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Silicon Nanowire Arrays – A New Catalyst for the Reduction of Nitrobenzene Derivatives

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Silicon nanowire arrays (SiNWAs) are under extensive investigation for solar cells and biomedical applications. This study reports for the first time that hydrogen fluoride-treated (H)-SiNWAs are an efficient catalyst for the reduction of nitrobenzene derivatives. We show that SiNWAs, after hydrogen fluoride treatment, have a high catalytic activity in *p*-nitrophenol (PNP) reduction. The conversion rate of PNP by H-SiNWAs increases with time and is almost complete within 30 min, which thus indicates catalytic activity comparable to that of platinum nanoparticles. The catalytic activity of SiNWAs is closely related to the chemical composition and specific morphology of the surface. Si–H bonds on the surface are essential for activity, and arrays with longer nanowires showed a higher catalytic activity. Moreover, the activity can be easily regenerated by hydrogen fluoride treatment. It was also found that H-SiNWAs exhibit a similar catalytic activity for the reduction of other nitrobenzene derivatives such as *p*-nitroaniline and sodium *m*-nitrobenzenesulfonate. It is concluded that H-SiNWAs may be considered as an environmentally friendly alternative to noblemetal-based catalysts for the reduction of nitrobenzene derivatives.

Introduction

Aminobenzene derivatives, the reduced analogs of nitrobenzene derivatives, have particular importance in the chemical and pharmaceutical fields. Among them, p-aminophenol (PAP) is a very important raw material and pharmaceutical intermediate, widely used in the production of dyes, developers, antipyretic analgesics, and acetanilide.^[1,2] The synthetic production of PAP is mainly by reduction of the nitro analog. The common synthetic methods for industrial production are based on the electrolytic reduction or catalytic hydrogenation of nitrobenzene, and the iron reduction or hydrogenation reduction of pnitrophenol (PNP). Among them, catalytic hydrogenation has received widespread interest because of its attractive features, such as fewer byproducts, high yield, and less environmental pollution.^[3-5] The catalytic hydrogenation of PNP requires a nickel-based catalyst or a noble metal catalyst, which is difficult to separate from the final product and tends to cause environmental pollution as well as physiologically toxic effects. Compared to catalytic hydrogenation, biological reduction can effectively reduce toxicity. It was found that type I nitroreductase can reduce nitrobenzene compounds in vivo in the presence of coenzymes [nicotinamide adenine dinucleotide (re-

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[⁺] These authors contributed equally to this work. duced; NADH) and nicotinamide adenine dinucleotide phosphate (reduced; NADPH)].^[6] However, this technology could not be widely adopted in industrial production because of the relatively harsh conditions required (e.g., in concentration, temperature, pH, and ionic strength), and the requirement of large amounts of coenzymes. Hence, it is of great importance and practical value to develop new catalysts for nitrobenzene reduction that have simple preparation methods, excellent catalytic performance, and little pollution of the environment.

Silicon-based nanoscale materials have several unique physicochemical properties, such as photocatalytic activity^[7,8] and photoluminescence.^[9,10] Silicon nanowire arrays (SiNWAs) are good candidate substrates for solar cells^[11,12] and are widely used in biomedical applications.^[13–18] Recent studies have found that the generation of reduced coenzyme I and II (NADH and NADPH), the two very important nicotinamide coenzymes in metabolism, can be triggered in a nonenzymatic system by hydrogen fluoride-treated SiNWAs (H-SiNWAs).^[19,20] Furthermore, the reduction effect of SiNWAs has also been utilized in systems catalyzed by lactate dehydrogenase and mitochondrial reductase. Therefore, SiNWAs can be used not only to produce the reduced coenzymes NADH and NADPH but also to reduce nitrobenzene derivatives.

Although reduced coenzyme I and II (NADH and NADPH) are necessary in many redox reactions in vivo, they can be easily inactivated and degraded under in vitro conditions. It was also found that the generation efficiency of NADH and NADPH is not high in the reduction reaction promoted by SiNWAs.^[19,20] So it is necessary to study the reduction of nitrobenzenes catalyzed by SiNWAs in the absence of NADH and NADPH. In this study we used H-SiNWAs in the reduction of PNP and demonstrated that H-SiNWAs possess unique properties as a reductive catalyst that have not been exploited thus far. SiNWAs, after a simple surface chemical treatment, can be use as a catalyst in the reduction of PNP to PAP; this effect is independent of any reductase or reduced coenzymes; and it is very similar to the catalytic effect of platinum nanoparticles. Furthermore, we studied the relationship between the surface properties of SiNWAs and its catalytic activity, and found that the surface chemical properties and topography of the material affect its reduction efficiency for PNP. At the same time, we also found that the role of H-SiNWAs is very broad and can be effective as a heterogeneous catalyst in reduction reactions for some other nitrobenzene derivatives.

