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Excellent Photocatalysis of HF-Treated Silicon Nanowires

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Heterogeneous photocatalysis is a promising method in the redox reaction.[1] As the selection of the photocatalysts offers special challenges, much effort was focused on looking for new photocatalysts.

Silicon as a main group semiconductor also has photocatalytic activity. In this work, HF-treated silicon nanowires (H-SiNWs) were employed as catalysts in the degradation of rhodamine B, as well as oxidization of benzyl alcohol to benzoic acid. To elevate the photocatalytic efficiency of the degradation, noble metal-modified SiNWs were employed, which were generally recognized as effective due to their easy separation of charges with electrons collected in metal particles.[2] In this work, platinum, palladium, gold, rhodium, and silver were chosen.

The unexpected and unusual results were that H-SiNWs exhibited better photocatalytic activity than Pd-, Au-, Rh-, or Ag-modified ones in the degradation of rhodamine B.

This discovery was pivotal in the application of silicon-related materials as they are normally employed as a catalyst carrier, e.g. silica, zeolites, and diatomite, due to their vast surface area, numerous and diameter-controlled voids, and acidic nature to balance the basity of active metal components.

Another unexpected phenomenon was that H-SiNWs maintained excellent photocatalytic activity even though they had been immersed in solution over one week. This stability in solution was also critical in the application of silicon materials.

The variation in the UV−vis absorption spectra of rhodamine B under these catalysts was shown in the Supporting Information. Figure 1 summarizes the degradation of rhodamine B vs time. The results reveal an unexpected fact: although H-SiNWs were not as good as Pt-modified ones in the photocatalytic activity, they did behave better than other metal-modified ones.

The photocatalytic activity of metal-semiconductor catalysts depends largely on the electron work function of metals, which is a key parameter in the electron transfer process from conducting band to metal. To make the transfer more rapid, a noble metal with a high value of electron work function is needed. Therefore, the Pt-modified SiNW catalysts were the best for photocatalysis with the highest value ($E_{Pt} = 5.65$ eV),[3] while Pd-, Au-, Rh- or Ag-modified ones follow by a decline in their values ($E_{Pd} = 5.12$, $E_{Au} = 5.1$, $E_{Rh} = 4.98$, $E_{Ag} = 4.26$ eV).[3]

Why do H-SiNW catalysts behave with excellent catalytic activity while pristine or HCl-treated SiNWs have no catalytic activity (Figure S6)? The answer might lie in the hydrogen atoms on the H-SiNW's surface.

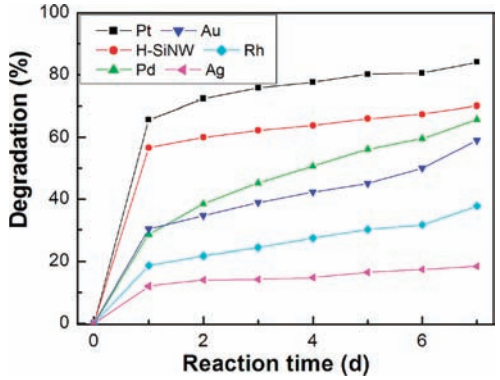

Figure 1. Degradation of rhodamine B under various SiNW catalysts at different times, which reveals the Pt-modified SiNWs have the best catalytic activity, followed by H-treated, Pd-modified, Au-modified, Rh-modified, and Ag-modified ones.

On the surface of H-SiNWs, there are monohydride (SiH), dihydride (SiH_2), and trihydride (SiH_3) species, which were confirmed by an FTIR spectrum.[4] *Ab initio* calculations showed that the charge on the H atom in these three hydrides is in the range 0.09−0.13 au;[5] therefore these H atoms are electron-deficient and may serve as an electron sink.

Figure 2 shows the schematic of electron−hole generation in an H-SiNW photocatalyst particle and part of the mechanism. When a photon with energy equal to or greater than the band gap of the H-SiNW reaches the catalyst's surface, it results in the generation of an electron in the conduction band and a hole in the valence band.

