

Generation of Ultra-Pure Hydrogen Gas Utilizing Nanoporous Silicon Technology

Dina Bashir

Alexandria University

Marwa Nabil

marwamoh2000@yahoo.com

City for Scientific Research and Technological Applications (SRTA-City)

Rafeek Baseily

Alexandria University

Morsy Abo-Yossef

Alexandria University

Abd El-Hady

City for Scientific Research and Technological Applications (SRTA-City)

Research Article

Keywords: Ultra-Pure hydrogen, Nanoporous silicon (NPS), wet alkali chemical etching process

Posted Date: October 29th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11012714/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Generation of Ultra-Pure Hydrogen Gas Utilizing Nanoporous Silicon Technology

Dina Bashir¹, Marwa Nabil^{2, *}, Rafeek Baseily¹, Morsy Abo-Yossef¹, Abd El-Hady Kashyout²

¹Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

²Advanced Technology and New Materials Research Institute, City for Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City, Alexandria, 21934, Egypt

*E-mail: marwamoh2000@yahoo.com

Abstract

Hydrogen energy is considered a renewable energy source as well as a future fuel choice. Nanoporous-silicon (NPS) is needed in many fields such as sensors, optoelectronics, drugs and hydrogen production. This study aims to produce ultra-pure hydrogen gas and (NPS-powder) from Si-powder processing at different KOH %weights as a base medium and different n-propanol % volumes as a wetting agent. Alkaline etching of Si-powder to produce (NPS) is also considered a source of H₂-production. The results show the high purity of H₂ gas (99.99%) produced through this process.

The method provides for generating H₂ gas at room temperature from commercial Si-powder is processing, without using any source of energy and at a stable, high generation rate (≈ 1 L / 20 min). XRD results confirmed the formation of (NPS), its particle size ranged (from 0.05 to 4.00 μ m). In addition, TEM measurements indicated the existence of a nano-ribbon structure with the polycrystalline nature of (NPS).

Keywords: Ultra-Pure hydrogen, Nanoporous silicon (NPS), wet alkali chemical etching process

1. Introduction

In many countries, hydrogen (H₂) is considered an important carrier of alternative energy and a promising path towards the future of sustainable energy. [1]. It isn't a primary source of energy that is freely found in nature, but it's a subsidiary form of energy which must be produced, such as electricity [2]. The primary energy sources can produce H₂ via various production technologies. [3]. The thermo-catalytic technique produces about half of all the H₂ production [4]; natural gas is the starting material in the gasification processes [5]; heavy oils and naphtha occupy the second largest source, then coal; in addition to the water splitting process [6]. Hydrogen production is a crucial factor in determining whether it meets the standards. Various sources can produce Hydrogen, such as water, biomass, boron hydrides, hydrocarbon fuels, hydrogen sulfide, and chemical elements containing hydrogen [7]. H₂ gas can be obtained during the synthesis of nanoporous silicon (NPS) powder process, which is a material widely used in various applications in several fields such as optics, energy photovoltaics, chemistry and biology. Here, we developed a zero-electricity electrolytic technology that converts a variety of waste gases into sustainable hydrogen. NPS has many properties such as compatibility with silicon-based microelectronics, low-cost, large surface area within a small volume that is compatible for H₂ gas production applications. In previous studies, the NPS synthesis is usually formed by anodizing a silicon wafer in hydrofluoric (HF) solution or a chemical acidic stain etching technique [8]. H₂ gas can be obtained during the stain etching of Si powder to produce nanoporous silicon (NPS). There are some advantages to extracting hydrogen from water environments in the presence of a small amount of NH₃, which are tenability and safety, in addition to the possibility to characterize NPS as a hydrogen source material in terms of hydrogen-effective shell and crystalline core conception [9].

This aims to produce ultra-pure hydrogen gas (99.99%) through the alkali chemical etching process using potassium hydroxide (KOH) and n-propanol (as a wetting agent) at room temperature with a high generation rate (≈ 1 L / 20 min) and high stability. This methodology is one of the promising techniques for the dual production of nanoporous-silicon (NPS) powder and ultra-pure H_2 gas (as shown in Table A.1), with respect to its low cost, simplicity, safety and zero energy consumption.

Table A.1: Comparison between previous studies and our current research.

Etching System / Composition	Si Nanostructure Achieved	Hydrogen Yield / Rate	Reaction Conditions	Fundamental Novelty / Mechanism	Ref.
Pure Aqueous KOH (High conc.)	Macroscopic dissolution / Coarse pyramids	High initial rate, rapid decay	High temp. $>80^\circ\text{C}$	Sacrificial Si consumption; no controllable nanoporosity.	[10]
Metal-Assisted Chemical Etching (MACE)	Nanowires / Nanopores	Extremely low / Negligible	Room temp., hazardous reagents	Focuses entirely on morphology; H_2 is trapped or minimized.	[11]
Electrochemical Etching {HF} {Ethanol}	High-quality Nanopores	Low / Intermittent	Requires external bias / electrical power	Driven by external current; scaling up is complex.	[12]
This Work (Optimized KOH/NPA)	Uniform Nanoporous Silicon (NPS)	High, sustained yield $0.0071\text{ L g}^{-1}\text{ min}^{-1}$	Mild/Room temp., single-step, no bias	NPA modulates kinetics, balances surface passivation and localized etching, enabling dual-functional synthesis.	Current Work

2. Materials & Methods

2.1. Setup

The developed technique combines both ultrasonication and alkaline chemical etching (wet technique) [13]. Si-powder as a precursor (silicon, Pulver-99%, 7 grams) was spread in a solution that carried different concentrations of potassium hydroxide {6, 7, and 8 wt % KOH}, and various concentrations of n-propanol {15, 20, and 25 Vol% NPA}; (as presented in Table 1) as a solution in ultrapure water (18 M Ω deionized water). So, the glass vessel was exposed to the ultrasonication waves for different times (30, 60, 90, 120, 150, 180 and 270 min), washing the produced nano-powders by using distilled water, and then drying them at 40°C (overnight) [13]. The system for the production of NPS and H_2 gas is shown in Fig. A.1.

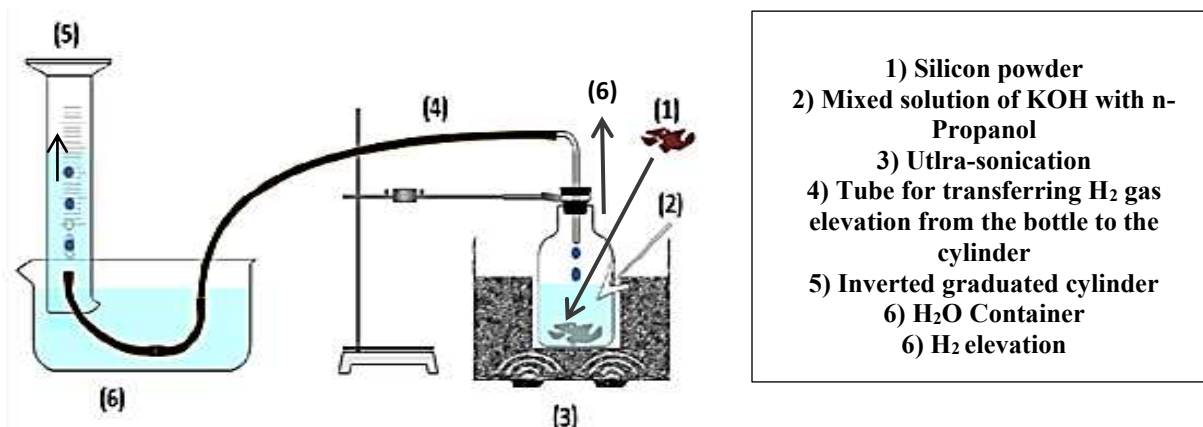


Fig. A.1. Schematic diagram for the production of NPS powders and H₂ gas evolution

2.2. Characterization of NPS powder product

The structure and crystallization of the NPS powder product are characterized by XRD (X-ray Ultra diffractometer, using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) at a scanning rate of 4° min^{-1} , 7000 Shimadzu diffractometer). In addition, the crystalline size of NPS is calculated using the XRD spectra through the Scherrer equation. The composition of the deposited powders is explored elementarily by JEOL-5300 scanning electron microscope embedded with EDAX microanalysis. An accelerating voltage of 20 kV was used. FTIR (Fourier Transform Infrared Spectrophotometer, Shimadzu- 8400s, Japan) and Raman Spectroscopy (Senterral, Bruker Raman micro-spectroscopy, at an excitation wavelength of 330 cm^{-1}) are used to record the chemical bonds of the NPS powder synthesis process. Raman spectroscopy (Senterral Bruker, Raman micro spectroscopy), with an excitation wavelength value of 514.5 cm^{-1} ; the used spectral range is $100 - 4000 \text{ cm}^{-1}$. The NPS powder morphology is inspected using SEM {Scanning electron microscopy, JEOL (JSM 5300), magnification (1000–30000), at an accelerating voltage of 20 kV} SEM is used for the determination of the shape, structure and size of NPS powder. JEOL- JEM-2100F is a FE (field emission) analytical electron microscope that provides the arrangement structure of sample atoms at the crystal arrays. The lattice image resolution was about 0.1 nm (ultra-high resolution). The point image reached about 0.19 nm, with an acceleration voltage range of 80-200 kV and magnification of 2,000-1,500,000.

The UV light spectrum (at wavelength 365 nm), in addition to Photoluminescence spectra (PL), is measured using the FP-8600 spectro-fluorometer (FP-8600), which uses a sensitive PMT to collect data from the UV region to the NIR region. The excitation wavelength ranges are (200- 850 nm) and also up to 1010 nm for fluorescence emission.

2.3. Characterization of the elevated Hydrogen gas product

H₂ gas volume is determined using the water displacement technique [14], as shown in Figure 1. The impurity of the product (elevated H₂) is determined by GC mass chromatography. Also, the amount of residue obtained, such as (CO, CO₂ and CH₄) is determined via an Agilent 6890N Network Gas Chromatograph. It is used to characterize the percentage of hydrocarbon (CO, CO₂ & CH₄), and H₂ gases. The range of suitable operating temperatures for all columns and chromatographic separations is $4 - 450^\circ \text{C}$. In addition, pressure is adjusted by increments of 0.01 psi.

3. Results & discussion

The main objective of this work is to achieve a high degree of hydrogen gas purity through the processing of NPS powder via chemical reaction from the commercial silicon powder. In the following sub-sections, the effect of changing concentrations of both KOH and n-propanol will be evaluated through the amount of hydrogen produced using both quantitative and qualitative analysis.

3.1. Characterization of Nanoporous Silicon (NPS) powders

3.1.1. X-ray Diffraction (XRD)

Fig. A.2 shows the XRD patterns for crystalline NPS powder with respect to the impact of different alkaline etchant (KOH) concentrations and the wetting agent (n-propanol; NPA) concentrations. The changes in peak intensity and position show the silicon (nc-Si) size and its concentration, which are obtained using alkaline etching and ultrasonic processing techniques to produce NPS powder [15]. The polycrystalline NPS powder is formed at etching conditions (alkaline etchant) $\text{KOH}_{\text{conc.}} = 6, 7, \text{ and } 8 \text{ wt } \%$, in addition, (wetting agent) $\text{NPA}_{\text{conc.}} = 15, 20, \text{ and } 25 \text{ Vol } \%$. The diagram of planes; peaks are around $2\theta = 28.23^\circ, 47.193^\circ, 56.023^\circ, 68.989^\circ, \text{ and } 76.2396^\circ$ that show nano-crystalline silicon planes $\{(111), (220), (311), (400), \text{ and } (312)\}$, correspondingly (JCPDS Card No. 01-079-0613 and 00-027-1402) [16].