Results and Discussion

Reduction of PNP by H-SiNWAs

PNP was significantly reduced by SiNWAs in our experiments. Although a similar reduction activity of SiNWAs has also been observed for oxidized coenzymes (NAD and NADP) and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide in previous studies,^[19,20] our results showed a marked reduction of PNP by H-SiNWAs (SiNWAs after treatment with HF for a short time), and the complete conversion of PNP to PAP was achieved in just 30 min. The reaction was confirmed by ¹H NMR spectroscopy (Figure 1 A). Compared with the reactant PNP,



Figure 1. ¹H NMR spectra (solvent D_2O). A) PNP before reduction, B) product of the reduction of PNP catalyzed by H-SiNWAs.

which showed typical signals at δ =8.165 and 6.987 ppm, the reaction product displayed a totally different profile with two new major peaks at δ =6.711 and 6.696 ppm (Figure 1B) as a result of the aromatic protons. Moreover, the reactant signals disappeared, which indicates the complete conversion of PNP to PAP.

The reaction kinetics was studied by UV/Vis absorption spectroscopy. The catalytic performance of H-SiNWAs for the reduction of PNP to PAP was thus evaluated. The much-studied reduction of PNP to PAP in the presence of NaBH₄ was chosen as a model system for comparison. It is well known that PNP has a strong absorption at 400 nm in the visible region. The corresponding reduction product shows a distinct blueshift to 298 nm in the UV region. This blueshift is a typical feature of the catalytic reduction of PNP to PAP.^[3-5] The absorbance of the PNP peak at 400 nm decreased from about 0.998 to 0.044 within 30 min, whereas the absorbance at 298 nm increased from 0.083 to 0.156 (Figure 2 A), which indicates that PNP was



Figure 2. Reduction of PNP catalyzed by H-SiNWAs. A) Time course of UV/Vis spectra (inset: expanded view of the 278–314 nm region); B) Conversion of PNP by H-SiNWAs versus time. Insets show the color change of the reaction mixture.

converted to PAP. The process was very fast with a conversion of PNP greater than 40% after only 3 min and greater than 99.2% after 30 min. The yellow color of the PNP solution grad-ually disappeared (inset in Figure 2 B), which confirmed that reduction occurred.

Pt nanoparticles (NPs) are commonly used as a catalyst for reduction reactions.^[21–24] Therefore, it was of interest to compare the catalytic activities of Pt NPs and the H-SiNWAs developed in this work. For Pt NPs (at a concentration of 27.7 μ g mL⁻¹) the conversion rate of PNP was 95% after 30 min (Figure 3) consistent with previous studies.^[23] For H-SiNWAs (at an area of 25 mm²) under the same conditions, the conversion rate of PNP was >99%. Thus H-SiNWAs may be seen as a catalyst for such reduction reactions comparable to Pt NPs. However, in contrast to the commonly used catalysts for reduction, H-SiNWAs do not contain any metal element related to hydrogen activation, such as Ni, Pt, Pd, Al, Cu, or Zn.

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Figure 3. Conversion of PNP using H-SiNWAs and Pt NPs as catalysts. Each column represents the mean of three independent experiments with bars as standard error (SE).

The effect of the surface properties of SiNWAs on the catalytic performance

The catalytic activity of the arrays was shown to depend largely on the chemical composition of the surface. The as-prepared SiNWAs were treated with either HF or "piranha" solution, referred to as H-SiNWAs and P-SiNWAs, respectively. Si reacts with HF to form Si–H bonds;^{125,26]} thus Si–H bonds can be introduced to the surface of the nanowire arrays by HF treatment.^[19,20,27] The chemical composition of the nanowires was investigated by Raman spectroscopy. For the H-SiNWAs, the band at 2100 cm⁻¹ was assigned to Si–H stretching (Figure 4A). In contrast, for the P-SiNWAs, there was no absorption



Figure 4. A) Raman spectra of H-SiNWAs and P-SiNWAs. B) Conversion of PNP by P-SiNWAs and H-SiNWAs over 15 min. The insets show the color of the reaction mixtures. The control is the reaction mixture without the addition of SiNWAs. Each column represents the mean of three independent experiments with bars as SE.

at 2100 cm⁻¹, which indicates that no Si–H bonds were formed on the surface (Figure 4 A). This difference may be related to the different effect of these materials on the reduction of PNP. From the UV/Vis absorption spectra it was estimated that > 90% of PNP was catalytically reduced after treatment with H-SiNWAs for 15 min, whereas P-SiNWAs had no effect (Figure 4B). These results suggest that Si–H bonds on the surface are essential for the catalytic activity of the H-SiNWAs. However, PNP is not reduced to PAP by H-SiNWAs in the absence of $NaBH_4$, which indicates that only in the presence of a reducing agent can the catalytic activity of H-SiNWAs be realized.

