On-Demand Hydrogen Generation using Nanosilicon: Splitting Water without Light, Heat, or Electricity

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ABSTRACT: We demonstrate that nanosize silicon (∼10 nm diameter) reacts with water to generate hydrogen 1000 times faster than bulk silicon, 100 times faster than previously reported Si structures, and 6 times faster than competing metal formulations. The H2 production rate using 10 nm Si is 150 times that obtained using 100 nm particles, dramatically exceeding the expected effect of increased surface to volume ratio. We attribute this to a change in the etching dynamics at the nanoscale from anisotropic etching of larger silicon to effectively isotropic etching of 10 nm silicon. These results imply that nanosilicon could provide a practical approach for on-demand hydrogen production without addition of heat, light, or electrical energy.

KEYWORDS: Silicon, hydrogen generation, water-splitting, fuel cell

Splitting water to produce hydrogen is of great interest in energy storage, catalysis, and fuel cell applications. Conventional means of splitting water include electrolysis, thermolysis, photocatalysis, and combinations thereof. Water can also be split chemically using a substance that can be oxidized by water, such as aluminum or silicon. The silicon-water reaction has not previously been exploited for on-demand hydrogen generation, because it is slow and can be self-limiting, via oxide formation. However, silicon can theoretically release two moles of H2 per mole of silicon, is abundant and safe, has high energy density, and releases no carbon dioxide. The scant literature on the subject shows that silicon is a promising material for hydrogen generation from water. It is stable and easy to transport, yet upon oxidation with water can generate 14% of its own mass in hydrogen, via overall reactions like

\[ \text{Si}(cr) + 4\text{H}_2\text{O}(l) \rightarrow \text{Si(OH)}_4(aq) + 2\text{H}_2(g) \]
\[ \text{Si}(cr) + 2\text{H}_2\text{O}(l) \rightarrow \text{SiO}_2(s) + 2\text{H}_2(g) \]

Because of their high surface area per volume, similar to that of other nanoparticles for hydrogen generation, silicon nanoparticles are naturally expected to generate hydrogen more rapidly than bulk silicon. Moreover, many properties of silicon nanocrystals are known to differ from those of bulk silicon in uniquely advantageous ways. Nonetheless, the advantages of silicon for rapid generation of hydrogen have not previously been investigated. Figure 1 provides a schematic showing our multidisciplinary, integrated approach from nanochemistry for generation of silicon nanoparticles; to the reaction with water under basic conditions which generates hydrogen on demand; to the use of generated hydrogen in a fuel cell for portable power.

To determine the size dependence of the hydrogen generation rate for base-catalyzed oxidation of silicon, we employed silicon particles with diameters of about 10 nm (synthesized in our lab) under 100 nm (Sigma Aldrich) and 325 mesh (<40 μm, Sigma Aldrich) using various aqueous bases and reaction conditions (see Supporting Information Methods). The particle structure (before reaction) from transmission electron microscopy and the corresponding hydrogen generation curves for the Si/KOH (1:8 molar ratio) combination are shown in Figure 2a–c. Clear differences distinguish the 10 nm Si nanoparticles from the larger ones. First, the 10 nm Si shows instantaneous generation of hydrogen that plateaus only after the silicon has been depleted, while larger particles exhibit an induction period. In addition, the hydrogen generated from the 10 nm silicon exceeds the expected 2 moles of H2 per mole of silicon. On the basis of time-of-flight-secondary-ion-mass-spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) results, this is attributed...
Figure 1. Schematic showing CO$_2$ laser pyrolysis synthesis of silicon nanoparticles transferred to a custom stainless steel prototype cartridge used to generate hydrogen for fuel cell applications.

