Tunable Metal/Silicon Hybrid Dots Catalysts for Hydrocarbon Selective Oxidation

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ABSTRACT: Metal (Au, Ag, and Pt)/silicon hybrid dots were facially prepared by a one-step reaction between Si quantum dots (SiQDs) and metal salts at room temperature without any templates and surfactants. The obtained Au/SiQDs were demonstrated to be a superior catalyst for selective oxidation of cyclohexene. By altering the composition of Au/SiQDs catalysts, the selectivity of main products can be tuned step-by-step.

1. INTRODUCTION  
High activity and special surface properties make inorganic nanoparticles (Au, Pt, CuO, TiO₂, etc.) possess excellent catalytic abilities and great potential applications as a new generation catalysts. The most attractive merit of nanocatalysts is that the activity and selectivity of a catalytic reaction can be manipulated by tuning the size, composition, and morphology of the nanocatalysts. For nanocatalysis, one of the main objectives is the design of nanocatalysts with strong and tunable chemical activity, selectivity, stability, and easy recovery.  

Besides metal and traditional semiconductor nanoparticles, silicon (Si) nanostructures are regarded as a promising candidate for nanocatalysts (or catalysts support) and have received considerable attention in photoreduced oxidation, hydrocarbon selective oxidation, and solar water splitting. Notably, the size-controlled photocatalytic abilities of Si quantum dots (SiQDs) are attributable to their tunable band gap and excellent photoconductivity properties. Here it should be pointed out that SiQDs (easily converted to Si−H surfaces by HF treatment) have the advantages of easy surface modification with various metals, organic groups, and oxides, large specific surface areas, and high chemical reactivity. By controlling the surface and band gap of SiQDs, one can expect to design and prepare more novel nanocatalysts via modification with different nanospecies (e.g., TiO₂, Au, Pt, C, etc.). Therefore, exploring and understanding the catalytic properties of SiQDs-based complex nanosystem is extremely important for nanocatalysis both fundamentally and technologically.  

In this article, we demonstrated one-step synthesis of metal/SiQDs hybrid dots (M/SiQDs, M = Au, Ag, and Pt) by reducing various metal salts with SiQDs (about 2−4 nm) in ethanol at room temperature, without any templates and surfactants. (See Figure 1a.) These hybrid dots (~5 nm) show high catalytic activity on the selective oxidation of cyclohexene with H₂O₂ as oxidant at room temperature. Notably, as shown in Figure 1b, by altering the composition (Au wt%) of Au/SiQDs, the selectivity for the main products (1,2-cyclohexanediol and 2-cyclohexene-1-ol) can be tuned step-by-step.

2. EXPERIMENTAL SECTION  
Silicon wafer (phosphorus-doped (p-type), 0.002 Ω sensitivity), hydrofluoric acid (HF), hydrogen peroxide, polyoxometalates

Received: June 2, 2012  
Revised: August 16, 2012  
Published: September 1, 2012
(POMs), HAuCl₄, K₂[PtCl₆], and AgNO₃ were purchased from Sigma-Aldrich. All chemicals were used as-received without additional purification.

H-terminated SiQDs were synthesized following our previous reports. In a typical procedure to synthesize the M/SiQDs hybrids, SiQDs were ultrasonically dispersed in 60 mL of ethanol solution and then divided into three parts; at the same time, metal salt solutions were prepared by dissolving 0.01 mmol HAuCl₄, K₂[PtCl₆] and AgNO₃ in 1 mL of distilled water. Under continuous magnetic stirring condition in a dark environment at room temperature, 20 μL metal salt solutions were added dropwise to SiQDs solution, respectively. The M/SiQDs hybrids were obtained 5 min later. To prepare hybrids with different Au loading, we added 20, 50, 100, 150, and 200 μL HAuCl₄ solutions dropwise to SiQDs solution, respectively, producing M/SiQDs hybrids with 15, 25, 35, 45, and 55 wt % Au loading. After thoroughly washed by DI water and ethanol, the final products were dried and kept in a vacuum dryer at room temperature.