The length of the nanowires in the arrays may also be expected to play a role in determining their catalytic performance. Different nanowire lengths were obtained by varying the etching conditions. Arrays with nanowires of length 3.8, 12.6, 23.0, and 55.8 μ m (measured by SEM) were prepared (Table 1). The diameter and spacing of the nanowires were sim-

Table 1. Conditions for the preparation of SiNWAs with different lengths of nanowires.				
Sample	НF [м]	AgNO₃ [mм]	Etching time [min]	Length of nanowires [µm]
S1	5.0	20	8	3.8
S2	5.0	50	10	12.6
S3	5.0	50	30	23.0
S4	7.5	50	30	55.8

ilar in the different arrays (Figure 5A). It was found that the catalytic activity of the H-SiNWAs was closely related to the length of the wires. An HF-treated Si wafer (zero wire length) had no measurable catalytic activity for PNP reduction, whereas H-SiNWAs, even of wire lengths less than 4 μ m, showed strong catalytic activity.

The conversion of PNP was greater than 95% at a nanowire length of 55.8 μ m. Shorter nanowire lengths gave a lower conversion, but even for wires of 3.8 μ m length, the conversion

was 75% (Figure 5B). The catalytic activity of H-SiNWAs is thus not only related to the surface morphology but also to the length of the nanowires, and longer nanowires showed a higher catalytic activity.

As shown above, H-SiNWAs have a high catalytic efficiency for the conversion of PNP to PAP. Most importantly, it was found that the catalytic activity of H-SiNWAs was retained over several reaction cycles of 30 min. Although the conversion decreased slightly after three cycles, it was still greater than 96% after five cycles (Figure 6), and the decreases were not statistically significant. The slight decrease in efficiency may be caused by oxidation of the nanowire surface during the reaction. As oxide layers can be removed and new Si–H bonds can be introduced by HF etching, the activity of the H-SiNWAs is readily recovered by treatment with HF.

Reduction of other nitrobenzene derivatives

Besides PNP, we also showed that H-SiNWAs are an effective catalyst in the reduction of several other nitrobenzene derivatives. For example, *p*-nitroaniline was reduced to *p*-phenylenediamine and sodium *m*-nitrobenzenesulfonate to sodium *m*-aminobenzenesulfonate with conversions of 98.1 ± 0.3 and 98.7 ± 0.5 %, respectively (Table 2). These results indicate that

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Figure 5. Effect of nanowire length on the reduction of PNP. A) SEM sideview images of H-SiNWAs with different nanowire lengths. Average lengths of nanowires: 3.8, 12.6, 23.0, and 55.8 μ m for samples S1–S4 (described in Table 1), respectively. Scale bar = 10 μ m. B) Conversion of PNP. The length of the HF-treated flat silicon surface is taken as zero. Each column represents the mean of three independent experiments with bars as SE.



Figure 6. Reusability of H-SiNWAs in the reduction of PNP over five cycles. For each cycle, the reaction time was 30 min. Each column represents the mean of three separate experiments with bars as SE.

the nanowire arrays have a high catalytic efficiency and may be widely applicable in the reduction of nitrobenzene derivatives. The reduction products obtained were PAP, *p*-phenylenediamine, and sodium *m*-aminobenzenesulfonate, respectively, which are important intermediates in the manufacture of many fine chemicals, such as dyes, developers, antioxidants, oil additives, paracetamols, and anticancer drugs. Therefore, H-SiNWAs have a great potential in industrial production and pharmaceutical preparation.



colorless products).

Compared to some noble metal catalysts and non-noble metal catalysts on the reduction of nitrobenzene derivatives, H-SiNWAs have several significant advantages. Firstly, all the Si nanowires of SiNWAs are attached to the block Si chip, and thus can be easily separated from the aqueous solution directly after reaction. Secondly, it is convenient to regenerate the catalytic activity of H-SiNWAs. If the catalytic performance of the H-SiNWAs decreases, one can regain the reduction activity by simple treatment of the SiNWAs with HF for 5 min. In addition, Si is biocompatible and its content in the Earth's crust is much higher than that of metal. Meanwhile, Si is a key component of organisms. Many studies have shown that Si plays an important role in animal bone and connective tissue development. Thus full utilization of the catalytic activity of H-SiNWAs in reduction reactions may have important implications to human health and social development.