Figure 2. Comparison of silicon particles of varying size in base-catalyzed reaction with water. (A–C) TEM images, before reaction, overlaid with plots of hydrogen generation vs time. (D–F) TOF-SIMS spectra from unreacted silicon particles. The red and blue regions highlight $m/z$ ratios corresponding to silicon/silicon hydride (red) and silicon hydroxide/heavier fragments (blue). (G–I) Mass spectra of the gas produced using D$_2$O and KOH (or using H$_2$O and KOH in the inset).
to the presence of hydrogen on the surface of the particles, which
remains from their production in a hydrogen rich environment,
otherwise their exposure to air. TOF-SIMS spectra shown in
Figure 2d–f confirm the presence of silicon hydride groups on
the nanoparticles. The ratios of silicon to silicon hydride peaks
were 0.92:1, 2.67:1, and 2.63:1 for the ∼10 nm, <100 nm, and
325 nm mesh particles, respectively. This confirms that the
10 nm silicon has higher silicon hydride content, despite the fact
that the experiments were all performed in air. Further details
of TOF-SIMS, XPS, SEM and EDX analysis of the particles are
provided in Supporting Information (Figures S1–7).

Bulk silicon is well-known to react with oxygen to form a
uniform passivating layer of oxide on its surface and, as expected,
the oxygen to silicon ratio increases with decreasing particle
size because of the increasing surface area-to-volume ratio.
Nonetheless, independent of their size and surface chemistry, all
silicon samples eventually reacted with basic water to produce
hydrogen as shown in Figure 2. The mass spectra of the gaseous
products are shown in the bottom panel. Upon reacting KOH in
D2O with any of the Si particles, only H2, HD, and D2O were
produced.

The difference in hydrogen production rate between the 10
and 100 nm silicon is much greater than can be accounted for by
the difference in the specific surface area. The surface areas
measured by nitrogen physisorption (BET method) were 204
and 32 m2/g corresponding to surface area mean diameters of
12.6 and 80.5 nm if the particles were spherical. The ∼150-fold
change in H2 production rate greatly exceeds the 6-fold change in
surface area between these two materials. To understand this
difference, we conducted experiments in which we stopped the
etching process before the silicon had been fully consumed.
The observed changes in structure of the silicon nanocrystals are
shown in Figure 3. Figure 3d,f shows particles from experiments
that were stopped when about half of the silicon had been
consumed. As silicon oxidation and hydrogen generation
proceed, the 10 nm particles decrease in size but do not change
shape. In contrast to the KOH etching of bulk silicon, the etching
appears to be isotropic. Figure 3e illustrates the result of isotropic
etching (removal of an equal number of lattice planes in each
direction) of the model shown in Figure 3b. The transmission
electron microscopy (TEM) images are representative; we
cannot image the exact same particle before and after the etching
process. Although the etching appears isotropic, the observed
behavior is compatible with the persistence of different etch rates
for different atomic planes. The etch rates of different atomic
planes in silicon are so vastly different that even if a small particle
were to be terminated by {111} planes the etching may be
entirely determined by the corners and edges of the crystal faces,
which have >100 times higher etch rates. In Supporting
Information Figure S11, we illustrate this concept to be true by
removing 110 and 100 planes from an initially quasi-spherical
∼10 nm nanocrystal. Even though no {111} planes were
explicitly removed, the decrease in particle size leads to a
decrease in the number of {111} planes and apparent isotropic
etching. Thus, the apparent isotropic etching need not reflect a
change in relative etch rates of different planes. It may be purely
an effect of geometry at small crystal size.

In contrast, for the 100 nm particles anisotropic etching is
observed with unexpected consequences. Comparing Figure 3,
panel c and f, which show typical 100 nm particles before and
after partial reaction, we see that the 100 nm particles are not
uniformly reduced in size, but form hollow shells or capsules.
These nanocapsules, to be described in greater detail in a separate
publication, have walls that consist of a few monolayers of silicon,
typically with the 111 plane parallel to the capsule wall.

