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# Synthesis of Functionalized Silica from Rice Husks Containing C-I End Group

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## Abstract:

In this paper, we have extracted Silica from rice husk ash (RHA) by sodium hydroxide to produce sodium silicate. 3-(chloropropyl)triethoxysilane (CPTES) functionalized with sodium silicate via a sol-gel method in one pot synthesis to prepare RHACCl. Chloro group in compound RHACCl replacement in iodo group to prepere RHACI. The FT-IR clearly showed absorption band of C-I at 580 cm$^{-1}$. Functionalized silica RHACI has high surface area (410 m$^2$/g) and average pore diameter (3.8 nm) within mesoporous range. X-ray diffraction pattern showed that functionalized silica RHACI has amorphous phase .Thermogravemitric analysis (TGA) showed two decomposition stages and SEM morphology of RHACI showed that the particles have irregular shape. Atomic force microscope (AFM) technique was proved that the RHACI has a nanostructure The XPS spectra of I 3d for all the studied surfaces are presented in the peak located at 618.5 eV binding energy was associated with C–I bond.

**Key words:** 3-(chloropropyl)triethoxysilane, Functionalized silica, Iodo group, Replacement, Rice husk ash

## Introduction:

Rice factories produce a large amounts of rice husk ash (RHA). The rice husk ash includes more than 94% of amorphous silica (1). The surface of silica contains two types of functional groups namely the siloxane (Si-O-Si) and silanol (O-H) groups. The prime modification route accrued via reaction of silanol groups on the surface of silica with particular molecule (2). The organic-chloro functionalization of amorphous silica is a significant starting material of synthesis more different of silica which includes a chloro end group can be utilized for immobilizing variety of organic moieties on the silica. RHACCl can also be utilized as a starting material for the synthesis heterogeneous catalyst (3). The silica functionalization with 3-(chloropropyl)triethoxysiloxane (CPTES) has been prepared in a simple method to yield RHACCl (4) and this simple method does not require (toxic reagents ,long time and high refluxing temperature) as previous methods (5). In this article we have replaced the chloro group in functionalization of amorphous silica RHACCl by iodo group to produce functionalization of amorphous silica RHACI.

purity and has been used directly without further purification. This consists sodium iodide (merck 99.9%), 3-(chloropropyl)triethoxysilane (sigma 98%), nitric acid (CDH 70%), sodium hydroxide (BDH 96%), and acetone (Romal 99.7%). The rice husk (RH) has been collected from rice milling in Mashkhab, Najaf, Iraq.

### Origin of Silica

The RH has been selected as an amorphous silica origin, it is obtainable in the exuberance. The silica has been obtained from rice husk as shown in the literature (6).

### Functionalization of RHA with CPTES

Depending on method reported in (4), 3.0g of amorphous silica (extracted from RHA) was stirred with 1.0 M sodium hydroxide in 250 mL in plastic receptacle at room temperature. The sodium silicate created was filtrated to exclude undissolved particles. About 6.0 mL CPTES solution was added to this mixture and titrated against nitric acid (3 M) until the solution reached an acidic pH (pH =3. The suspension allowed to age for two days, then the aged suspension was centrifuged at 4000 rpm for 8 min to obtain the gel. The aforesaid isolation protocol repeated six times to insure a significant yield. The yield was washed with acetone, then dried in oven at 100°C for 24 hrs. Finally, the product was grounded to give white powder labeled as RHACCl.

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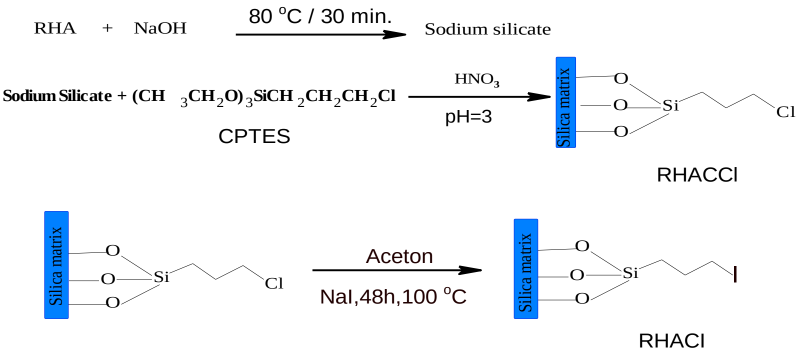
### Iodide-Exchanged Polymers

One gram of RHACCl was mixed with (4g) of sodium iodide in (50) mL of dry acetone. The reaction mixture then refluxed for up to 60 hrs. The solution was then filtered and the solid washed with water, ether, and methanol. Then it was dried under vacuum at 110°C, the product was labeled as RHACI (7). The synthesis of RHACI is shown in Scheme 1.



