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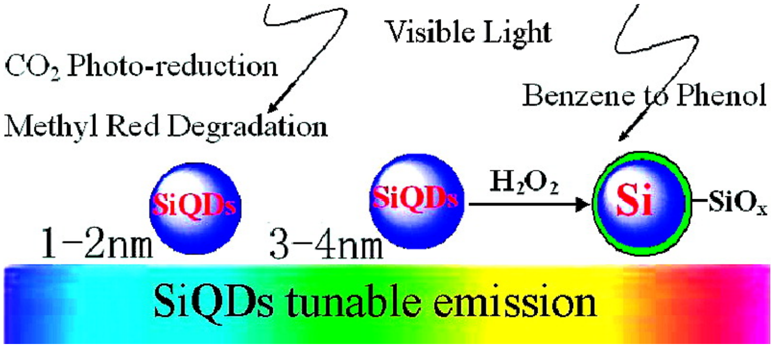

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Silicon Quantum Dots: A General Photocatalyst for Reduction, Decomposition, and Selective Oxidation Reactions

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Photocatalysis is important for many current environmental and energy issues.[1−3] Semiconductors are commonly selected as photocatalysts on the basis of their band gaps to absorb light over a wide spectral range. To perform photocatalysis, a semiconductor absorbs energy equal to or larger than its band gap to form electron/hole (e^-/h^+) pairs.[1] A good photocatalyst should be able to utilize visible and/or near UV light and be photostable (against photocorrosion), inexpensive, and nontoxic.[1−3] Nanoscience research can greatly impact the development of new and more potent catalysts via design and control of photocatalyst properties, especially in terms of energy gap, chemical composition, and surface modification.

Silicon (Si) and carbon nanostructures are particularly interesting in this regard.[4−6] Carbon nanotubes and graphite nanofiber-based systems have shown promising catalytic activity and selectivity despite their very small energy gaps.[6a−c,7] Because of unique properties and huge Si-based microelectronics market, Si nanostructures are arguably the most important semiconductor nanomaterial. Porous Si and Si nanoparticles are good photosensitizers because of singlet oxygen generation in solution.[6d−f] In particular, size-controlled Si quantum dots (SiQDs) show tunable emission from near-infrared to blue wavelength,[6c] making them promising candidates for photocatalysts. Here, we demonstrate that 1−2 nm SiQDs can function as excellent photocatalysts for CO_2 reduction and dye (methyl red) degradation, while 3−4 nm SiQDs are effective photocatalysts for selective oxidation of benzene. The versatility of an SiQD as a general photocatalyst is summarized in Scheme 1, which shows the size dependence of emission and photocatalytic activity of SiQDs for different reactions.

Hydrogen-terminated SiQDs (H-SiQDs) were prepared by electrochemical etching method.[6c] Figure 1a shows the transmission electron microscopy (TEM) image of as-prepared SiQDs. Photoconductivity of thin films of SiQDs formed between two gold electrodes via gentle evaporation of SiQDs colloidal solution (SiQDs/*n*-hexane) are shown in Figure 1b. It reveals that the photocurrent is 3×10^{-11} A under a normal microscope light, and only about 10^{-13} A in the dark. The 100 times difference in current shows the good photoconductivity of SiQDs. The photoluminescence (PL) spectrum of 1−2 nm and 3−4 nm SiQDs is respectively depicted in Figure 1c and 1d (TEM images shown in Supporting Information, Figure S1). The red shift of the PL band with increasing SiQDs size may be due to the quantum confinement effect in SiQDs.[6c] The PL data show 1−2 nm SiQDs have band gaps of 2.3−3.5 eV and absorb green to near-UV light, while 3−4 nm SiQDs have band gaps of 1.5−2.2 eV and absorb red to green light. Therefore, 1−4 nm SiQDs may serve as photocatalyst, especially the 1−2 nm ones.

