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Nanostructured Catalysts

Visible-Light-Driven Oxidation of Organic Contaminants in Air with Gold Nanoparticle Catalysts on Oxide Supports**

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One of the great challenges in catalysis is to devise new catalysts that have high activity when illuminated by visible light.[1] Solving this challenge will allow us to use sunlight, an abundant and clean low-cost energy source, to drive chemical reactions. Visible light (wavelength $\lambda > 400$ nm) constitutes around 43% of solar energy,[2] and the energy of sunlight to the Earth is about 10000 times more than the current energy consumption of the world.[3] Many approaches have been proposed to develop visible light photocatalysts, including doping TiO_2 with metal ions or metal atom clusters,[4,5] incorporating nitrogen[6] and carbon[7] into TiO_2, and employing other metal oxides or polymetallates as catalyst materials.[2,4,5,8] Research has been mainly concentrated on semiconductor oxides. Sulfides have also been studied, but they are not suitable catalysts because of their poor chemical stability.[1,4] However, searching for catalysts that can work under visible light should not be limited to semiconductor materials with band-gap structure, but can be extended to other materials, such as gold nanoparticles.

It can be said that glaziers in medieval forges were the first nanotechnologists who produced colors with gold nanoparticles of different sizes,[9] although they had little understanding of the modern day principles which have become a hot topic in the last two decades. In recent years there have been numerous studies on the optical properties of gold nanoparticles.[10] Gold nanoparticles absorb visible light intensely because of the surface plasmon resonance (SPR) effect.[10,11] The electromagnetic field of incident light couples with the oscillations of conduction electrons in gold particles, resulting in strong-field enhancement of the local electromagnetic fields near the rough surface of gold nanoparticles.[12] The enhanced local field strength can be over 500 times larger than the applied field for structures with sharp apices, edges, or concave curvature (e.g. nanowires, cubes, triangular plates, and nanoparticle junctions).[13] The SPR absorption may cause rapid heating of the nanoparticles.[14,15]

Gold nanoparticles supported on metal oxides are efficient catalysts for important oxidation process, including selective oxidation of hydrocarbons and oxidation of various volatile organic compounds (VOCs), such as CO, CH_3OH, and HCHO at moderately elevated temperatures.[16,17] Therefore, the combination of the SPR absorption and the catalytic activity of gold nanoparticles presents an important opportunity: if the heated gold nanoparticles could activate the organic molecules on them to induce oxidation of the organic compounds, then oxidation on gold catalysts can be driven by visible light at ambient temperature. Moreover, the SPR is a local effect, limited to the noble metal particles, so that the light only heats gold nanoparticles, which generally account for a few percent of the overall catalyst mass.[16] This leads to significant saving in energy consumption for catalyzing organic compound oxidation.

To verify the possibility of driving the VOC oxidation with visible light at room temperature, we prepared gold particles supported on various oxide powders. ZrO_2 and SiO_2 powders were first chosen as supports, because their band gaps are circa 5.0 eV[18] and circa 9.0 eV,[19] respectively, which are much larger than the energies of the photons of visible light (less than 3.0 eV). Thus, the light cannot excite electrons from the valence band to the conduction band. It is also impossible for the gold nanoparticles on ZrO_2 to reduce the band gaps of ZrO_2 enough for visible light photons to be absorbed and excite electrons in ZrO_2. Thus, the catalytic activity is not caused by the same mechanism as occurs in semiconductor photocatalysts, but is due to the SPR effect of gold nanoparticles. The changes in the concentrations of the reactant (HCHO, 100 ppm) and product (CO_2), when gold supported on ZrO_2 was used as the catalyst, are depicted in Figure 1a.