Scheme 1: Preparation routes of RHACI from RHACCl.

### Sample Characterization

The synthesis RHACI was characterized by FT-IR spectroscopy (Shemadzo-8400s, Japan), elemental analysis (Eager 300 for EA1112), , powder X-ray diffraction (XRD-6000, shimadzu), scanning electron microscope ((EDS)-Hidch su 750, Oxford Instrumental), nitrogen adsorption-desorption isotherm (Nova 2000, quantachrome, USA), (AFM) using CSPM-AA3000, thermal analysis TGA/DTG (TGAQSO, United Kingdom) and X-ray photoelectron spectroscopy XPS by (PECS phoibs 100 analyzer, And SPES X-ray source).

## Result and Discussion:

### Infrared Spectroscopy of Analysis

FT-IR spectrum for RHACI (Fig.1) has been showed the stretching frequency of SiO-H and $H_2O$ adsorbed on the surface of silica at 3553 $cm^{-1}$. The stretching vibration frequency of siloxane (Si-O-Si) in RHACI appeared at 1085 $cm^{-1}$ (8). In a previous study, the stretching vibration frequency of C-Cl appeared at 702 $cm^{-1}$ (4), while the FT-IR spectrum for RHACI shows the appearance of new band at 580 $cm^{-1}$ belong to C-I bond(9). The appearance of this band and disappearance of C-Cl band are good evidence to the presence of C-I bond in the compound RHACI.

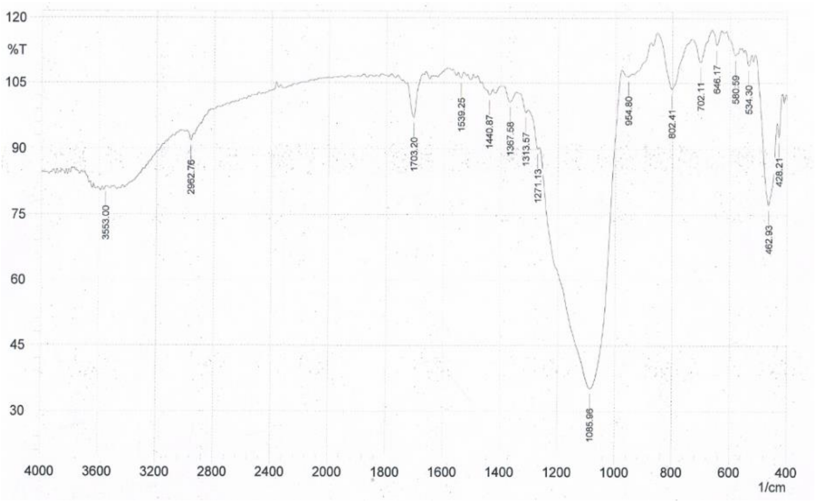


Figure 1. FT-IR spectrum for RHACI

### X-ray Diffraction Pattern

X-ray diffraction pattern of RHACI (Fig. 2) has been showed a broad diffraction band at $2\theta$ angle of ca. 22°. This band indicates amorphous formula of silica in RHACI(10).

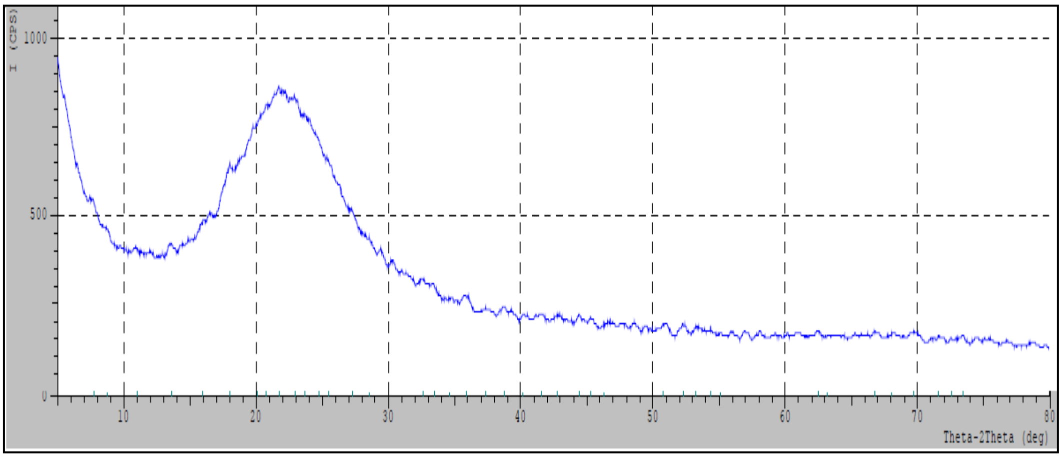


Figure 2. Powder X-ray for RHACI show natural amorphous.