Conclusions

Hydrogen fluoride-treated silicon nanowire arrays (H-SiNWAs) have been shown to be an efficient, recyclable catalyst for the reduction of a wide range of nitrobenzene derivatives. The catalytic performance is related to the surface chemical composition and the length of the nanowires. The activity of the arrays appears to be a result of the presence of Si–H bonds on the material surface and is determined by the length of the nanowires. H-SiNWAs with longer nanowires in the range of 3.8–55.8 μ m have a higher catalytic activity than shorter ones. The silicon-based catalyst may be seen as environmentally friendly relative to conventional noble metal materials. Moreover, silicon is abundant, commercially available, and biocompatible. Thus the use of H-SiNWAs as a substitute for catalysts based on noble metals (e.g., platinum, palladium) may help to

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reduce environmental pollution and toxic effects on organisms.

Experimental Section

Materials

Si wafers (n-doped, (100)-oriented, 0.56 mm thick, and 100 mm in diameter) were purchased from the Guangzhou Institute of Semiconductor Materials (Guangzhou, China). The as-received Si wafers were cut into 5×5 mm square chips. *p*-Nitrophenol (PNP, Aladdin) and NaBH₄ (Aladdin) were used as received. Pt nanoparticles (2 nm) were synthesized using NaBH₄ as a reduction initiator based on a standard citrate reduction method.^[28] Deionized water, purified by using a Millipore water purification system to give a minimum resistivity of 18.2 M Ω cm, was used in all experiments. N₂ gas was of high purity grade. All other solvents were purified according to standard methods before use.

Preparation of SiNWAs

SiNWAs of different lengths were prepared by chemical etching of the Si wafer in AgNO₃/HF aqueous solution.^[29-31] Briefly, the Si wafers were cleaned in a freshly prepared "piranha" solution (H₂SO₄/H₂O₂=7:3, v/v) at 90 °C for 30 min and were then rinsed with deionized water and dried in a stream of N₂. The cleaned Si wafers were immersed in an etching solution containing HF and AgNO₃ of varying concentrations at 50 °C for different times. The resulting surfaces were immersed in 20% HNO₃ for 1 min and then rinsed extensively with deionized water.

Surface treatment of the Si wafer and SiNWAs

The Si wafer and SiNWAs were immersed in HF solution (5% in deionized water, v/v) for 5 min. After treatment, the materials were rinsed with deionized water and then dried in a N₂ stream. The HFtreated Si wafer and SiNWAs were named H-Si and H-SiNWAs, respectively.

SiNWAs were also treated in "piranha" solution at 90 °C for 2 h. After treatment, the materials were rinsed with deionized water and then dried in a stream of N₂. The prepared materials were named P-SiNWAs.

Surface characterization

The surface morphology of different SiNWAs was observed by using a field-emission scanning electron microscope (FESEM, S-4800, Japan). In situ Raman spectra of H-SiNWAs and P-SiNWAs were recorded by using a confocal Raman system (Horiba Jobin Yvon HR800, France). A 632.8 nm He-Ne laser was employed as the excitation source. The laser beam was focused on the samples through a $50 \times$ objective with a long working distance. The slit and pinhole were 200 µm in width and 800 µm in diameter, respective-ly. The data acquisition time was 60 s.

H-SiNWAs as a catalyst in the reduction of PNP

The reduction of PNP was performed in 2.0 mL centrifuge tubes. An aqueous solution of PNP (3 μ L, 10 mM) was added to deionized water (57 μ L), and NaBH₄ (90 μ L, 0.1 M) was added at once. After mixing, a single piece of nanowire array was added to the reaction

solution as a catalyst. The product solution was then taken into another centrifuge tube and centrifuged at 12 000 rpm for 1 min. UV/ Vis absorption spectra were measured by using a Varioskan Flash Multimode Reader (Thermo Fisher Scientific Inc). The formation of PAP was also confirmed from the ¹H NMR spectrum of the product in D₂O (Varian UNITY INOVA 400, USA).

Repeated reduction experiments of PNP with a single batch of the H-SiNWAs catalyst were performed over five cycles. After each cycle, the H-SiNWAs were washed thoroughly with deionized water before putting into another fresh reaction mixture for the next cycle.

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