For the calculation of the average size of the crystalline nc-Si, the full width at half maximum (FWHM) of all atoms is used, such as the Scherrer equation [17]. It may be differentiated because of the wet alkali chemical etching technique conditions via the etchant solution (alkaline etchant and wetting agent) concentrations. Scherrer equation can be used for the calculation of the crystal size value.

$$D = \frac{K\lambda}{B \cos \theta} \quad \text{Eq. (A.1)}$$

At D (nm): the crystallite size, $k = (0.9 \text{ as Scherrer's constant})$, λ (nm) = 0.15406 as the wavelength of radiation used (CuK α in this case), β (radians): the full width at half maximum intensity of the diffraction peaks (FWHM), θ (radians): the diffraction angle of the concerned diffraction peak.

XRD patterns of the polycrystalline NPS powder at different wetting agent concentrations (15, 20, and 25 Vol% n-propanol) are presented in Fig. A. 2, in addition to Table A.2. The peaks are in good agreement with the joint committee on powder diffraction (JCPDS Card No. 01-079-0613 and 00-027-1402) data. The corresponding reflecting planes are (111), (220), (311), (400), (331), (422) and (511), respectively. The NPS powder product's average crystallite size values are influenced by the difference between the alkaline etchant concentration (wt% KOH) and the wetting agent concentration (Vol% NPA).

As shown in Fig. A.2.a, in samples 1, 2, and 3, the highest value of (FWHM) corresponds to the plane (111) that is followed by planes (220), (311), and (422). There is a direct proportional relationship between the concentration (Vol% NPA) and the value of crystalline size of polycrystalline NPS powder at (8 wt% KOH). On the other hand, Fig. A.2.b shows data of samples 4, 5, and 6 that have the same order of (FWHM) values with respect to the peak intensity values. But, there is a slight difference in that some of the peaks have equal intensities, as a result of the different value of KOH_{conc} (7 wt% KOH). Also, the smallest crystallite size of NPS powder is recorded at (25 Vol% NPA), and there isn't a regular relationship between the (Vol% NPA) and the value of crystallite size of polycrystalline NPS powder as shown in the previous one. Fig. A.2.c presents the highest value of (FWHM) that corresponds to the plane (111); however, there is a good equality of (FWHM) values of planes (220) and (311). At (6 wt% KOH), the smallest crystallite size of the NPS powder is recorded at (25 Vol% NPA), with a value of 23 nm.

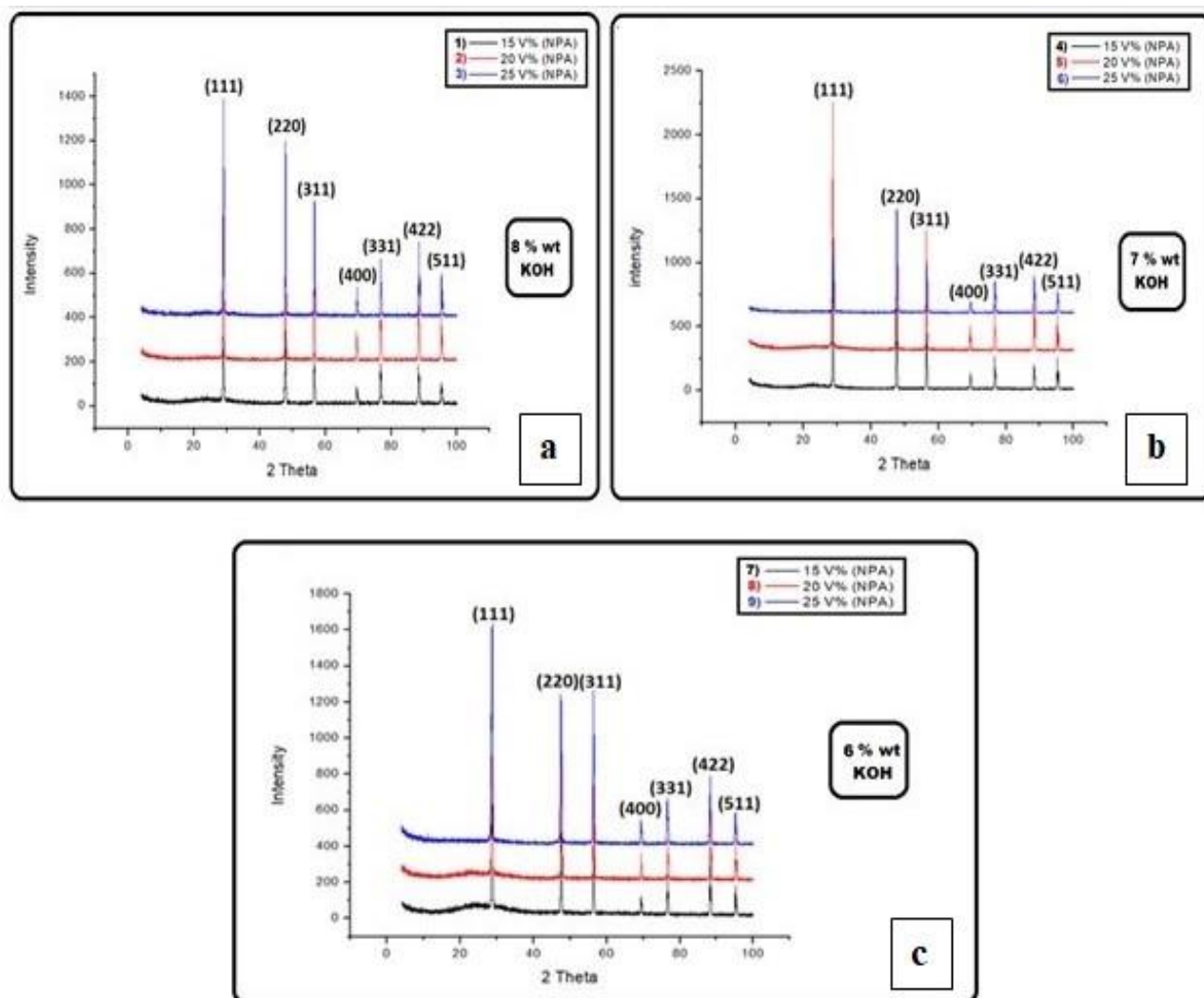


Fig. A.2 : XRD spectra of various polycrystalline NPS powder at different (Vol% NPA); a) at 8wt% KOH, b) at 7wt% KOH, and c) at 6wt% KOH

Table A.2: Standard values of the polycrystalline NPS-powders, XRD diffraction peaks obtained by different wet alkali chemical etching conditions and crystallite size

Sample number	Wt% KOH	Vol% NPA	Diffraction peaks (2θ)°							Crystallite size (nm)
			planes							
			(111)	(220)	(311)	(400)	(331)	(422)	(511)	
1	8	15	29	47.88	56.66	69.65	76.88	88.50	95.38	23
2		20								25
3		25								29.3
4	7	15	28.6	47.7	56.54	69.5	76.7	88.3	95.2	29.5
5		20								39.7
6		25								24.6
7	6	15	28.6	47.5	56.54	69.3	76.6	88.3	95.2	30.1
8		20								31.4
9		25								26

3.1.2. Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared absorption analysis reveals information on powders' surface chemistry and how it is changed as a function of the alkaline etchant and wetting agent concentrations. The FTIR spectrum of the silicon powder after alkali chemical etching is depicted in Fig. A.3. FTIR spectrum of NPS powder shows a clear spectrum of bands in the region (1000–1300) cm^{-1} , which is assigned to Si–O asymmetric stretching at various concentrations of the mixture of etchants. The stretching and bending of the Si-(O₂Si₂), Si-(O₃Si) and Si-(O₄) are noticed in band range 450 - 470 cm^{-1} . The broadband of 3000 to 3750 cm^{-1} correlates with O-H expansion patterns in SiOH and H₂O assemblies in addition, the frequency range 2000-2300 cm^{-1} is due to the presence of the Si-H group. [18-21]

As shown in Table A.3 and Fig. A.3.a, samples 1, 2 and 3 show the FTIR spectra of NPS powders at 8 wt% KOH and various values of NPA concentrations (as 15, 20, and 25 Vol% NPA), respectively. It shows an abroad band at around 3400 cm^{-1} that is attributed to ν (OH) in O–H stretching bands of Si–OH groups, i.e. 3700–3200 cm^{-1} [21]. The FTIR stretching band for ν (Si-H_x) appears around 2340 cm^{-1} for NPS. Also, that's the agreement of the presence of rocking motion of the O atom, which is perpendicular to the Si–O–Si plane, as shown in figure 3.a.the Si-H group is identified by a band in the range 2280-2080 cm^{-1} ; it's the exact position band which is very sensitive to the electronegativity of the groups attached to the silicon [24]. In addition to symmetric vibration bands, ν_s (Si-O₂) and ν_{as} (Si-O₂) bands in the region 1945 cm^{-1} [23], and an asymmetric stretching band at 1079 cm^{-1} . So, the FTIR band attributed to ν_s (Si-O₂) of NPS is in red shift and appears in the range 1640- 1655 cm^{-1} . But, the FTIR spectrum for ν_{as} (Si-O₂) band is in blue shift and appears around 1080 cm^{-1} , representing the δ (O-Si-O) stretching vibration [24]. The FTIR bands at 457, 461 and 463 cm^{-1} for NPS samples, 1, 2 and 3, respectively, are attributed to the rocking motion of the O atom, which is perpendicular to the Si–O–Si plane [25].

Fig. A.3.b presents the FTIR spectrum of NPS samples 4, 5, and 6 at 7 wt% KOH and different V% NPA concentration values and is shown in Table A.2. The broad band ν (OH) in the (O–H) stretching band of the Si–OH group appears in the same regions in Fig. A.3.a. The FTIR stretching band for ν (Si-H_x) appears at 2343.6 and 2347.5 cm^{-1} for NPS samples 4 and 5, respectively. It disappears in sample 6 in the FTIR spectra. Also, the FTIR band attributed to ν_s (Si-O₂) for NPS is in a red shift. On the other hand, the ν_{as} (Si-O₂) band makes a blue shift and

appears at 1084 and 1086 cm^{-1} for NPS samples 4 and 6, respectively. The FTIR bands at 794.7, 788.9 and 773.5 cm^{-1} for NPS (samples 4, 5 and 6) represent the δ (O-Si-O) stretching vibration [24].

Fig. A.3.c shows FTIR spectrum of NPS powder with 6 wt% KOH and 25, 20 & 15 Vol% NPA, “7, 8 & 9”, has abroad bands at 3458.5, 3441 & 3443 cm^{-1} , respectively which is attributed to $\nu(\text{OH})$, where the O–H stretching bands of Si–OH groups appear in the same region as alcohols, i.e. 3700–3200 cm^{-1} [25]. The IR stretching band for $\nu(\text{Si-H}_x)$ appears at 2345.5, 2253 and 2355 for samples “7, 8 and 9”, respectively. The Si-H group is characterized by a spectral band in the 2280–2080 cm^{-1} range. There is no interference from other spectral bands in this part of the spectrum. The precise location of this band is strongly influenced by the electronegativity of the silicon-bound groups [27]. $\nu_s(\text{Si-O}_2)$ and $\nu_{as}(\text{Si-O}_2)$ bands, respectively, where it exhibits two absorption IR bands, a symmetric vibration in the region 1945 cm^{-1} [28] and an asymmetric stretching band around 1079 cm^{-1} [29]. So, the IR band attributed to $\nu_s(\text{Si-O}_2)$ for NPS samples 7, 8 & 9 is red-shift and appears at 1658.8, 1653 and 1662.7 cm^{-1} respectively. While FTIR spectrum for $\nu_{as}(\text{Si-O}_2)$ bands makes a blue shift and appears at 1084, and 1084 cm^{-1} for NPS powder 7 and 9 respectively. But it makes a little red-shift in sample 8 at 1076 cm^{-1} . The band at 785, 763.8 and 763.8 cm^{-1} for NPS 7, 8 and 9 represents the δ (O-Si-O) stretching vibration. The IR bands at 457 and 428 cm^{-1} for NPS 7 and 8 are respectively attributed to the rocking motion of the O atom which is perpendicular to the Si–O–Si plane [30]. But, this band disappears at NPS sample 9.