The initial concentration of HCHO in the glass vessel was 100 ppm. HCHO content decreased by 64% in two hours under the irradiation of six light tubes of blue light (with wavelength between 400 and 500 nm and the irradiation energy determined to be 0.17 $W\,cm^{-2}$ at the position of glass slides coated with the gold catalysts), and the CO_2 content in the vessel increased accordingly. These results confirm that the oxidation of formaldehyde to carbon dioxide proceeds to a large extent at ambient temperature. The turnover frequency was calculated as being about 1.2×10^{-3} molecules of

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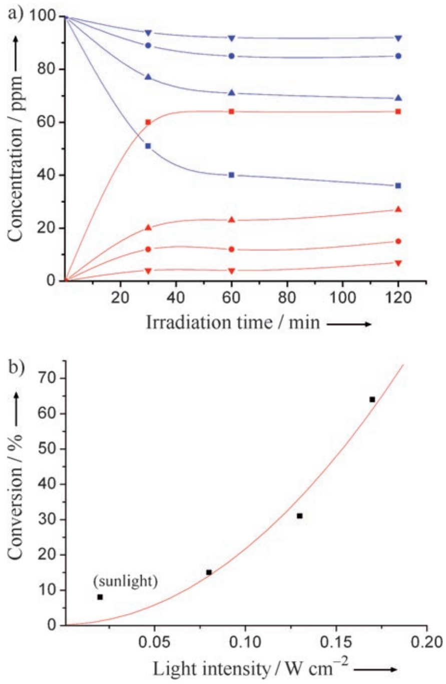

Figure 1. Oxidation of 100 ppm HCHO on gold nanoparticles supported on ZrO_2 (Au/ZrO_2) under blue light or sunlight at 25 °C. a) Changes in reactant HCHO (blue lines) and product CO_2 (red lines) under different light intensities (■ 0.17, ▲ 0.13, ● 0.08, and ▼ 0.02 W cm^{-2}) as a function of irradiation time. b) The relationship between HCHO conversion and light intensity.

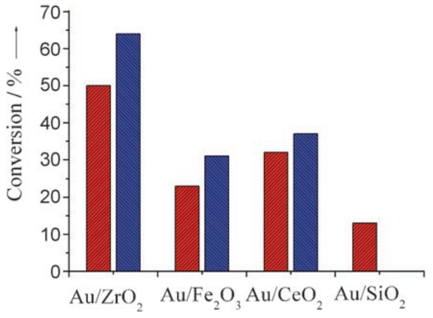

Figure 2. Influence of the oxide support on the activity of HCHO oxidation reaction. Blue bars: HCHO conversion (%) under illumination of blue light; red bars: conversion under red light.

HCHO per gold atom per second. This frequency is comparable to those for the CO oxidation on gold catalysts by heating the reaction system to 80 °C or above, which is between 10^{-2} and 10^{-3} molecules of CO per gold atom per second.[20]

The catalytic activity was dependent on the intensity of light irradiation. When the experiment was conducted without light irradiation, no changes in HCHO content were observed and no CO_2 was detected. When the light intensity was reduced by turning off two and four of the six light tubes, the conversion of HCHO decreased correspondingly (Figure 1 a). Sunlight was also used as the light source for the HCHO oxidation, and 8 % of HCHO was converted into CO_2 in two hours. The intensity of the sunlight is much lower (0.02 W cm^{-2}) than those of the light tubes. The HCHO conversion rate is plotted against the light intensity (Figure 1 b), which clearly demonstrates the dependence of conversion on light intensity. When a red light with wavelengths between 600 and 700 nm was used, the catalytic activity of Au/ZrO_2 catalyst is slightly lower compared with that of the blue light; 50 % of HCHO was oxidized in two hours (Figure 2). These facts indicate that the reaction is undoubtedly driven by visible light.

As the SPR effect involves enhanced local electromagnetic fields, the oscillating fields should interact more intensively with polar than nonpolar molecules and chemical bonds. This conclusion was verified experimentally by conducting the oxidation of methanol and cyclohexane using Au/ZrO_2 catalyst under the same experimental conditions. 18 % and 16 % of methanol was oxidized under irradiation of six blue and red light tubes in two hours, respectively, whereas no oxidation was observed for cyclohexane. The polarity of a molecule is in proportional to the value of its dipole moment. The dipole moments of formaldehyde, methanol and cyclohexane are 2.3, 1.7 and 0 Debye, respectively. The results demonstrate that for the reactant molecules of similar structural features, the molecule with higher polarity is much easier to activate and thus be oxidized on gold nanoparticles under visible light.