In a typical catalytic experiment, the oxidation of cyclohexene (Sigma-Aldrich, 95%) under mild condition was performed in a 50 mL round-bottomed flask connected to a water condenser and equipped with a magnetic stirrer. In brief, 25 mg of Au/SiQDs was first dispersed in 10 mL of cyclohexene; then, 10 mL of H₂O₂ was added to the solution drop-by-drop. The reaction was carried out in air at ambient pressure at 60 °C in oil bath with stirring for 2.5 h. The sample was extracted from the reaction system every 0.25 h. Analysis of products was carried out by using gas chromatography−mass spectrometry measurements.

Transmission electron microscopy (TEM) images of SiQDs were obtained with a FEI/Philips Tecnal 12 BiO/TWIN TEM. For the TEM observations, the samples were dispersed in ethanol and then dried on a holey carbon film Cu grid. UV−visible spectra were obtained with an Agilent 8453 UV−vis diode array spectrophotometer. The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2500 V PC diffractometer using Cu Kα radiation. For XRD observations, the samples were dispersed in ethanol and then dried on a Ti film. X-ray photoelectron spectroscopy (XPS) was obtained by using a KrATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatized Mg Kα X-ray. Gas chromatography−mass spectrometry measurements were performed using an Agilent 6890 GC system coupled to an Agilent 5973 quadrupole mass-selective detector equipped with a HP 5MS column (30 m long, 0.25 mm i.d., 0.25 μm film thickness).

3. RESULTS AND DISCUSSION

Hydrogen-terminated SiQDs (H-SiQDs, 1 to 2 nm) were prepared by using the electrochemical method developed by our research group. M/SiQDs (Au/SiQDs, Ag/SiQDs, or Pt/SiQDs) hybrid dots were briefly obtained by mixing the metal salt solutions (HAuCl₄, K₂[PtCl₆], or AgNO₃) and SiQDs solution (SiQDs in ethanol) under continuous magnetic stirring condition in a dark environment at room temperature. Figure 2 shows the photographs of the M/SiQDs samples in aqueous solution at room temperature. The UV−vis absorption spectra of SiQDs and Au/SiQDs are compared in Figure 3a. As shown, a broad absorption peak from 260 to 400 nm is observed in the red curve for SiQDs, whereas for Au/SiQDs hybrid dots, the absorption peak (black curve) shows an obvious red shift to ~545 nm, which indicates the formation of Au nanoparticles and is also responsible for its red color (Figure 2). Similarly, for Ag/SiQDs hybrid dots, the absorption peak at 435 nm is associated with Ag nanoparticles and is corresponding to its yellow color (Figure 2). The absorption spectrum (Figure S1 of the Supporting Information) of Pt/SiQDs is similar to that of SiQDs because PtNPs have no obvious absorption peaks at λ > 200 nm, and this result is also coincident with the Pt colloids reported in previous studies.

Figure S2a of the Supporting Information shows the TEM image of Au/SiQD hybrid dots as shown, the resultant Au/SiQDs hybrid particles appear as spherical dots with good monodispersity. Figure 3b displays the high-resolution TEM (HRTEM) image of the single as-prepared Au/SiQDs hybrid dots, clearly exhibiting the firmly contacted boundary between SiQD and Au nanoparticle. Moreover, Si dot keeps its single-crystalline structure in the obtained Au/SiQDs, and the lattice fringe spacing of ~0.31 nm agrees well with the (111) plane spacing of Si crystal. Whereas the well-resolved lattice fringe spacing of ~0.24 nm is attributed to the (111) plane of Au crystal with excellent crystalline nature. The TEM and HRTEM images of Pt/SiQDs and Ag/SiQDs hybrid dots are shown in Figures S2 and S3 of the Supporting Information.