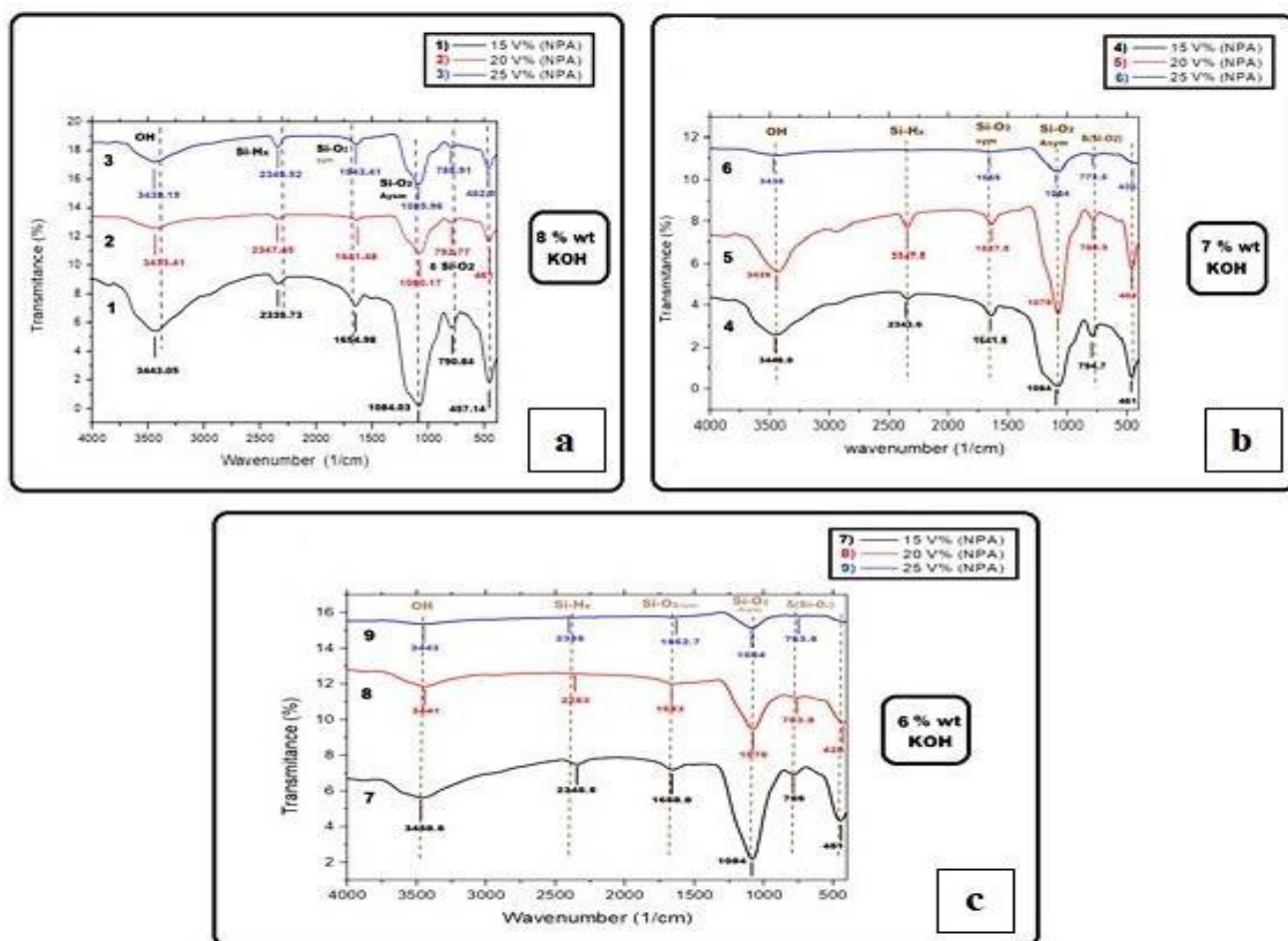


Fig. A.3 : FTIR spectra of various polycrystalline NPS powder at different (Vol% NPA); a) at 8wt% KOH, b) at 7wt% KOH, and c) at 6wt% KOH

Table A.3: By using various wet alkali chemical etching conditions, the FTIR spectrum bands of the polycrystalline NPS-powders are obtained.

Number of sample	ν (O-H) (cm ⁻¹)	ν (Si-H _x) (cm ⁻¹)	ν_s (Si-O ₂) (cm ⁻¹)	ν_{as} (Si-O ₂) (cm ⁻¹)	δ (O-Si-O) (cm ⁻¹)	rocking motions [O atom] (cm ⁻¹)
1	3443.05	2339.73 (s)	1654.98	1084.03 (strong)	790.84	457.14
2	3433.41	2347.45 (s)	1641.48	1080.17	792.77	461.00
3	3439.19	2345.52 (m)	1643.41	1085.96	788.91	462.93
4	3448.84	2343.59	1641.48	1084.03	794.70	461.00
5	3435.34	2347.45	1637.62	1078.24	788.91	461.00
6	3435.34	-----	1654.98	1084.03	773.48	426.28
7	3458.48	2345.52	1658.84	1084.03	785.05	451.36
8	3441.12	2253.00	1653.05	1076.32	763.8	428.21
9	3443.05	2355.00	1662.69	1084.03	763.84	-----

3.1.3. Raman Spectroscopy

Fig. A.4.a shows the Raman spectrum of sample 2, that shows five peaks at the KOH concentration (8 wt %) and (20 Vol % of NPA). Each peak corresponds to a transition of electrons between energy levels, as follows: band (a) shows sharp peak as the highest Raman intensity with red-shifted to 504.3 cm⁻¹ with respect to the peak obtained from commercial silicon powder. Also, band (b) is detected at 922.7 cm⁻¹ which is due to 2T0 overtones that are completely in agreement with the existing literature [28]. In addition, peaks (c and d) at 291.8 and 230 cm⁻¹. And, peak (e) which is at 72.9 cm⁻¹.

While the Raman spectra of sample 6 (NPS) shown in Fig. A.4.b present four peaks, which has some differentiate than the existing literature. The red-shifting of peak (a) is recorded at 514.8 cm⁻¹. Peaks (b, c, and d) appear at (940, 966, and 295.8 cm⁻¹), respectively. On the other hand, Fig. A.4.c shows the Raman spectrum of NPS powder, sample 7. Band (a) is red-shifted and broadened relative to 519.5 cm⁻¹ sharp line compared with the spectrum obtained from commercial silicon powder. The second band, (b), appear at 947.5 cm⁻¹ which corresponding to 2nd order TO phonon (NPS) [32]. And band (c) appears at 306 cm⁻¹ due to 2TA phonon [33].

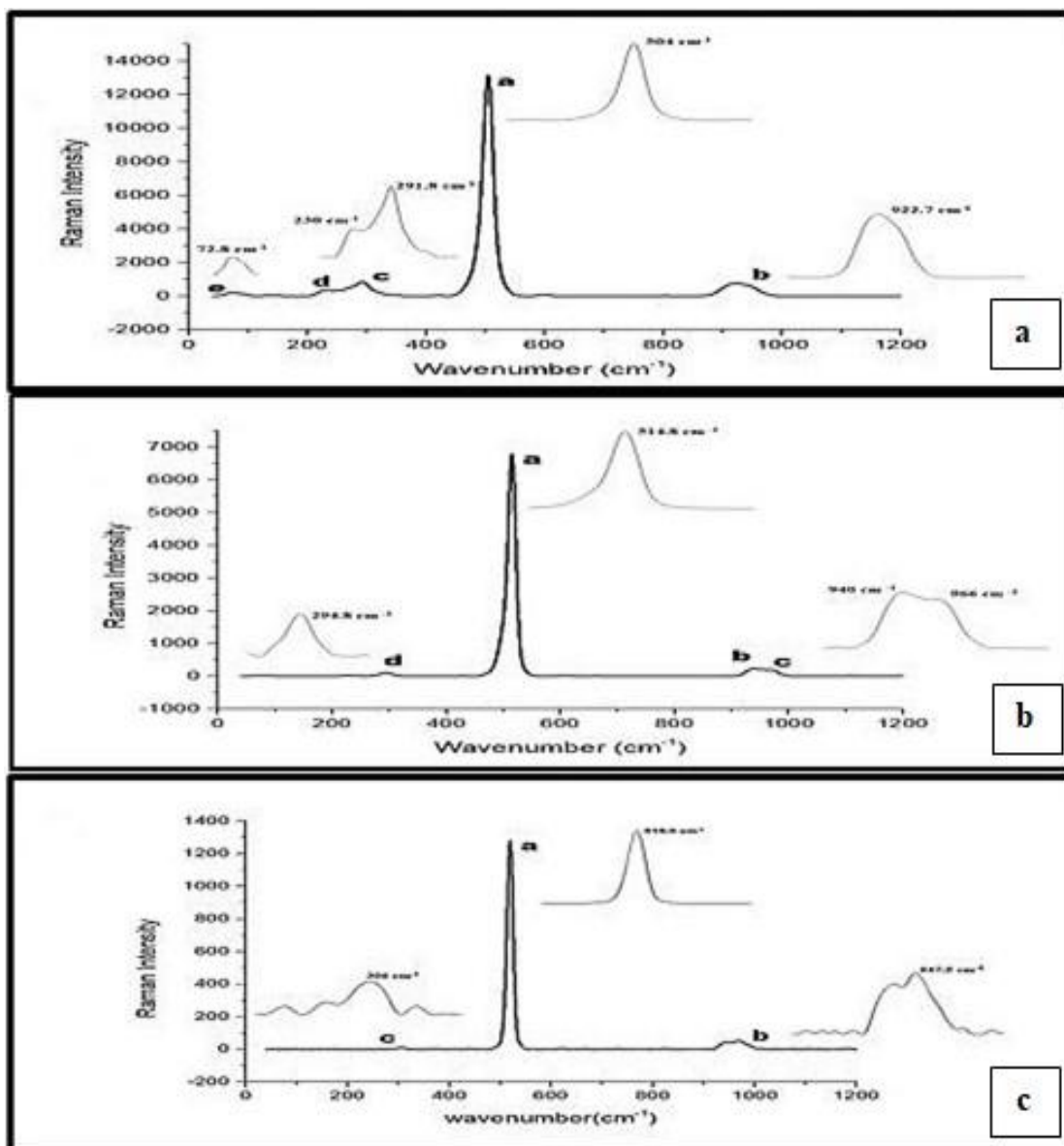


Fig. A.4. Raman Spectra of; a) NPS powder sample 2; 8 wt % KOH, 20 Vol % NPA, b) sample 6; 7 wt % KOH, 25 Vol % NPA, and c) sample 7; 6 wt % KOH and 15 Vol % NPA at etching time 180 min.