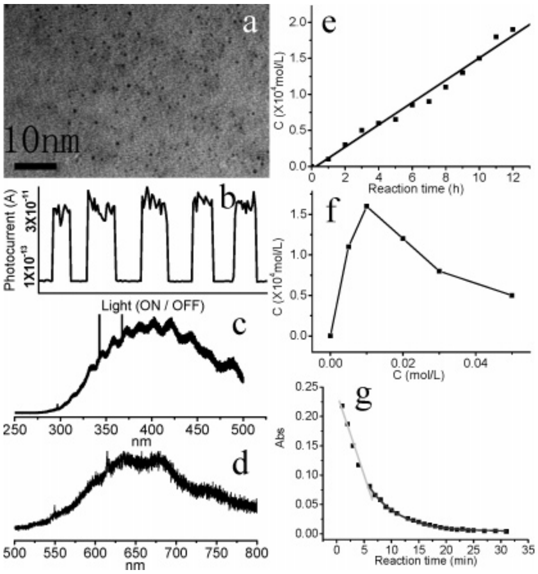
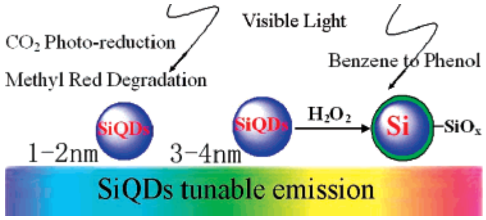


Figure 1. (a) TEM images of SiQDs and (b) photoresponse of SiQDs film; PL spectra of (c) 1−2 nm and (d) 3−4 nm SiQDs, respectively; (e) product ($CH_2O/HCOOH$) concentration versus reaction time; (f) reduction rate or ($CH_2O/HCOOH$) concentration (reaction time 12 h) versus [CO_3^{2-}]; (g) methyl red concentration versus reaction time.

Scheme 1 . Different Diameters SiQDs for Different Reactions



We selected the photochemical reduction reaction of CO_2/CO_3^{2-} to study the photocatalytic ability of 1−2 nm SiQDs for their band-gaps of 2.3−3.5 eV. Photochemical reduction was carried out in a 100 mL conical flask containing 0.01 M CO_2-saturated Na_2CO_3 solution and a suitable amount of 1−2 nm SiQDs as catalyst, using a 150 W halogen lamp for illumination. The concentration of the reduction product (formaldehyde, CH_2O, and formic acid, HCOOH) was determined by Nash reagent ($\lambda_{max} = 412$ nm),[8] while other products were not monitored. Figure 1e shows that the product concentration increases roughly linearly with reaction time indicating a zeroth-order reaction (apparent kinetics), which is consistent with surface reaction being the major pathway in the photochemical reaction.[1−3] The reduction rate of CO_2/CO_3^{2-} (or ($CH_2O/HCOOH$) concentration) is highly dependent on Na_2CO_3 concentration as depicted in Figure 1f. It shows the rate first increases with increasing [CO_3^{2-}] until 0.01 M of [CO_3^{2-}], above which the rate begins to fall and decrease with increasing [CO_3^{2-}], probably due to the influence of Na^+.[8b] As 1−2 nm SiQDs may also photocatalyze degradation of dyes, we studied photodegradation of methyl red

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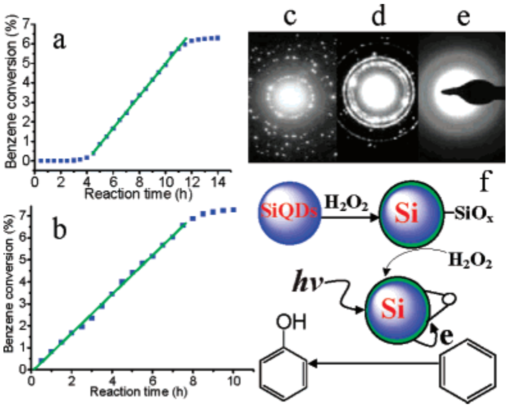

Figure 2. Benzene conversion versus reaction time for (a) 3−4 nm H-SiQDs as photocatalyst and (b) partially oxidized 3−4 nm SiQDs as photocatalyst; ED patterns of (c) H-terminated, (d) partially oxidized, and (c) fully oxidized SiQDs, respectively; (f) mechanism for photocatalytic conversion of benzene to phenol.