### $N_2$-Nitrogen Adsorption analysis

Figure 3 shows the $N_2$ adsorption desorption for RHACI in addition to the pore size distribution graph. The range of $0.4<p/{}^{\circ}p<1.0$; shows the H1 hysteresis loop (11). The BET of RHACI showed that the specific area was 410 $m^2$/g, while the specific surface area of RHACCl was 633 $m^2$/g (4). Therefore, the decrease in surface area of RHACI is caused by the reduction of surface sites to the replaced a large size iodo species. The RHACI showed narrow pore size ranges between 2.2 -11.7 nm which fall within the mesoporous region. The result obtained by BET $N_2$ adsorption-desorption analysis of RHACCl and RHACI is summarized in Table1.

Table 1. The physical parameters obtained for RHACI and RHACCl

| Sample | Specific surface area $m^2$/g | Average pore diameter (nm) | Average pore volume cc $g^{-1}$ | Ref. |
|---|---|---|---|---|
| RHACCl | 633 | 6.07 | 0.705 | (4) |
| RHACI | 410 | 3.86 | 0.397 | |

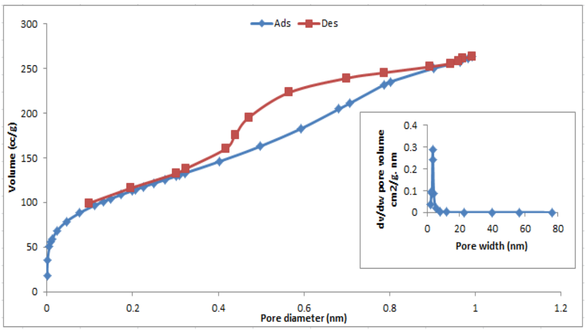


Figure 3. The $N_2$ adsorption-desorption for RHACI.

### The Scanning Electron Microscope (SEM) of RHACI.

The morphology of RHACI has been studied using SEM technique, Fig. 4 shows the morphology of RHACI that has irregular shape and size. The shape of RHACI particles resembles shell shape (12).

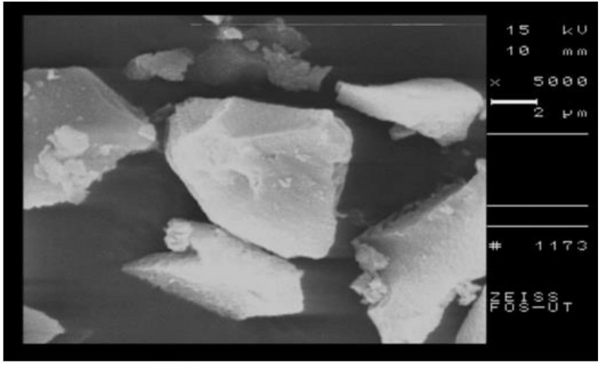


Figure 4. The SEM micrograph of RHACI powder.

### The Atomic Force Microscope (AFM) of RHACI.

The dense packing of the RHACI particles was illustrated by AFM. The shapes of prepared compound are showed that the silica particles were packed tightly three dimensionally in the nanoparticles(13) . The particle sizes for the RHACI is 63 nm as shown by granularity cumulation distribution Fig. 6.