3.1.4. UV Emission lamp & Photoluminescence Spectroscopy (PL)

The photoluminescence (PL) of nanoporous silicon (NPS) has been extensively studied and many models of its mechanism have been proposed, but to date the photoluminescence mechanism of PS remains controversial. Some groups have observed the blue and even violet light emission from oxidized NPS (OPS), and suggested that it originated from the Si oxide in NPS [34]. Fig. A.5 shows the violet light UV lamp emission for NPS powders with different concentrations of KOH and different concentrations of n-propanol wetting agent. The samples 2 and 7 show similar behavior of UV emission, while sample 6 (Fig. A.5.b) shows a different color of light purple. This may be attributed to the NPS (PL spectra) obtained by PL spectroscopy system, [Model FP-8600 in the range (200 -1010 nm)], also the value of energy gap is obtained via Eq. (A.2) [35].

$$E_g = hv / \lambda$$

$$\text{Eq. (A.2)}$$

Where, E_g (eV) is the optical energy gap, h (joules. sec) equal to 6.626×10^{-34} which is Planck's constant, v (m/sec) is equal to 2.99×10^8 m/sec, velocity of light, λ (nm) is the wavelength of absorption peak value

The optical properties of NPS were further studied using photoluminescence spectroscopy. Photoluminescence spectra show a single broad band that is similar to a Gaussian curve-like shape [36]. Fig.6 shows the NPS photoluminescence spectra etched at various concentrations of KOH and NPA. The NPS can illuminate visible violet PL range with a peak wavelength that falls in (319-320) nanometers. This effect is due to the surface types and the quantum confinement effect that develops on porous nanoparticles during the etching process. [37]. The PL intensities are nearly similar with different wt % KOH concentrations and different V % (NPA). This result can be attributed to the same porosity and total surface area of all NPS powders. By comparison the impact of KOH and NPA concentrations of samples 2 and 6, respectively; at Table A.4, etched NPS has a broader PL peak centered at 319 nm as shown in Fig. A.6.a and b, as compared to the other concentrations of sample 5, that have the PL peak a little redshift to higher wavelength at 320 nm (Fig. A.6.c). The values of energy gap for NPS powders specified via equation (A.3) lie between the regions of 3.89 eV to 3.87 eV that is more than the standard value for p-type silicon (1.11 eV). Also, the gap range can be attributed to quantitative confinement [38].

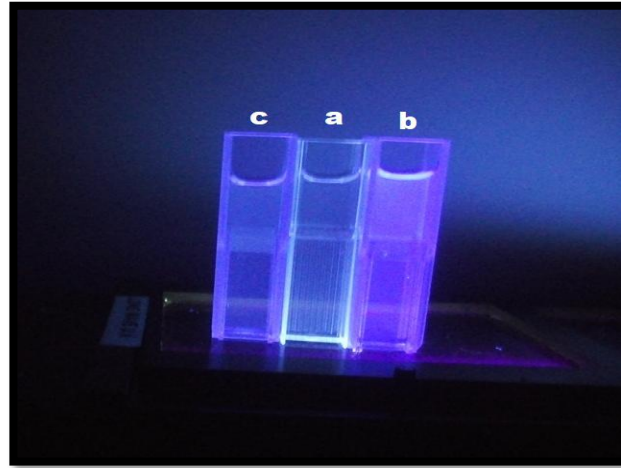


Fig. A.5 . UV lamp emission for NPS powders at different concentrations of KOH and NPA; a) sample 2, b) sample 6, and c) sample 7.

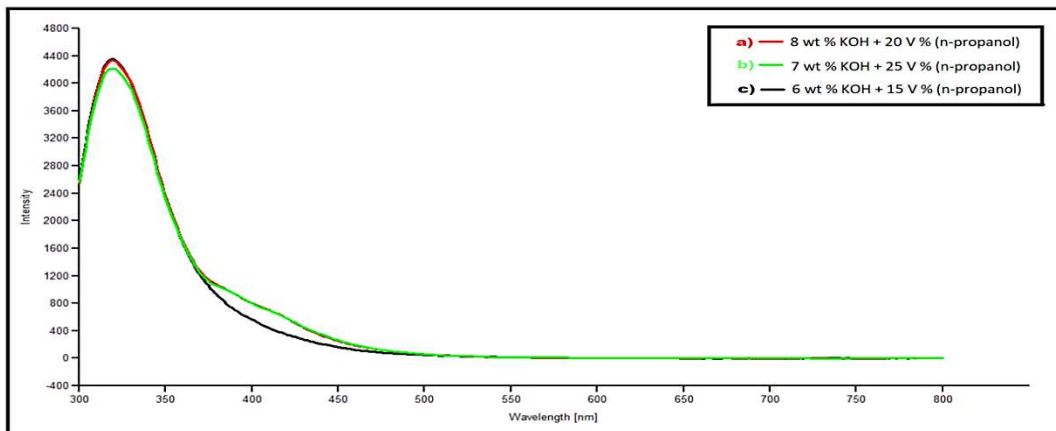


Fig. A.6. PL intensity for NPS powders; a) sample 2, b) sample 6, and c) sample 7.

Table A.4 tabulates all the values of PL peak intensity, wavelength, and energy gap values that are determined for the NPS powders etched via various concentrations of KOH and various NPA concentrations as the wetting agent.

Table A.4 The Peak intensity, PL peak wavelength and energy gap values determined for the production of NPS via various wt % KOH and Vol% (n-propanol) concentrations.

Sample number	NPS powder	KOH (wt %)	NPA (Vol %)	PL Peak Wavelength (nm)	PL peak intensity (a.u)	Energy gap (eV)
2	a	8	20	319	4331	3.89
6	b	7	25	319	4214	3.89
7	c	6	15	320	4352	3.87

Then, this enhanced charge separation mechanism is further supported by the PL and FTIR results. The surface states identified via PL serve as intermediate energy levels that efficiently trap photo- or chemically-excited electrons, suppressing recombination. As verified by the FTIR functional group analysis, these active surface sites promote strong chemical binding with the alkaline etchant, ensuring rapid interfacial charge transfer and accelerating the reduction process to yield higher H₂ output.

3.1.5. Scanning Electron Microscope (SEM)

Fig. A.7 shows the morphology of the synthesized NPS powder samples (1, 2, and 3) at different etching conditions with various n-propanol concentrations (15, 20, and 25 Vol% NPA), respectively. The used sonication time is 180 min. It shows the etched silicon powder surface, where some nearly uniform cracks are observed throughout the sample at lower magnification. At higher magnification small nanopores are observed. Fig. A.7.a and a' shows the layer thickness of sample 1 is in the range (0.05 -0.07 μm) and the pore size (70-100 nm). The pore size is directly proportional with the wetting agent concentration as shown in Fig. A.7.b, and b'. The pore size value in sample 2 is in the range (400-900 nm). But, Fig. A.7. c and c' show the morphology of sample 3, which has the largest value of the layer thickness (2.32 - 4.00 μm) and the smallest pore size (40-60 nm). The uniform cracklings are in some places on the edge surface due to the anisotropic etching process of NPS powder using NPA as a wetting agent at drying the samples in air. In addition, Fig. A.8 shows the morphology of synthesized NPS powder samples (4, 5, and 6). The layer thickness is in the range (1.42 to 3.94 μm) and the pore size values are in the range (40 to 80 nm).

Fig. A.9 shows the morphology of synthesized NPS powder samples (7, and 8). The layer thickness of sample 7 is in the range (1.21 -1.27 μm) and the pore size value is in the range (40- 50 nm) as shown in Fig. A.9. a, a'. On the other hand, the value of the layer thickness is inversely proportional with the NPA concentrations. As shown in Fig. A.9. b, b', layer thickness is in the range (0.05 -0.08 μm) and pore size (60-70 nm).

The micro-pores of NPS are filled by an alkaline etchant (KOH), so the surface tension is increased and capillary stresses are formed that cause uniform cracking [39]. The shape morphology is changed due to changing the alkaline etchant concentration. The rod arrays are formed at (7 wt% KOH), and NPS sheets are formed at (6 wt% KOH).

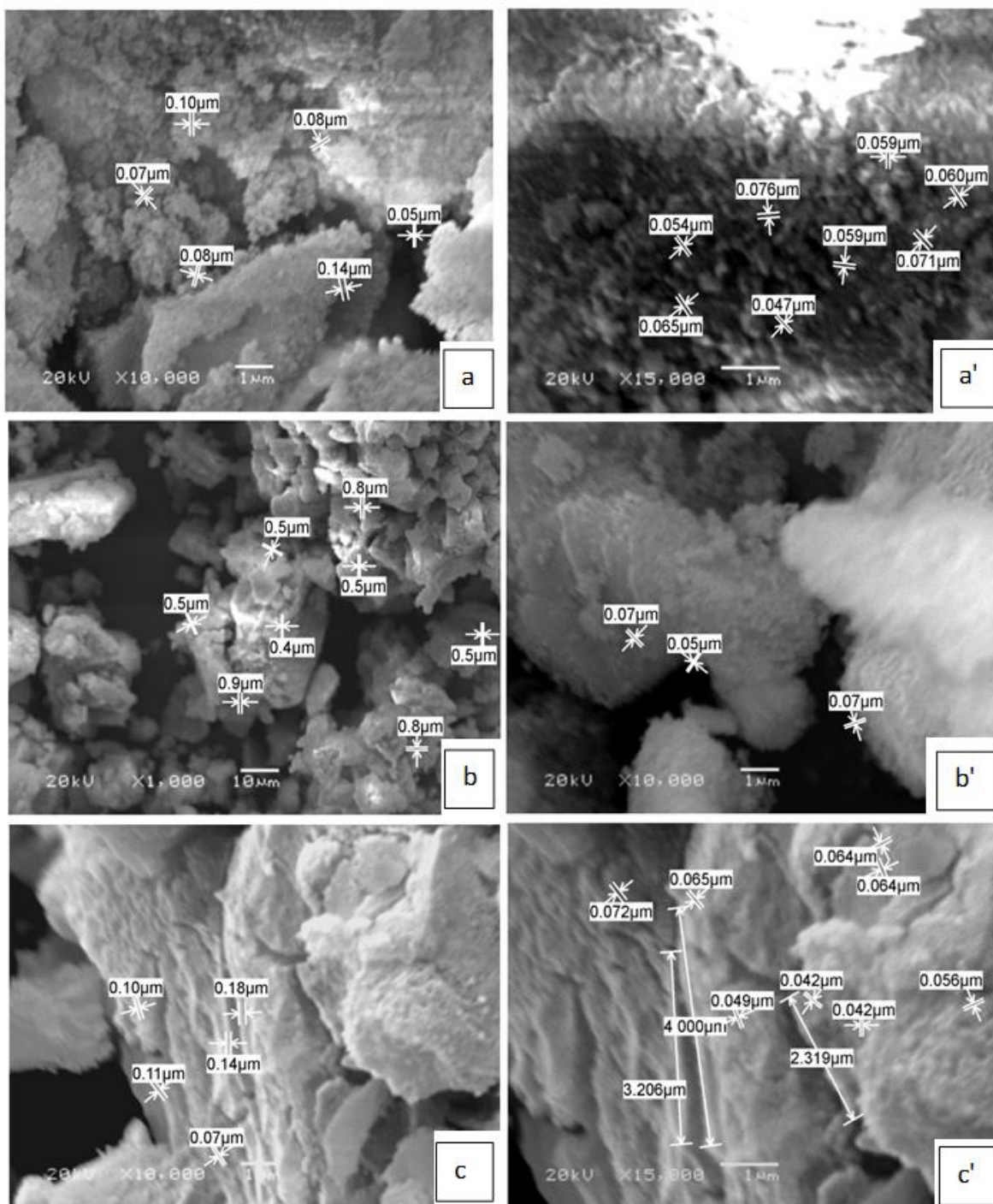


Fig. A.7. SEM images of NPS powder using 7 gm Si Powder and 8 wt % KOH; a, a') sample 1 at 15 Vol% (NPA), b, b') sample 2 at 20 Vol% (NPA), and c, c') sample 3 at 25 Vol% (NPA).