using similar conditions to CO_2/CO_3^{2-} reduction. Methyl red was determined spectrophotometrically at $\lambda_{max} = 490$ nm. Figure 1g plots methyl red concentration versus reaction time. It shows the reaction rate is initially zeroth-order (apparent kinetics) at 0−7 min, but changes to first-order (apparent kinetics) at a longer reaction time as methyl red concentration reduces. In sharp contrast to 1−2 nm SiQDs, when 3−4 nm SiQDs (with amounts 1−3 times more) are used as catalyst, the same experiments showed no photochemical reduction of CO_2/CO_3^{2-} and little or no photodegradation of methyl red. The striking difference in reactivity may be attributed to the larger e^-/h^+ pair energy of 1−2 nm SiQDs than that of 3−4 nm SiQDs, so that the former has sufficient energy to induce photochemical reduction of CO_2/CO_3^{2-} and degradation of methyl red.

We next investigate whether 3−4 nm SiQDs with a smaller band gap of 1.5−2.2 eV can also be a potent photocatalyst. The following experiments show that 3−4 nm SiQDs indeed can function as a photocatalyst for hydroxylation of aromatic hydrocarbons. Hydroxylation of benzene by H_2O_2 with 3−4 nm SiQDs as photocatalyst was performed at room temperature and under illumination of a 150 W halogen lamp. Figure 2a plots benzene conversion against reaction time. It shows in the initial 2 h no phenol was formed, and from 5 to 11 h benzene conversion was approximately linearly proportional to the reaction time. Finally after 12 h hydroxylation reaction changes to first order (kinetic analysis is in supporting materials). We explain the reaction process as follows. In the first 2 h the as-prepared SiQDs were primarily hydrogen terminated (electron diffraction (ED) pattern in Figure 2c), and catalytically inactive. Subsequently, H-SiQDs were gradually oxidized by H_2O_2 into a Si/SiO_x core−shell structure, which served as the actual catalyst for benzene hydroxylation. In support of the above explanation, Figure 2b shows the relationship between benzene conversion and reaction time when partially or lightly oxidized SiQDs (ED pattern in Figure 2d, TEM images in Figure S1) were used as photocatalyst. It reveals clearly that right from the beginning hydroxylation reaction was already operative and first order, which was distinctively different from the first 2 h reaction in Figure 2a. It is important to point out that hydroxylation of benzene yielded almost 100% phenol and light was essential for the high selectivity, since control experiments in the dark produced less than 95% phenol and byproducts from over-oxidation of phenol. However, if fully oxidized SiQDs (ED pattern shown in Figure 2e, TEM images in Figure S1) were used as catalyst, phenol selectivity was also poor (<95%) even under illumination. Further experiments show that photooxidation of toluene also predominantly occurred at the benzene ring, yielding a mixture of cresols (ortho/meta/para isomer ratio ≈ 3.0:1.0:5.0) with high ~80% selectivity, and the ratio of ring oxygenation to methyl group oxygenation was about 7.8.

Active oxygen species are known to be nucleophilic, electrophilic, or radical. Since oxygen attacks selectively the benzene ring during hydroxylation, negatively charged oxygen species are unlikely the active ones because they are nucleophilic. On the other hand, if radicals are the main active species, then more benzyl alcohol and benzaldehyde should be produced instead of cresols in toluene hydroxylation.[9] Therefore, we deduce the active oxygen species responsible for hydroxylation is more likely to be electrophilic. Oxene, an active oxygen species produced by H_2O_2 decomposition, can readily add to carbon−carbon double bonds, such as those in benzene. This kind of oxygen addition is 10^3 times faster than hydrogen abstraction from methyl group.[7,9] While its exact identity is unclear, it may be certain that the active oxygen species has a strong oxene character. From the above results and discussion, we propose the mechanism of photocatalysis as depicted in Figure 2f: H-SiQDs were partially oxidized by H_2O_2 and formed the Si/SiO_x core−shell structure, on which H_2O_2 molecules adsorbed and decomposed into active oxygen species with oxene characteristics, which are electrophilic and prone to oxidize benzene ring to phenol. Significantly, the products (phenols) are protected by the photoelectron reductive environment, which prevents further oxidation of phenols, thus yielding high selectivity of phenol formation.