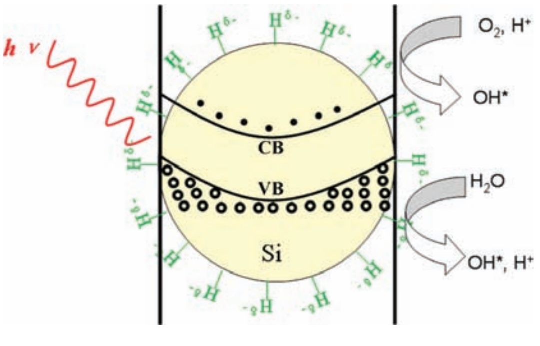

Figure 2. Schematic of the electron−hole generation in H-SiNW photocatalyst and some of the mechanisms involved: (left) Ray promotes the formation of the electron and hole; (middle) the electron transfer to hydrogen atom on the surface; (right) hole is used in the formation of the OH* groups promoting oxiding processes.

The induced hole receives the electron from adsorbed water and results in OH* free radical groups.

Hydrogen atom has a large Pauling electron negative value of 2.2; consequently, the terminated hydrogen atom with a charge of

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0.09−0.13 au may serve as an electron sink and accelerate the separation of the electron and hole.

Here, terminated hydrogens accelerate the separation of photoinduced electrons and holes and promote the photocatalytic efficiency.

Finally, the reactive OH* radicals oxidize and degrade organic adsorbed pollutants.

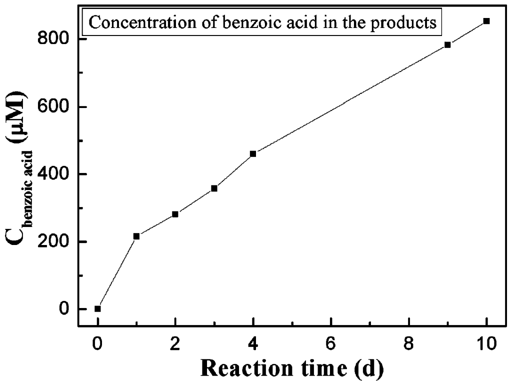

Figure 3. Concentration of benzoic acid vs reaction time.

To further investigate catalytic activity, 20 mg of SiNWs were etched and employed as catalysts by adding them to 50 mL of acetonitrile solution with an initial reagent concentration of 0.2 M benzyl alcohol. Figure 3 indicates the concentration of benzoic acid increases with increasing reaction time, clearly revealing catalytic activity of the H-SiNWs since benzyl alcohol cannot change to benzoic acid in the absence of H-SiNWs. For comparison, two contrast experiments were performed by keeping all other conditions constant except when using SiNWs or HF solution in place of H-SiNWs; the oxidation reaction could not take place.

Another unexpected phenomenon was that the H-SiNW catalysts still had excellent catalysis after being immersed in solution over one week. To gain a full understanding of the stability of this system, XPS measurements have been employed to analyze the composition and surface state of the H-SiNW catalysts.

In the F1s core XPS spectrum of H-SiNWs (see Supporting Information) there exists a symmetrical peak centered at 687.4 eV. The peak may belong to a Si−F bond because the F1s peak of LiF is located at 684.9 eV and that of Na_2SiF_6 at 686.4 eV.[6] This F1s peak reveals that the H-SiNWs are partially terminated with a fluorine ion. The atomic ratio of F/Si is calculated as 0.26:1. Fluorine as the most electronegative element stands for the most stable terminator[7] and would help H-SiNW catalysts maintain excellent photocatalytic activity. After the H-SiNWs were immersed in water for one week and characterized with XPS, the surface atomic ratio of F/Si decreased to 0.04:1.

The present results suggest a new feature of the catalytic properties of the main group elements. H-SiNWs exhibited excellent photocatalytic activity even though they were immersed in solution over one week. This stability might be due to the fluorine terminator. It is hoped that our findings will stimulate further investigations and have potential application.

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Supporting Information Available: Experimental procedures for nanomaterials, SEM and TEM image, and photocatalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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