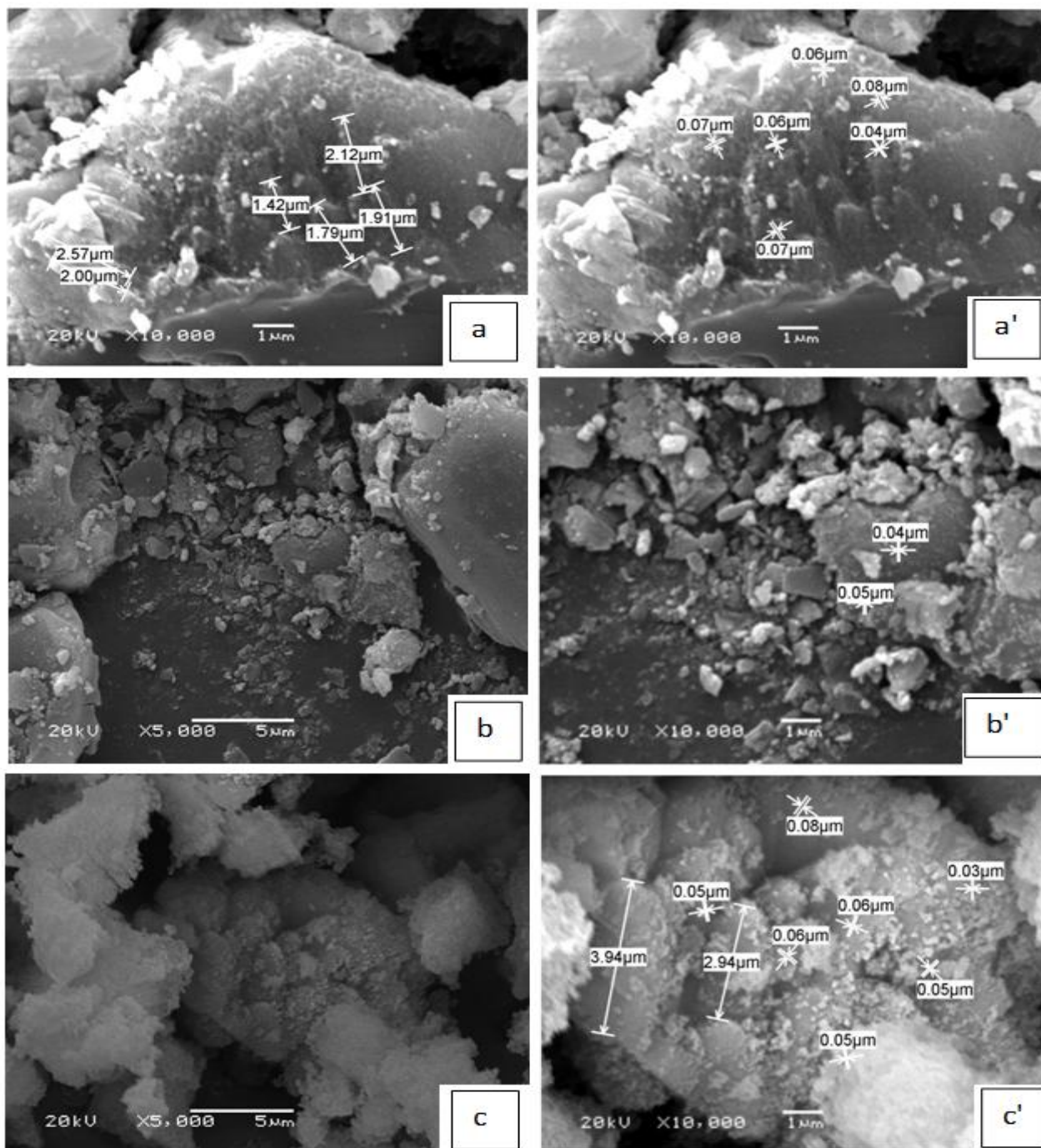


Fig. A.8. SEM images of NPS powder using 7 gm Si Powder and 7 wt % KOH; a, a') sample 4 at 15 Vol% (NPA), b, b') sample 5 at 20 Vol% (NPA), and c, c') sample 6 at 25 Vol% (NPA).

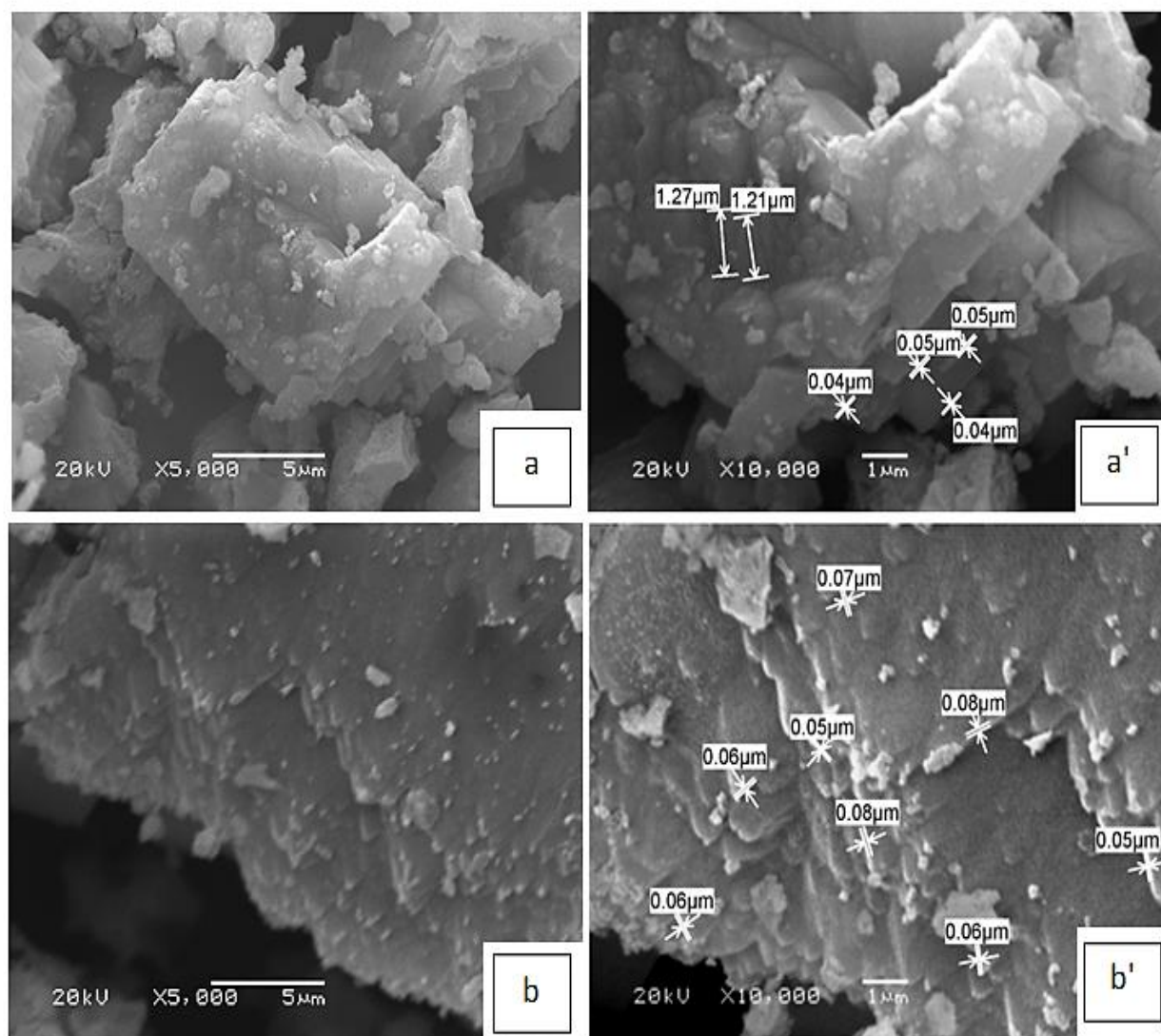


Fig. A.9. SEM images of NPS powder using 7 gm Si Powder and 6 wt % KOH; a, a') sample 7 at 15 Vol% (NPA), and b, b') sample 8 at 20 Vol% (NPA).

3.1.6. Field Emission Transmission Electron Microscope (FE-TEM)

Fig. A.10 shows HRTEM images of the etched silicon powder for producing both nanoporous silicon [40] and hydrogen gas under different etching conditions of both KOH and n-propanol and at 180 minutes as the etching time.

Clear enhancements of the nano-pores of the nano-powder are exhibited in sample 2; in addition, the existence of the nano-ribbon nature is clearly indicated in Fig. A.10.a, a'. The selected area electron diffraction (SAED) in the inset of Fig. A.10.a indicates clearly the different planes of the polycrystalline nature of the NPS as confirmed by XRD data. On the other hand, the image of sample 6 shows a great effect on maximizing the nano-ribbons and minimizing the nanoparticles, as shown in Fig. A.10.b, b'.

The SAED still gives the polycrystalline nature and fringes of 0.3 nm that indicate the good crystallinity of the etched nano-powder. At lower concentrations of the etching solution (sample 7); the etched powder exhibits a mixed structure of silicon nanoparticles of about 50-70 nm accompanied by wide nano-ribbons with 3-4 layers of NPS as shown in Fig. A.10.c and its inset. High resolution of this nano-powder shows nano-pores with dimensions ranging from 2-5 nm and the nano-ribbons have the silicon fringes with a dimension of 0.3 nm of the (111) plane as shown in Fig. A.10.c, c'.

So, the formation of nanopores and nanoribbons, observed via SEM and HRTEM, plays a pivotal role in accelerating the hydrogen generation performance. The network of nanopores significantly increases the accessible surface area, exposing a higher density of active catalytic sites. Concurrently, the unique 1D morphology of nanoribbons provides a continuous pathway for rapid electron transport and minimizes mass transfer resistance. This structural synergy facilitates the immediate release of generated H₂ bubbles, preventing catalyst surface blocking and sustaining high reaction kinetics

3.2. Hydrogen Production

Silicon element is capable of reacting with alkali etchant mixture (KOH and n-propanol) and producing hydrogen gas in aqueous solutions at ambient conditions [41]. In addition, the qualitative and quantitative analyses of hydrogen gas are presented as follows.

3.2.1. Qualitative analysis of hydrogen gas production

For the determination of H₂ gas volume, using water displacement technique for quantification and collection the evolved H₂ gas, as shown in the Fig. A.1. The qualification and purity percent of the evaluated H₂ are determined by GC mass chromatography [42] (Methanizer Agilent 6890N) as mentioned before. In addition, some impurities of hydrocarbons like (CO, CO₂ and CH₄) of some NPS powder samples (2, 6, and 7), are determined too by GC mass chromatography (Hp 6890 series). The hydrogen purity for all samples is ~ 99.99 %.