In summary, we demonstrate that 1−2 nm SiQDs can function as photocatalysts for CO_2 reduction and dye (methyl red) degradation, while 3−4 nm SiQDs are effective photocatalysts for selective oxidation of benzene into phenol. Thus, a SiQD may serve as a general photocatalyst for reduction, decomposition, and selective oxidation. Such capabilities of SiQDs are attributable to their tunable band gap and excellent photoconductivity properties. By controlling the surface and band gap of SiQDs, one can expect to design and prepare more novel catalysts via modification with different nanospecies (e.g., TiO_2, Au, Pt, C, etc.).

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Supporting Information Available: Experimental details, detailed characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Bhatkhande, D. S.; Pangarkar, V. G.; Beenackers, A. *J. Chem. Technol. Biotechnol.* **2001**, *77*, 102.
(2) Kabra, K.; Chaudhary, R.; Sawhney, R. L. *Ind. Eng. Chem. Res.* **2004**, *43*, 7683.
(3) Linsebigler, A. L.; Lu, G.; Yates, J. T. *Chem. Rev.* **1995**, *95*, 735.
(4) Morales, A.; Lieber, C. M. *Science* **1998**, *279*, 208.
(5) (a) Ma, D. D. D.; Lee, C. S.; Au, F. C. K.; Tong, D. S. Y.; Lee, S. T. *Science* **2003**, *299*, 1874. (b) Sun, X. H.; Li, C. P.; Wong, N. B.; Lee, C. S.; Lee, S. T.; Teo, B. K. *J. Am. Chem. Soc.* **2002**, *124*, 14856. (c) Wang, N.; Tang, Y. H.; Zhang, Y. F.; Lee, C. S.; Lee, S. T. *Phys. Rev. B* **1998**, *58*, R16024.
(6) (a) Kang, Z. H.; Wang, E. B.; Gao, L.; Lian, S. Y.; Jiang, M.; Hu, C. W.; Xu, L. *J. Am. Chem. Soc.* **2003**, *125*, 13652. (b) Kang, Z. H.; Wang, E. B.; Mao, B. D.; Su, Z. M.; Gao, L.; Lian, S. Y.; Xu, L. *J. Am. Chem. Soc.* **2005**, *127*, 6534. (c) Kang, Z. H.; Tsang, C. H. A.; Zhang, Z. D.; Zhang, M. L.; Wong, N. B.; Zapien, J. A.; Shan, Y. Y.; Lee, S. T. *J. Am. Chem. Soc.* **2007**, *129*, 5326. (d) Kovalev, D.; Fujii, M. *Adv. Mater.* **2005**, *17*, 2531. (e) Fujii, M.; Kovalev, D.; Goller, B.; Minobe, S.; Hayashi, S.; Timoshenko, V. Y. *Phys. Rev. B* **2005**, *72*, 165321. (f) Fujii, M.; Usui, M.; Hayashi, S.; Gross, E.; Kovalev, D.; Künzner, N.; Diener, J.; Timoshenko, V. Y. *J. Appl. Phys.* **2004**, *95*, 3689.
(7) Kang, Z. H.; Wang, E. B.; Mao, B. D.; Su, Z. M.; Gao, L.; Niu, L.; Shan, H. Y.; Xu, Lin. *Appl Catal., A* **2006**, *299*, 212.
(8) (a) Nash, T. *Biochem. J.* **1953**, *55*, 416. (b) Yang, Q. H.; Cui, X. L.; Fu, X. X. *Chin. Chem. Lett.* **2005**, *68*, 320.
(9) (a) Niwa, S.; Eswaramoorthy, M. S.; Nair, J.; Raj, A.; Itoh, N.; Shoji, H.; Namba, T.; Mizukami, F. *Science* **2002**, *295*, 105. (b) Otsuka, K.; Yamanaka, I.; Hosokawa, K. *Nature* **1990**, *345*, 697. (c) Clerici, M. G.; Ingallina, P. *Catal. Today* **1998**, *41*, 351. (d) Neumann, M. G.; Jonathan, N. *J. Chem. Soc. B* **1970**, *167*, 1970. (e) Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115.

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