While the TEM images are illustrative and representative of
the sample as a whole, they obviously show only a single particle
for each case. Powder X-ray diffraction provides an ensemble
measurement that supports the interpretation of isotropic
etching of 10 nm particles and anisotropic etching of larger
particles. For silicon, etching reactions are typically slower on the
111 plane because they require breaking three Si–Si bonds rather
than two.21 The ratio of etch rates for bulk silicon has been
reported as 160:1:1 for (110)/(100)/(111) crystal planes at
room temperature in KOH solution.22 The powder XRD
patterns from the 10 nm structures show almost identical
relative intensities of peaks corresponding to different lattice
planes before reaction and after partial reaction (Figure 3g).
This suggests that etching is isotropic. Note also the slight peak
broadening after partial etching. The crystallite diameters
obtained by applying the Scherrer equation to the 111, 220,
and 311 peaks of the XRD pattern of unetched ∼10 nm particles
were 9.9, 9.0, and 9.0 nm, respectively. The corresponding peaks
for the partially etched sample gave crystallite diameters of
8.8, 7.4, and 7.4 nm, respectively. Reduction of a spherical
particle from 9.9 to 8.8 nm corresponds to removal of 30% of the
particle volume, whereas reduction from 9.0 to 7.4 nm would
correspond to removal of 44% of the particle volume. Given
the uncertainties in crystallite sizes from XRD measurements, this
observed size reduction is consistent with a model of isotropic
size reduction.

In contrast, for 100 nm particles and microparticles, the XRD
patterns show decreased intensity of the 111 reflection relative to
the other lattice planes. This demonstrates that the etching is
anisotropic. Because the 111 plane is the slow-etching plane, one
might expect the relative abundance of 111 planes to increase
after reaction. The relative decrease in the intensity of the 111
reflection is attributed to the unusual etching dynamics that lead
to the formation of hollow nanocapsules. Etching along other
directions within the interior of the particles leaves behind thin
shells like the one shown in Figure 3f, which have predominantly
111 planes parallel to their surface. This produces a decrease in
diffraction from the 111 planes. Lower magnification TEM
images of the 100 nm particles are shown in the Supporting
Information (Figure S12). The XRD patterns from the 325 mesh
particles were similar to those from the 100 nm particles (see
Supporting Information, Figure S13). The reaction may also be
limited by diffusion of OH through a shell of product as
illustrated in Figure 3j. This would also produce a size-
dependence that is more than linearly proportional to the
surface to volume ratio. For a given extent of reaction (fraction
reacted), particles that were initially larger will not only have less
surface area per unit volume, but also a proportionally thicker
layer of reaction product through which reactant and product
diffusion must occur.

The difference in etching behavior between 10 and 100 nm
particles is also evident from analysis of the apparent linear
etching rate as a function of time. If one assumes a shrinking core
model with monodisperse spherical particles decreasing in size,
one can compute an apparent linear etch rate from the
measurements of hydrogen production versus time. To apply
this analysis to the 10 nm silicon particles, we assume that
the excess hydrogen, beyond the stoichiometric 2 mol per
mol silicon, is released first, followed by etching, as illustrated
in Figure 3i. As shown in Supporting Information (Figure S14), the
apparent linear etch rate for 10 nm particles starts at about
0.3 nm/s and decreases approximately linearly until it reaches zero when the particles are consumed. In contrast, the apparent linear etch rate for 100 nm particles starts at zero, reaches a maximum of about 0.05 nm/s when about one-third of the silicon has been consumed, then decreases back to zero. This behavior of 100 nm particles cannot readily be explained by a shrinking-core model, but one can imagine formation of shells like the one shown in Figure 3f occurring by an initially slow process that exposes fast-etching planes, followed by rapid and self-limiting hollowing out of the interior. Such a scenario would be consistent with the observed sigmoidal curve for hydrogen production and the apparent linear etch rates.

Similar behavior was observed with other bases as etchants. Results using sodium hydroxide and using hydrous hydrazine were similar to those using KOH (Supporting Information Figure S15−S22) but the absolute rates were slower. The reaction of silicon in an ethanol−water mixture produced hydrogen without addition of a base but at a much slower rate.