XPS was carried out to check the surface composition and chemical environment of the obtained M/SiQDs hybrid dots. Figure S4 shows the typical full survey spectra of M/SiQDs: S4a, S4b, and S4c for Au/SiQDs, Ag/SiQDs, and Pt/SiQDs, respectively. A weak C1s feature at 285.0 eV was observed in the wide scan XPS spectra, indicating the presence of a minor carbonaceous component commonly found as a result of sample handling in air. The O1s spectra for these samples consist of a feature at a binding energy of ~532.9 eV, indicating the slight oxidation on the Si particle surface. The detailed XPS spectra of Au/SiQDs are shown in Figure 3c,d. The Si 2p core level spectra (Figure 3c) can be deconvoluted typically into four component peaks with binding energies at about 100, 102.3, 103.1, and 104 eV, respectively. The lower binding energy peak at ~100 eV corresponds to the Si0 of Au/SiQDs, whereas the higher binding energy peaks at about 103.1 and 104 eV are attributable to the Si⁺ and Si²⁺ of the oxidized state due to the formation of SiO₂ on SiQDs surface. Notably, the obvious peak at ~102.3 eV in Si2p line (Figure 3c, shaded peak) can be assigned to the formation of metallic Si alloy in Au/SiQDs. As shown in Figure 3d (the Au4f XPS spectra of Au/SiQDs), the binding energies for Au4f doublet (4f₇/₂ and 4f₅/₂) appeared at about 84.8 and 88.5 eV can be assigned to metallic gold, which are slightly higher than that of bulk Au (84.0 and 87.7 eV), further indicating the partially formation of AuSi in the hybrid dots. Combining the UV−vis, HRTEM, and XPS results, it can be concluded that the Au/SiQDs hybrids are not the simple mixture of SiQDs and Au dots but the hybrid dots with partial alloy (AuSi) nature. The XPS spectra of Pt/SiQDs and Ag/SiQDs are given in Figure 4, and similar to Au/SiQDs, Pt/SiQDs and Ag/SiQDs also show the formation of partial metal/Si alloy (PtSi and AgSi).

The catalytic performance of Au/SiQDs was investigated for the selective oxidation reaction of cyclohexene at 60 °C using H₂O₂ as oxygen donors. The detailed conversion of cyclohexene...
and selectivity for oxidation products with Au/SiQDs (Au, 55 wt %) as catalysts is shown in Figure 5a. In the beginning of the oxidation reaction (within 0.75 h), the selectivity for 1,2-cyclohexanediol (one of the main products) was only ∼8%, which increased with reaction time, and reached up to 20% after 2.5 h of reaction (see pink line). In this process, the selectivity of 2-cyclohexene-1-ol (the other main product) was kept at ∼52% (see blue line). Epoxyclohexane and 2-cyclohexene-1-one, as byproduct, have only a very slight decrease when increasing the reaction time (see red and green line in Figure 5a).

In the followed studies, a series of catalytic experiments were carried out to investigate further the catalytic behavior of Au/SiQDs hybrid dots with different Au loadings. In those experiments, Au/SiQDs hybrid dots with Au loadings of about...
15, 25, 35, 45, and 55 wt % were prepared, respectively (HRTEM images and EDX analysis shown in Figure 6), and used as catalysts directly for the oxidation of cyclohexene. Figure 5b reveals the relationship between conversion of cyclohexene and the reaction time by using these Au/SiQDs samples as catalysts (reaction profiles shown in Figure S5 of the Supporting Information). From it we can see that Au loadings have no obvious effect on the conversion of cyclohexene during the catalytic oxidation process. However, it is significant to note that the Au loadings can strongly affect the selectivity of the main oxidation products (2-cyclohexene). As shown in Figure 5c, the selectivities for main products (2-cyclohexene-1-ol and 1,2-cyclohexanediol) are changed gradually by altering the Au loadings of Au/SiQDs step by step: lower Au loading (15 wt %) is more preferable to the formation of 1,2-cyclohexanediol (selectivity about 52%), and higher Au loading (55 wt %) is favorable for the formation of 2-cyclohexene-1-ol (selectivity about 50%), whereas, the selectivities for the byproduct (epoxycyclohexane and 2-cyclohexene-1-one for about 25 and 5%, respectively) are not strongly affected by Au loadings during the catalytic process (Figure 5d). These results indicate that catalytic selectivity of Au/SiQDs hybrid dots may be tunable via careful selection of Au loadings.