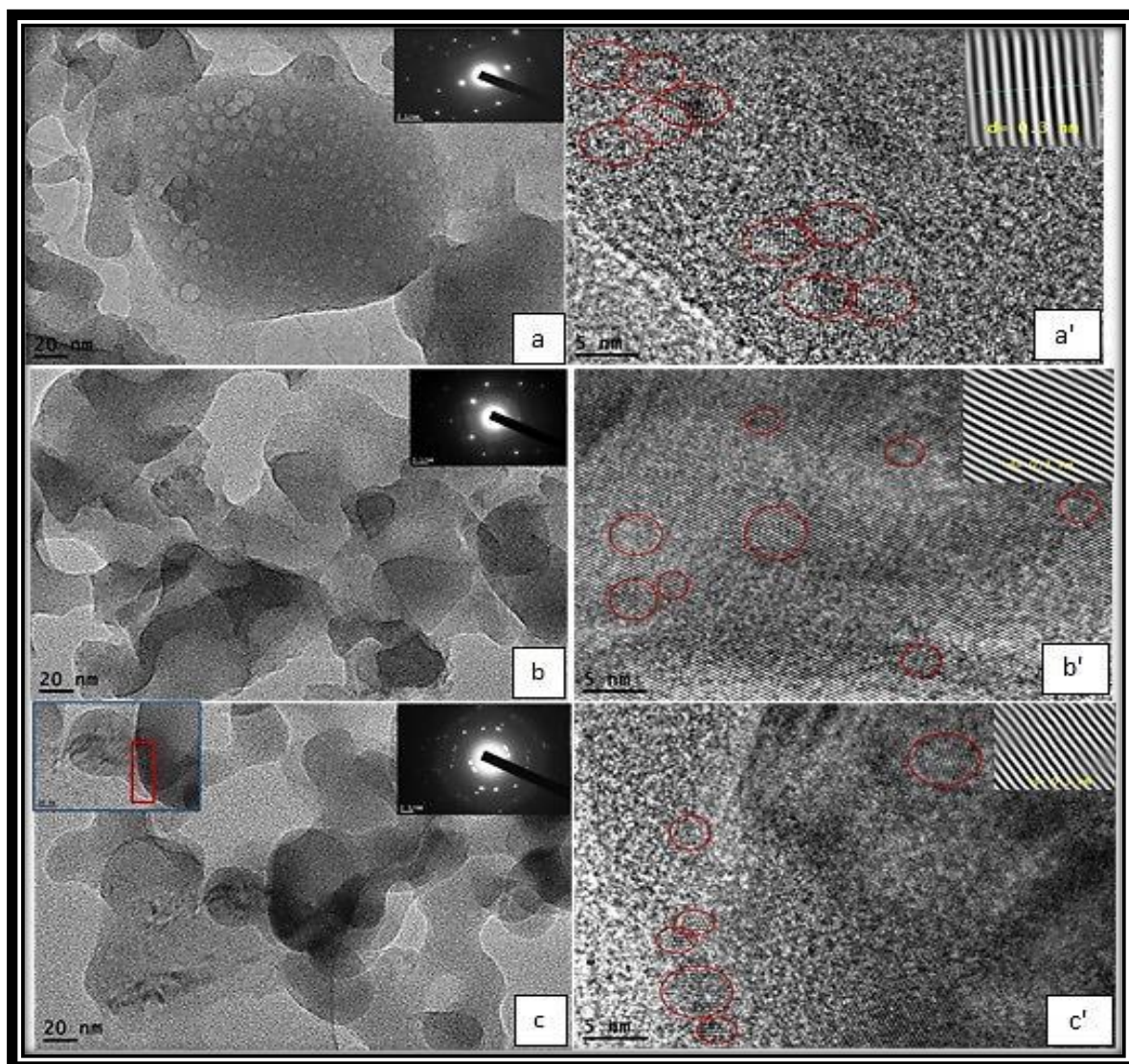


Fig. A.10. HRTEM of etched silicon powder for producing both NPS and hydrogen gas at different etching conditions; a, a') sample 2, b, b') sample 6, and c, c') sample 7.

Table A.5: Hydrogen purity and concentration of CO, CH₄ and CO₂

Components	Method	Result		
		Sample 2	Sample 6	Sample 7
H ₂ (vol %)	UOP 603	99.99	99.99	99.99
CO (ppm)		7	3	3
CH ₄ (ppm)		4	3	2
CO ₂ (ppm)		107	115	61

3.2.2. Quantitative analysis of hydrogen production

For the determination of H₂ gas volume, we applied the water displacement technique for quantification and collection the evolved H₂ gas [43], as mentioned before in the Fig. A.2. As well known, the density is the ratio of the weight of substance to its volume, so the weight accumulated (wt.) of hydrogen gas evolved can be calculated from Eq. (A.3).

$$\text{Wt. (gm)} = C * [V \text{ (ml)} * 10^{-3}] \quad \text{Eq. (A.3)}$$

Where, wt. (g): weight of the calculated of hydrogen gas evolved in grams, V (ml): Volume of hydrogen gas evolved in milliliters, C (g/L): = 0.08988, a constant which is the density of hydrogen gas

Fig. A.11, shows the elevation process of hydrogen gas with 7 gm Si powder, during preparation samples (1, 2 and 3) which starts approximately at 22, 27 and 20 min, respectively. For sample 1, elevation of hydrogen gas records one liter after 30 min of the reaction starting. Hydrogen quantity increases gradually until reach to the constant rate at 70 min which equivalent to about 3000 ml. While for sample 2, it registers one liter after 40 min of the reaction, also hydrogen elevation increases gradually till constant rate at 70 min which equivalent to about 3500 ml. For sample 3, shows the production of hydrogen which starts approximately at 20 min then complete to one liter after 30 min of the reaction, hydrogen quantity increases gradually until reach to the constant rate at 100 min which equivalent to about 4080 ml .

According to Equation (4) the accumulated weight of H₂ (the equivalent volume and weight of H₂ at different times) for sample 1, at 180 min, is about 0.28 gm. And the value of accumulated weight of H₂ for sample 2 and 3, are 0.55, and 0.38 gm, respectively. So the highest value of the accumulated weight of H₂ at concentrations 8wt% KOH and 20 Vol% NPA, at 180 min as the etching time, as shown in Fig. A.11.a.

Fig. A.11.b shows the production of hydrogen due to synthesis process of NPS via different etchant mixture concentrations, that corresponding to samples 4, 5, and 6. For sample 4, it shows the hydrogen production which starts approximately at 25 min then complete to 1000 ml after 45 min of the reaction, hydrogen increases gradually till reach to the constant rate of elevation at 90 min which equivalent to about 4000 ml. And in case of sample 5, it shows the time of hydrogen production is at 30 min then complete to 1000 ml after 58 min of the reaction, hydrogen increases gradually until reach to a constant rate at 110 min which equivalent to about 4150 ml. While for sample 6; 27 min is the time of the beginning of H₂ gas elevation and then produces 1000 ml after 32 min of the reaction, hydrogen increases gradually until reach to the constant elevation rate at 100 min which is equivalent to about 5100 ml. The accumulated weight for hydrogen calculated from equation (4) is about 0.47, 0.45, and 0.54 gm, it corresponding to samples 4, 5 and 6, respectively.

The production of H₂ gas during preparation of samples 7, 8, and 9 is presented in Fig. A.11.c. For sample 7, H₂ gas elevation starts approximately at 30 min then complete to one liter at 50 min from starting of the reaction, H₂ increases gradually until reach to the constant rate at 90 min which is equivalent to about 3830 ml, according to equation (4) the accumulated weight is about 0.49 gm. In case of sample 8, the H₂ is produced at 23 min and one liter at 44 min of the reaction, H₂ increases gradually until reach to the constant rate at 130 min which equivalent to about 4150 ml, so the accumulated weight is about 0.39 gm. While for sample 9, the production of H₂ starts approximately at 31 min then complete to one liter after 45 min of the reaction, H₂ increases gradually until reach to the constant rate at 100 min which equivalent to about 4000 ml, the accumulated weight is about 0.47 gm in 180 min for reaction.

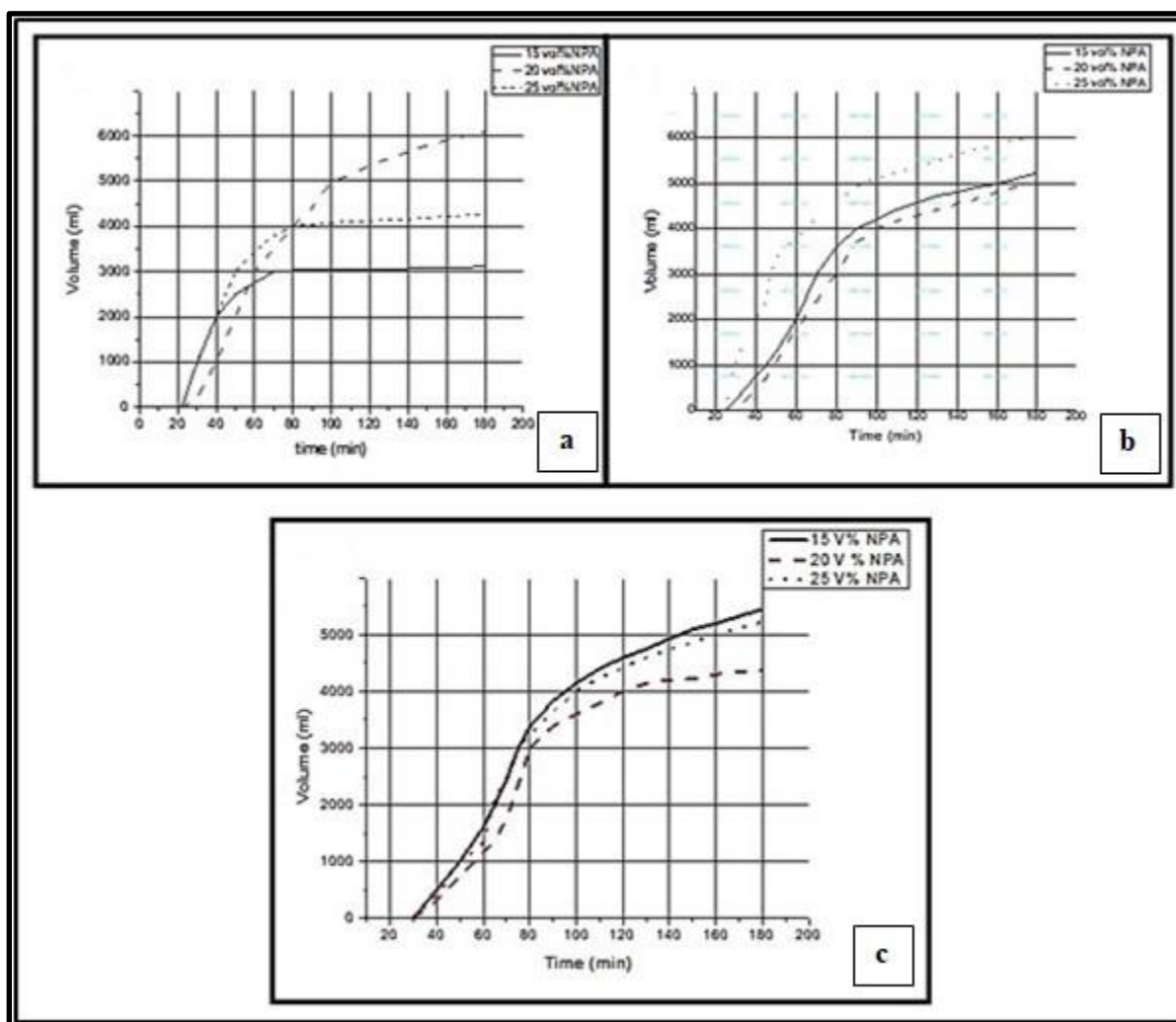


Fig. A.11: the accumulated elevation hydrogen gas (H_2) during preparation process of; a) samples 1, 2, and 3, b) samples 4, 5, and 6, and c) samples 7, 8, and 9.

So, as shown in Table A.5, the best amounts of H_2 gas in grams at constant weight amount of Si powder (7 gm) and constant time of ultrasonic reaction at 180 min. Thus, it's observed that at 8wt% KOH and 20 V% NPA, sample 2 has the highest amount of H_2 gas which is equal to 0.55 gm rather than the two other concentrations of NPA. While at concentrations 7 % wt KOH and 25 Vol% (NPA), the best amount of H_2 gas production is observed (Sample 6), 0.54 gm comparing with the other two concentrations. And sample 7 at etchant mixture concentrations (6 wt %KOH, and 15 Vol% (NPA)), the best value of accumulated H_2 gas is 0.49 gm.