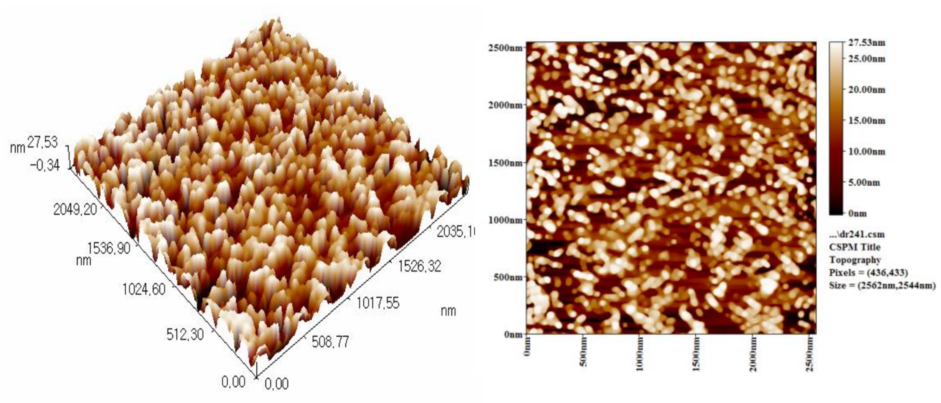


**Figure 5. Three-dimensional AFM images for RHACI.**

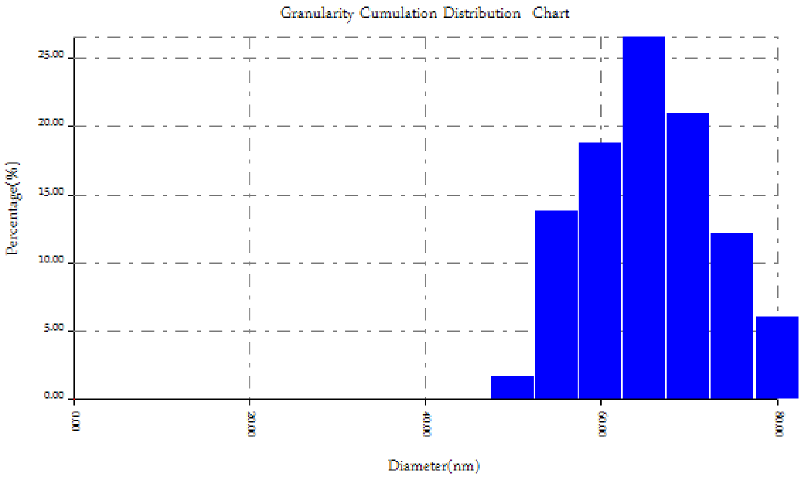


**Figure 6. Granularity normal distribution chart of RHACI**

### Thermal Analyses (TGA)

The thermogravimetric analysis result for RHACI is shown in Fig. 7. The TGA of RHACI showed two character decomposition stages, The first starts between (26.68-130 °C) attributed to the loss of water that adsorbed onto silica surface (ca.2.482%), the second weight loss (ca.28.09%) was between (130-590 °C) assigned to loss of organic moiety (iodopropyl) that incorporated to silica(14).

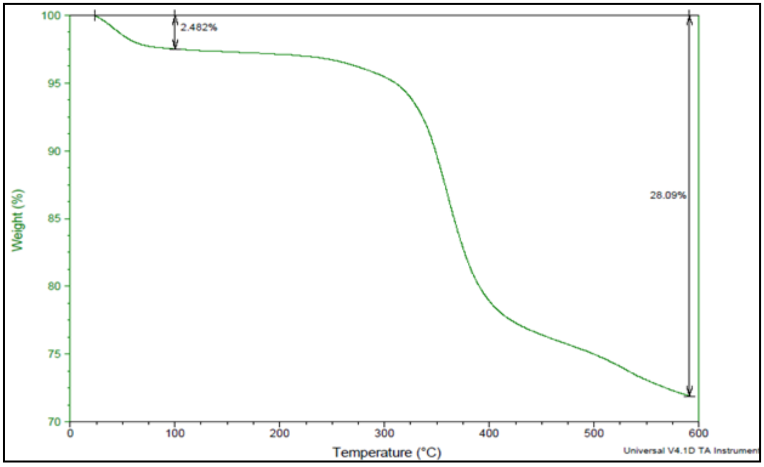


**Figure 7. The thermal analysis TGA of RHACI.**

### X-ray Photoelectron Spectroscopy (XPS)

The composition of elemental in the surface was estimated by XPS. The results in Fig. 8 clearly show that after the RHACCl treatment with iodide, the chloride content decreases 3.3% and the iodide increases 30%. The percent elemental composition for chloride and iodide were studied by dividing the intensity of the elemental line by the sum of the intensities of the elemental lines observed for the specimen(15).

The XPS spectrum of the Si 2p in a peak was found at ca. 101.5 ev binding energy (16). The O 1S BE was found at 531.0 ev for RHACI (17). The XPS spectra of iodide(I 3d) for all the studied surfaces are presented in the peaks located at 618.5 eV and 630 eV binding energies are associated with C–I and Na-I bonds, respectively (18). The XPS spectrum of the C 1s in peak at ca. 284 ev is associated to C-Si and C-H (19). The XPS also appears a peak at 199 ev is associated to Cl 2p that is a residue from replacement process or that not replacement in CPTES . Then XPS has also indicated peak at ca. 1070 ev linked with of Na is species, the existence of Na is due to the replacement operation of the chloro group by iodide group (20). It can be clearly seen in Figure 6 that there is (Cl) group content in RHACI that is very small compared with high concentration of iodide group. The XPS produces good evidence to successful replacement process to form RHACI.