In the final set of experiments, for comparison, we investigated the cyclohexene oxidation in the presence of SiQDs and Au nanoparticles as catalysts directly (comparison details, see Table S1 of the Supporting Information). Under the same reaction conditions, the conversion efficiency of cyclohexene was only ∼5%, whereas the selectivity for 1,2-cyclohexanediol reached ∼96% when SiQDs were used as catalysts directly, which may be attributed to the weak Lewis acid sites of SiO$_2$ on SiQDs. (H-SiQDs can be partially oxidized by H$_2$O$_2$ and transformed into Si/SiO$_2$ core shell structure.) Further detailed investigation on the cyclohexene oxidation reveals that when using the same amount of Au nanoparticles as catalysts (Au nanoparticles show poor stabilities), 2-cyclohexen-1-ol was the major final product with selectivity of ∼73%, and the relatively high conversion efficiency of cyclohexene of ∼36% would be attributed to the strong catalytic abilities of Au nanoparticles on H$_2$O$_2$ decomposition. However, in these control catalytic experiments, no obvious changes in the selectivity for main products (1,2-cyclohexanediol or 2-cyclohexene-1-ol) can be observed, even if a different amount of Au nanoparticles or a mixture of SiQDs and Au nanoparticles were used as catalysts. In general, a good catalyst should be stable under repeated catalytic application. To test the repeatability of the Au/SiQDs hybrids, ten times catalytic experiments were carried out with the recycled catalysts. As shown in Table S2 of the Supporting Information, Au/SiQDs hybrids are stable enough under repeated application with nearly constant conversion.

On the basis of the above experimental results, the excellent catalytic properties of Au/SiQDs can be roughly explained as follows. Au dots were first formed by reacting Si–H with Au$^{3+}$ (Si–H bonds have strong reducing reactivity) and then stabilized...
or anchored on SiQDs and isolated or separated from other Au dots. These features are the key factors for the enhanced catalytic activity (high conversion) and good repeatability of Au/SiQDs hybrids. Furthermore, the high surface area of Au/SiQDs hybrid dots (particles size less than 5 nm) is also another possible reason for their high catalytic activity. Notably, the unique alloy nature of Au silicide in Au/SiQDs hybrids may change the factor strongly the catalytic properties is now in progress.

4. CONCLUSIONS

In summary, we present a facile one-step synthesis of M/SiQDs hybrid dots at room temperature without any templates and surfactants. The obtained Au/SiQDs hybrids (<5 nm) were shown to exhibit high catalytic activity for the selective oxidation of cyclohexene with H2O2 as oxidant. Remarkably, the Au loadings in Au/SiQDs hybrids were found to affect strongly the selectivity to the main products but have no obvious effect on the conversion of cyclohexene. That is to say, the catalytic ability of Au/SiQDs hybrids is tunable. This approach can be extended to the preparation of other noble metals or their alloys nanoparticles on SiQDs. Furthermore, the M/SiQDs hybrid dots system can be regarded as an ideal model of complex nanosystem for catalyst design. On the basis of the active surface and tunable band gap nature of SiQDs, further work on the surface modification by different nanospecies (TiO2, Cu, Pt, Ag, C, etc.) may offer unique opportunities for a myriad exciting applications in nanocatalysis, catalyst design, and new energy.

ASSOCIATED CONTENT

1. Supporting Information
Materials characterizations and results of catalytic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the National Basic Research Program of China (973 Program) (No. 2012CB825800), National Natural Science Foundation of China (NSFC) (No. 51132006, 21073127, 21071104), a Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (FANEDD) (No. 200929), a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), a Suzhou Planning Project of Science and Technology (ZXG2012028), and a project supported by the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 11KJB150015).

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