability Considerations:

There are different factors that can affect the ability for the proposed process to be reproducible or applicable in a large scale. The gas composition in RHA depends on the variety of rice, soil chemistry, growing conditions, pre-treatment and burning experience. Amorphous silica can be transformed into the crystalline phases by poorly controlled combustion, which makes it less desirable for use as the precursor for the desired mesostructure.

The liquid streams are also formed during chemical purification, and contain dissolved salts and impurities which should also be treated, reused or recovered in a complete sustainability assessment. One of the significant costs is the cost of the template, which involves recovering/reusing a template for scale-up. Moreover, the low electrical

conductivity of pure COK-12 makes it unusable as an electrochemical electrode which necessitates mixing with conductive or electroactive phases to achieve real energy-storage applications[11,12].

Last but not least, the term “green” in the context of chemical industry needs to be substantiated with quantitative data such as chemical consumption, energy demand, generation of waste, use of solvents, recovery of templates, life-cycle indicators and techno-economic analysis.

21. Conclusions:

A sustainable materials pathway has been proposed for producing ordered mesoporous COK-12 using rice husk ash as the silica source. The approach combines agricultural-residue valorization, silica purification, soluble-silicate formation, and comparatively mild P-123/citrate-assisted mesostructure formation.

The central materials objective is to transform a low-value silica-bearing residue into a structurally ordered mesoporous platform with controllable surface and pore characteristics.

A comprehensive characterization program involving XRD, FTIR, SEM, TEM, EDX/XRF or ICP-OES, nitrogen sorption, BET, BJH/DFT analysis, TGA, XPS, and, where available, ^{29}Si MAS NMR can establish the relationship between precursor quality, synthesis conditions, mesoscopic order, condensation state, and surface chemistry.

The material may subsequently be explored as a catalyst support, functionalized adsorbent, environmental-remediation medium, host for active nanoparticles, template for ordered carbon, and structural component of silicon/carbon or other hybrid energy materials.

The main scientific challenge is the combination of waste-resource utilization and ordered mesoporous-material engineering, while minimizing the degree of chemical and thermal severity in the synthesis. Future experimental study should be focused on systematic optimization of purification of RHA, formation of COK-12, quantitative structural characterization, catalytic and adsorption tests, electrochemical tests, recovery of templates, Life-cycle assessment and techno-economic analysis. To transform the current proposed framework into a

completely tested experimental materials platform, these investigations are required.

22. References

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