Table A.6. Quantitative comparison between weight and volume accumulated of H₂ gas evolution with different concentrations of KOH and n-propanol

Concentrations			Time of Reaction in ultra-sonication system is 180 min	
7 gm (si-powder)	wt % (KOH)	Vol % (NPA)	Volume accumulated (ml)	Weight accumulated (gm)
	8%	15%	(3110)	(0.28)
		20%	(6100)	(0.55) (Best Result)
		25%	(4280)	(0.38)
	7%	15%	(5200)	(0.47)
		20%	(5000)	(0.45)
		25%	(6050)	(0.54) (Best result)
	6%	15%	(5450)	(0.49) (Best Result)
		20%	(4370)	(0.39)
		25%	(5230)	(0.47)

Then, the H₂ evaluation depends on several parameters as shown in the following; a) *Influence of KOH concentrations*: the hydrogen evolution rate scales [nearly linear] with KOH concentration within the range of [6 to 8 wt%]. Quantitatively, increasing KOH enhances the concentration of reactive OH⁻ ions, accelerating the nucleophilic attack on the silicon backbone. However, beyond [8 wt%], excessive isotropic etching leads to a decrease in active surface area, stabilizing or reducing the net H₂ output. b) *Influence of NPA concentrations*: it serves a dual quantitative role as a surface tension reducer and a kinetic moderator. At an optimal value of [20 vol%], NPA maximizes bubble detachment (reducing H₂ bubble pinning on pores) and improves wetting. Exceeding this concentration limits the diffusion of OH⁻ to the silicon interface, slowing down the reaction kinetics. c) *Influence of sonication time*: Increasing the sonication time from 30 to 270 minutes yields a [196%] increase in the initial hydrogen generation rate. This is attributed to the continuous mechanical removal of passivating byproduct layers K₂SiO₃propoxides) and the accelerated mass transport of reactants into the deep nanopores. And, d) *Influence of morphology*: SEM imaging confirms that the transition from a (e.g., macro-porous to a dense nanoporous network) directly governs the reaction kinetics. The highly interconnected nanoporous structure minimizes the diffusion path for alcohol molecules.

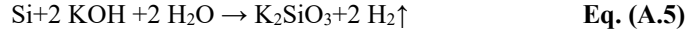
To evaluate the practical significance and efficiency of the proposed alcoxylolation process, the key performance metrics were standardized against the mass of the starting material. Based on the consumption of 7.0 g of silicon powder to generate 1.0 L of H₂ over a 20-minute interval, the system demonstrated a hydrogen productivity (yield) of 0.1429 L g⁻¹ Si and an average production kinetic rate of 0.4286 L g⁻¹ Si h⁻¹. Given the 1:2 stoichiometric ratio of Si to H₂ defined by the reaction equation, the theoretical maximum hydrogen output is 11.17 L (at STP), yielding a reaction conversion efficiency of 8.95% (8.20% at 25 °C). This baseline evaluation establishes a benchmark for future optimization of the catalyst or reaction conditions to overcome potential kinetic bottlenecks.

4. Suggested chemical reaction mechanism via dual formation of NPS and H₂ gas

In the presence of a strong base catalyst KOH, silicon directly reacts with n-propanol CH₃CH₂CH₂OH to yield tetra-n-propoxysilane (or soluble propyl-silicate complexes) and hydrogen gas. The overall stoichiometrically balanced equation for a single silicon active unit is:

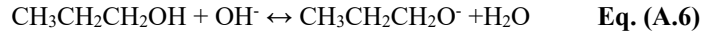


If water is present in the KOH solution, a competitive/cooperative hydrolysis and etching reaction occurs simultaneously, which is balanced as follows:

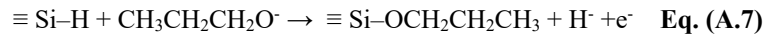


The reaction mechanism contained the following steps:

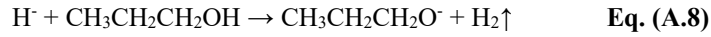
- a) *Deprotonation of n-Propanol (Catalytic Activation)*: The hydroxide ions (OH^-) from KOH abstract protons from the n-propanol molecules, generating highly nucleophilic propoxide ions ($\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$)



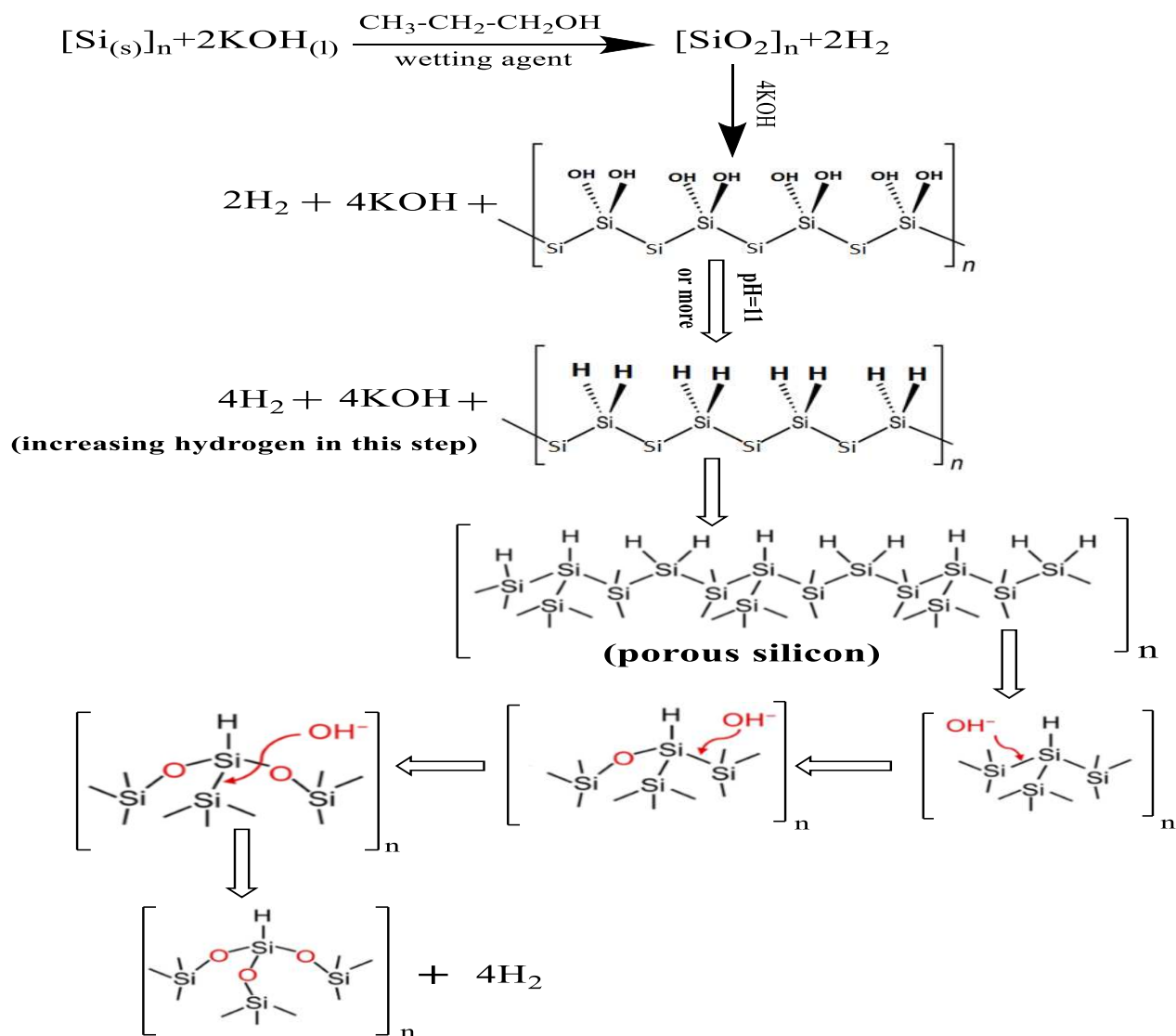
- b) *Nucleophilic Attack on the Silicon Surface*: The propoxide ions $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$ perform a nucleophilic attack on the polarized surface $\{\text{Si}-\text{Si}\}$ backbones or $\{\text{Si}-\text{H}\}$ terminated bonds. This leads to hydride displacement and temporary formation of surface-bound alkoxide groups:



- c) *Hydrogen Evolution Kinetics*: The displaced hydride ions H^- or electrons instantly reduce nearby protons from the alcohol or water molecules to form molecular hydrogen gas H_2 , returning the hydroxyl/propoxide catalysts to the cycle:



So, scheme 1 shows the suggested mechanism for dual formation of NPS and H_2 gas production. Firstly, commercial Si powder reacts with KOH (as an alkaline medium) in the presence of NPA as a wetting agent. Si oxidized and forms SiO_2 and also during oxidation process two molecules of hydrogen gas are produced. SiO_2 during the basic medium, converts into $\text{Si}(\text{OH})_2$ and also produces hydrogen. Then, the reaction will accelerate and concentration of KOH increases due to increasing pH of the reaction. At pH = 11 or more, the PS powders formed with producing double amounts of hydrogen than the last step. After that, the corrosive alkaline medium breaks the bond between Si-Si to form Si-O-Si, producing four molecules of H_2 .



Scheme 1. Chemical reaction mechanism for dual formation of NPS and H₂ gas

While older research of hydrogen generation from porous silicon proved that the reaction was possible, it was highly inefficient for practical applications because [44]: The moment silicon reacts with water; it forms a native silicon dioxide {SiO₂} layer. In past studies, this oxide shell immediately choked the reaction, leaving the bulk inner core of the silicon completely unreacted. NPS particles tend to clump together (agglomerate) when wet. This severely reduces the accessible surface area, slowing down the hydrogen generation rate. In addition, most previous setups required continuous external energy such as high temperatures, constant stirring, or dedicated light sources to sustain even a modest hydrogen flow.

But in our research, instead of adding porous silicon to an external chemical bath or heating it, the new method co-embeds the necessary elements directly into the porous matrix. KOH dissolves the passivating oxide layer as soon as it forms, while the NPA prevents the nanopowder from clumping. Finally, allowing the porous silicon to achieve its true theoretical hydrogen yield spontaneously as an economical and environmentally friendly method.

Conclusion

The main goal of this work is the production of high-purity hydrogen gas at room temperature, without using any source of energy and at a stable great generation rate ($\approx 1 \text{ L} / 20 \text{ min}$). This process combines ultrasonic processing with wet alkaline chemical etching. Porosification process of commercial silicon powder occurs via using alkaline medium (KOH). The different characterization techniques confirmed that PS powders product in Nano scale and its thickness in the range (0.05 to 4.00 μm), in addition XRD peaks show the reflecting planes (111), (220), (311), (400), (331), (422) and (511). SEM and HRTEM present morphological shapes of NPS; i.e. nano-ribbon with polycrystalline nature of the NPS and confirmed the superstructure nature of NPS powders.

For the determination of H_2 gas volume, we applied the water displacement technique for quantification and collection the evolved H_2 gas. At etchant solution concentrations (8wt% KOH with 20 Vol% NPA), the highest amount of H_2 gas is obtained that equal 0.55 gm rather than the two other concentration of NPA. While at 7 % wt KOH, the best amount of hydrogen observed at 25 Vol% (NPA), is 0.54 gm comparing with other two concentrations. On the other hand, at 6 wt %KOH, 0.49 gm of hydrogen accumulated was observed which is the best one at 15 Vol% (NPA).

Qualitative analysis for hydrogen is measured by GC mass chromatography shows the percentages of H_2 gas and some impurities hydrocarbon like (CO , CH_4 and CO_2). So, the hydrogen product purity is at least 99.999 Vol % (dry). Thus, allowing the product to be used in many fine industries.

Acknowledgement

This work is a part of the research program of Advanced Technology and New Materials Research Institute, City for Scientific Research and Technology Applications References, Alexandria, Egypt.

Data Availability: All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Competing Interests and Funding

Funding: The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Financial interests: Author A, B, C, D, and E declare they have no financial interests.

Conflict of interest: The authors declare that they have no conflict of interest.