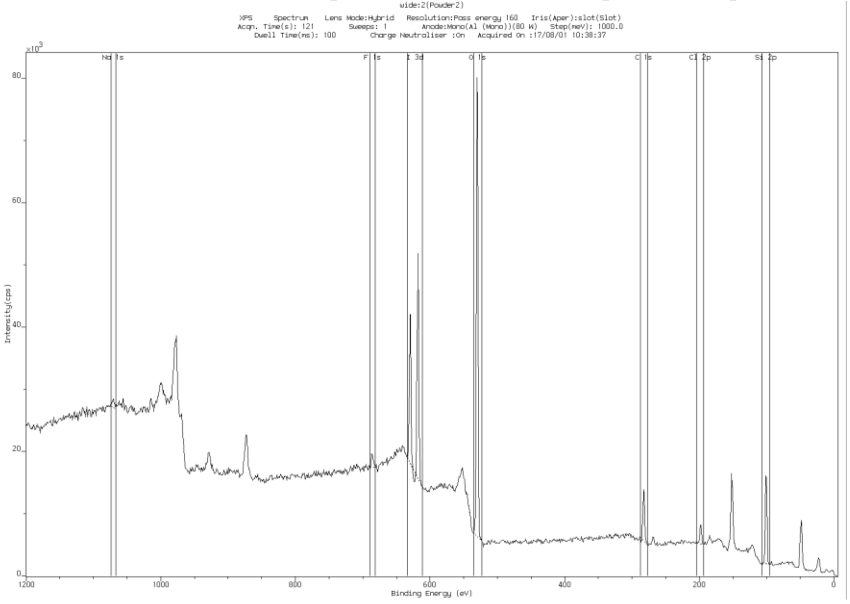


Figure 8. XPS spectrum of RHACI the C, O, Si, Cl and I content shown

## Conclusion:

In the present work, we depended on a method used to functionalize silica extracted from rice husk ash with CPTES using a low-cost, and environment-friendly method. In this method, the rice husk was used to prepare silica immobilized with CPTES to prepare RHACCl . The second step replacement functional group (chloro group) in organic part of RHACCl was done by iodo group to form RHACI. The spectral measurements used in this study showed that the CPTES had been immobilized into sodium silicate and replacement chloro with iodo group occurred. We believe the procedure offered here is the most simplified route to the modification replacement of chloro group with iodo group it synthesis RHACI. We currently study the immobilized of advantageous ligand onto RHACI which could be important and easier than RHACCl in chemical syntheses especially in synthesis of catalyst.

## Acknowledgments

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# تحضير سليكا وضيفيه من قشور الارز تحتوي على مجموعة نهائيةC-I

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## الخلاصة

في هذا البحث، قمنا باستخلاص السليكا من رماد قشرة الأرز (RHA) بواسطة هيدروكسيد الصوديوم لإنتاج سيليكات الصوديوم. سيليكات الصوديوم عوملت مع 3- (كلورو بروبيل)ثلاثي اوكسي سلين عن طريق تقنية sol-gel بسيطة لتحضير RHACCl الحاوي على مجموعة الكلورو .قمنا باستبدال مجموعة الكلورو بمجموعة ايدو لتحضير RHACI .أظهرت نتائج FT-IR بوضوح حزمة امتصاص C-I عند 580 سم $^{-1}$. السليكا الوضيفية RHACI لديها مساحة عالية (410 م $^2$ / جم) ومتوسط قطر المسام (3.8 نانومتر) والذي هو ضمن نطاق mesoporous.أظهر نمط حيود أشعة إكس أن RHACI ذو طبيعة غير متبلورة. أظهر التحليل الحراري (TGA) مرحلتين للتحلل، اما مورفولوجيا SEM لـ RHACI أظهر أن الجسيمات لها شكل غير منتظم. أثبتت تقنية مجهر القوة الذرية (AFM) أن RHACI لها بنية نانوية. اظهرت نتائج أطياف XPS لـ I 3d انها تقع عند طاقة ربط 618.5 اكترون فولت.

**الكلمات المفتاحية**: 3- (كلورو بروبيل)ثلاثي اوكسي سلين ، السليكا الوظيفية، مجموعة الايدو، استبدال، رماد قشر الأرز