The maximum and the average rates of hydrogen generation for different silicon formulations are shown in Figure 4. The maximum rate, time required to generate 1 mmol of H2, and total hydrogen produced were as follows: 0.06 gH2 s$^{-1}$ gSi$^{-1}$, 5 s, and 2.58 mol H2 per mol Si for 10 nm particles; 0.0004 gH2 s$^{-1}$ gSi$^{-1}$, 811 s, and 1.25 mol H2 per mol Si for 100 nm particles; 0.0003 gH2 s$^{-1}$ gSi$^{-1}$, 3075 s, and 1.54 mol H2 per mol Si; and 0.00007 gH2 s$^{-1}$ g$^{-1}$Si, 12.5 h, and 1.03 mol H2 per mol Si for a 110 silicon wafer. The maximum H2 generation rate with 10 nm Si was 150 times that achieved with 100 nm particles which, in turn, was only 1.3 times that achieved with 44 μm particles. These differences cannot be accounted for by differences in specific
surface area, the BET surface area. The maximum hydrogen generation from our 10 nm silicon is substantially higher than rates previously reported for silicon, as illustrated in Figure 4b. Goller et al.\textsuperscript{13} reported $2 \times 10^{-8}$ gH\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1}Si; Zhan et al.\textsuperscript{16} showed that hydrogen stored in porous silicon could be released at a maximum rate of $2 \times 10^{-8}$ gH\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1}Si; Litvinenko et al.\textsuperscript{13} showed that stain etching of nanoporous silicon generated H\textsubscript{2} at $1.7 \times 10^{-5}$ gH\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1}Si at 60 °C using nanoparticles embedded in porous silicon; Bahruji et al.\textsuperscript{15} reported $2 \times 10^{-8}$ gH\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1}Si by photoactivated reaction under ultraviolet light. The other two nontoxic, air-stable hydrogen generating materials are aluminum and zinc, and the fastest rate reported using these materials is 0.01 gH\textsubscript{2} s\textsuperscript{-1} g\textsuperscript{-1}Si.\textsuperscript{17,23}

Direct application of hydrogen generated from silicon and water was demonstrated using a small fuel cell (TDM fuel cell technology, 20 stack polymer electrolyte membrane). This provides a straightforward demonstration that the gas produced is hydrogen with no byproducts that could interfere with fuel cell operation. A 200 mg sample of 10 nm Si was placed in a stainless steel reaction vessel, and the activator (KOH) and water were added. For comparison, the fuel cell was also run using an amount of H\textsubscript{2} equal to 14 wt % of the silicon used (stoichiometric amount of H\textsubscript{2} for pure Si) delivered using a mass flow controller. Hydrogen generated from silicon produced more current and voltage than the theoretical amount of pure H\textsubscript{2} as seen in Figure 4c. The current and voltage difference for the 10 nm particles is attributed to the additional hydrogen generated (beyond the theoretical 14 wt %) from the Si nanoparticles as observed in Figure 3i. For the larger Si particles, the total energy was lower than that obtained using pure H\textsubscript{2}. These lower values are attributed to the larger particles being unable to produce the theoretical value (14 wt %) of hydrogen. The larger particles have higher silicon content but a lower effective energy density. The fuel cell ran for about 4 min and characteristic results are depicted in Figure 4d.

In summary, we have demonstrated that hydrogen generation from ultrasmall silicon nanoparticles proceeds much more rapidly than expected based upon extrapolation of rates obtained using larger particles. This accelerated reaction rate reflects a transition from anisotropic to effectively isotropic etching of the nanoparticles with decreasing size, along with effects of surface properties and surface to volume ratio. Silicon nanoparticles may be of practical use for on-demand hydrogen generation, based upon their enhanced activity relative to other air-stable hydrogen-generating materials such as aluminum and zinc. Integration of nanosilicon with appropriate cartridge technologies could provide a “just add water” hydrogen-on-demand technology that would promote adoption of hydrogen fuel cells in portable power applications. However, scalable and energy-efficient processes for nanoparticle production must be
implemented to expand the potential use of silicon-based H\textsubscript{2} generation beyond niche applications. Laser pyrolysis has been demonstrated at kg/h scales, and thus it may be one such process.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information includes materials and methods, supporting text, extensive characterization by EDX, SEM, and XRD, along with hydrogen generation curves for a range of different conditions and activators (KOH, NaOH, hydrazine). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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