References

- [1] Megía, P.J., Vizcaíno, A.J., Calles, J.A. & Carrero, A. Hydrogen production technologies: from fossil fuels toward renewable sources, *ENERG. FUEL*. 35, 16403-16415 (2021).
- [2] Openshaw, D., Lang, W.L., Goldstone, L., Wildsmith, J., Freeman, B. & Bagnato, G. Hydrogen storage methods by lithium borohydride, *Int. J. Hydrogen. Energy*. 69, 1188-1198 (2024).
- [3] Singh, S., Jain, S., PS, V., Tiwari, A.K., Nouni, M.R., Pandey, J.K. & Goel, S. Hydrogen: A sustainable fuel for future of the transport sector, *Renew. Sustain. Energy. Rev.* 51, 623-633 (2015).
- [4] Jang, H.T. & Cha, W.S. Hydrogen production by the thermocatalytic decomposition of methane in a fluidized bed reactor, *Korean. J. Chem. Eng.* 24, 374-377 (2007).

- [5] Li, Y., Guo, L., Zhang, X., Jin, H. & Lu, Y. Hydrogen production from coal gasification in supercritical water with a continuous flowing system, *Int. J. Hydrogen. Energy.* 35, 3036-3045 (2010).
- [6] Liao, C.-H., Huang, C.-W. & Wu, J.C.S. Hydrogen production from semiconductor-based photocatalysis via water splitting, *Catal.* 2, 490-516 (2012).
- [7] Weng, H.H., Chen, J.-S. & Chen, P.C. Effects of green innovation on environmental and corporate performance: a stakeholder perspective, *Sustain.* 7, 4997-5026 (2015).
- [8] Coyopol, A., Díaz-Becerril, T., García-Salgado, G., Rosendo, E., Juárez, H., López, R., De- La-Rosa, E., Pacio, M. & Galeazzi, R. Morphological and optical properties of porous silicon annealed in atomic hydrogen, *Superf. Sci.* 25, 226-230 (2012).
- [9] Litvinenko, S., Alekseev, S., Lysenko, V., Venturello, A., Geobaldo, F., Gulina, L., Kuznetsov, G., Tolstoy, V., Skryshevsky, V., Garrone, E. & Barbier, D. Hydrogen production from nano-porous Si powder formed by stain etching, *Int. J. Hydrogen. Energy.* 35, 6773-6778 (2010).
- [10] Mortada, M., Youssef, Y.M., Hassan, I., Ibrahim, M.A.M. Green Hydrogen gas production using an adapted electrolysis method, *Egypt. J. Chem.* 66, 241-254 (2023).
- [11] Kolasinski, K.W. Metal-Assisted Catalytic Etching (MACE) for nanofabrication of semiconductor powders, *Micromachines.* 12, 776-795 (2021).
- [12] Zhang, Y., Zhu, W., Fang, J., Xu, Z., Xue, Y., Pei, J., Sui, R., Wang, X., Zhang, X., Zhuang, Z., Electrochemical converting ethanol to hydrogen and acetic acid for large scale green hydrogen production, *Nano Research*, 17, 1542-1551 (2024).
- [13] Nabil, M., Mahmoud, K.R., Nomeir, R., El-Maghraby, E.M. & Motaweh, H.A. 3D porous silicon (nanorods array, nanosheets, and nanoclusters) production, *Egypt. J. Chem.* 63, 1269-1278 (2020).
- [14] Mousa, A.M., Sayed, H.A.A., Ali, K.A.M., Elkaoud, N.S. & Mahmoud, W.A.E. Energy-conversion efficiency for producing oxy-hydrogen gas using a simple generator based on water electrolysis, *Sci. Rep.* 14, 25312-25324 (2024).
- [15] Pal, S., Jana, S., Singh, D.K., Ganesan, V., Azad, U.P. & Prakash, R. Engineered Ni-Fe prussian blue analogue nanocubes and their transformation into nanocages and mixed oxide for applications as bifunctional electrocatalyst, *Int. J. Hydrogen. Energy.* 50, 52-65 (2024).
- [16] Bosu, S. & Rajamohan, N. Recent advancements in hydrogen storage - Comparative review on methods, operating conditions and challenges, *Int. J. Hydrogen. Energy.* 52, 352-370 (2024).
- [17] Garcia-Villalva, R., Biset-Peiro, M., Alarcon, A., Bacariza, C., Murcia-Lopez, S. & Guilera, J. Comparison of methane reforming routes for hydrogen production using dielectric barrier discharge plasma-catalysis, *Int. J. Hydrogen. Energy.* 59, 1367-1375 (2024).
- [18] Kashyout, A.E.-H. & Nabil, M. Production of high throughput nano-porous silicon (NPS) powder with different architectures, *Mater. Chem. Phys.* 216, 454-459 (2018).
- [19] Kashyout, A.E.-H., Soliman, H.M.A., Nabil, M. & Bishara, A.A. Fabrication of nano-porous silicon using alkali etching process, *Mater. Lett.* 100, 184-187 (2013).
- [20] Kashyout, A.E.-H., Soliman, H., Nabil, M. & Bishara, A. Impact of Congo red dye in nano-porous silicon as pH-sensor, *Sens. Actuators. B: Chem.* 216, 279-285 (2015).
- [21] Predoi, D., Groza, A., Iconaru, S.L., Predoi, G., Barbuceanu, F., Guegan, R., Motelica-Heino, M.S. & Cimpeanu, C. Properties of Basil and Lavender essential oils adsorbed on the surface of hydroxyapatite, *Mater.* 11, 652-668 (2018).
- [22] Elbendary, N., Abdelsalam, H., Ibrahim, M.A., Tawfik, W. & Khalil, M.M.H. Environmental implications of Si₂BN nanoflakes in pharmaceutical pollutant detection and removal: insights from first-principle calculations, *Sci. Rep.* 15, 8555-8572 (2025).
- [23] Karlsson, A., Singh, S.K. & Albertsson, A.C. Controlled destruction of residual crosslinker in a silicone elastomer for drug delivery, *J. Appl. Polym. Sci.* 84, 2254-2264 (2002).
- [24] Borrajo, J.P., Liste, S., Serra, J., González, P., Chiussi, S., León, B., Pérez-Amor, M., Ylänen, H.O. & Hupa, M. Influence of the network modifier content on the bioactivity of silicate glasses, *KEM*, 254-256, 23-26 (2004).

- [25] Mart'inez, F.L., Toledano-Luque, M., Gand'ia, J.J., Carabe, J., Bohne, W., Rohrich, J., Strub, E. & I Martil, I. Optical properties and structure of HfO₂ thin films grown by high pressure reactive sputtering, *J. Phys. D: Appl. Phys.* 40, 5256-5265 (2007).
- [26] Fengwei, D., Qiying, Z., Ge, H., Hanzhong, D. & Xun, Z. Infrared spectrum characteristics and quantification of OH groups in coal, *ACS. Omega.* 8, 16519-17336 (2023).
- [27] Kopani, M., Mikula, M., Kosnac, D., Gregus, J. & Pincik, E. Morphology and FT IR spectra of porous silicon, *J. Electr. Eng.* 68, 53–57 (2017).
- [28] Karlsson, A., Singh, A.S. & Albertsson, A.C. Controlled destruction of residual crosslinker in a silicone elastomer for drug delivery, *J. Appl. Polym. Sci.* 84, 2254-2264 (2002).
- [29] Akl, M.A., Mostafa, M.M., Abdel Hamid, A.I., Hassanin, E.E. & Abdel-Raouf, M. Assessment of the antimicrobial activities of trioctylphosphine oxide modified silica nanoparticles, *Egypt. J. Chem.* 63, 1325-1339 (2020).
- [30] Zdaniauskiene, A., Ignatjev, I., Charkova, T., Talaikis, M., Lukša, A., Šetkus, A. & Niaura, G. Shell-isolated nanoparticle-enhanced Raman spectroscopy for probing riboflavin on grapheme, *Materials.* 15, 1636-1649 (2022).
- [31] Gregora, I., Champagnon, B. & Halimaoui, A. Raman investigation of light-emitting porous silicon layers: Estimate of characteristic crystallite dimensions, *J. Appl. Phys.* 75, 3034-3039 (1994).
- [32] Liu, F.M., Ren, B., Wu, J.H., Yan, J.W., Xue, X.F., Mao, B.W. & Tian, Z.Q. Enhanced-Raman scattering from silicon nanoparticle substrates, *Chem. Phys. Lett.* 382, 502-507 (2003).
- [33] Kumar, P., Hofmann, T., Knorr, K., Huber, P., Scheib, P. & Lemmens, P. Tuning the pore wall morphology of mesoporous silicon from branchy to smooth, tubular by chemical treatment, *J. Appl. Phys.* 103, 024303-024308 (2008).
- [34] Jimenéz-Vivanco, M.R., García, G., Carrillo, J., Agarwal, V., Díaz-Becerril, T., Doti, R., Faubert, J. & Lugo, J.E. Porous Si-SiO₂ based UV microcavities, *Sci. Rep.* 10, 2220-2240 (2020).
- [35] Al-Douri, Y., Badi, N. & Voon, CH. Etching time effect on optical properties of porous silicon for solar cells fabrication, *Optik.* 147, 343-349 (2017).
- [36] Vasquez, M.A., Rodriguez, G.A., Salgado, G.G., Paredes, G.R. & Sierra, R. FTIR and photoluminescence studies of porous silicon layers oxidized in controlled water vapor conditions, *Rev. Mex. Fis.* 53, 431-435 (2007).
- [37] Sagidolda, Y., Tuokedaerhan, K., Azamat, R., Darmenkulova, M., Zhumatova, S., Ibraimov, M., Tezekbay, Y., Zhazitov, M., Abdullah, M., Akilbekov, B., Karibayev, M., Duisebayev, T., Aldongarov, A., Piskunov, S. & Toktarbaiuly, O. The effect of Ti, W, Ag and TiO₂ particles on the structural and optical properties of porous silicon obtained in various electrolytes, *Sci. Rep.* 16:16820-16835(2026).
- [38] Sheng, C.K., Yunus, W.M., Yunus, W.Z., Talib, Z.A. & Kassim, A. Characterization of thermal, optical and carrier transport properties of porous silicon using the photoacoustic technique, *Phys. B: Cond. Mat.* 403, 2634-2638 (2008).
- [39] Lemus, R.G., Rodriguez, C.H., Hander, F.B. & Duarte, J.M.M., Anodic and optical characterization of stain-etched porous silicon antireflection coatings, *Sol. Energy. Mater. Sol. Cells.* 72, 495-501 (2002).
- [40] Nabil, M., Mahmoud, K.R., Nomier, R., El-Maghraby, E.-M. & Motaweh, H. Nano-porous-silicon powder as an environmental friend, *Materials.* 14, 4252-4265 (2021).
- [41] Annuar, A.B.M., Liu, Y., Bhattacharjee, S., Slaughter, J., Mikulska, I., Sayed, F.N., Grey, C.P., Wright, D.S. & Reisner, E. Photoreforming of solid waste on 1 m² scale using single-source precursor-derived co-catalyst films, *Nat. Chem. Eng.* 3, 351-362 (2026).
- [42] Varlet, V., Smith, F. & Augsburg, M. Indirect hydrogen analysis by gas chromatography coupled to mass spectrometry (GC-MS), *J. Mass. Spectrom.* 48, 914-918 (2013).
- [43] Campari, A., Ustolin, F., Alvaro, A. & Paltrinieri, N. A review on hydrogen embrittlement and riskbased inspection of hydrogen technologies, *Int. J. Hydrogen. Energy.* 48, 35316-35346 (2023).
- [44] Mussabek, G., Yar-Mukhamedova, G., Orazbayev, S., Skryshevsky, V., Lysenko, V. Silicon nanostructures for Hydrogen generation and storage, *Nanomaterials.* 15, 1531- 1568 (2025).