The function of the oxide supports in the catalysts used in the present study may be similar to that of the oxide supports of the gold catalysts used for the thermal oxidation.[16,21] If an oxide of a transition metal or rare earth element is used as support, the gold catalysts exhibited marked activity (Figure 2), whereas a gold catalyst on SiO_2 exhibited moderate activity under red light only. This situation is similar to that of the thermal oxidation of CO with gold catalysts, in which the oxide supports in the gold catalysts have been classified into inert and active supports.[21] Silica is an inert support, which has the function of stabilizing the small gold nanoparticles but does not adsorb oxygen, whereas the active supports, such as transition metal oxides and rare earth oxides, can adsorb oxygen molecules. To understand the function of the oxide supports in the catalytic oxidation driven by light, we conducted the catalytic reaction with the Au/ZrO_2 and Au/SiO_2 catalysts, respectively, in pure nitrogen (99.99 %), instead of dry air while maintaining the other experimental conditions unchanged. About 5 % of HCHO was degraded on the Au/ZrO_2 catalysts under blue light, but no HCHO oxidation was observed on the Au/SiO_2 catalysts. The results indicate that oxygen, the oxidation agent for the reaction, mainly comes from air. If we replaced air with pure nitrogen, there was no oxygen for the oxidation with Au/SiO_2 catalyst, therefore no oxidation was observed. However, for Au/ZrO_2 catalyst, the strongly adsorbed oxygen remained on ZrO_2 support after air was replaced with nitrogen, and was thus able to take part in the oxidation. The adsorbed oxygen on the active supports also explains the high activity of the catalysts on these supports when the reaction proceeds in dry air.

As seen in transmission electron microscopy (TEM) images (Figure 3), the size of the gold nanoparticles on

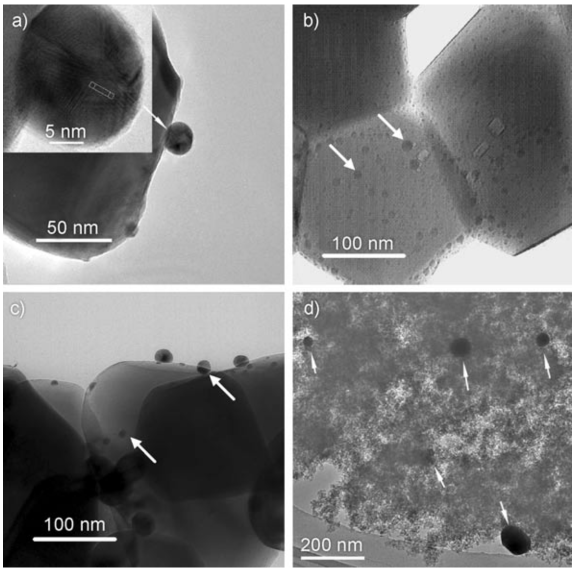

Figure 3. TEM images of the gold catalysts on different oxide supports. a) Au/ZrO_2, b) Au/CeO_2, c) Au/Fe_2O_3, d) Au/SiO_2. Arrows indicate gold nanoparticles.

different oxides can be different. The size distributions of the gold nanoparticles on four supports were calculated from the TEM images (see the Supporting Information, Figure 1). The distributions on ZrO_2 and SiO_2 are broad, and have peak values at 27 and 53 nm, respectively. Most of the gold nanoparticles on CeO_2 are below 10 nm, and most of the particles on Fe_2O_3 supports are between 10 and 30 nm. The mean sizes of gold particles are in the order Au/CeO_2 < Au/Fe_2O_3 < Au/ZrO_2, and the performance of the catalysts on the three oxides are in the order Au/ZrO_2 > Au/CeO_2 > Au/Fe_2O_3. It appears that gold particle size is not the determining factor, and the synergistic effect of the active metal oxide has as a much stronger influence on the catalytic activity than particle size.

Nonetheless, on the same metal oxide support, such as ZrO_2, the smaller the gold nanoparticle, the better the catalytic activity. When the Au/ZrO_2 catalysts was heated at 500 °C, the gold particles in this catalyst increased from about 20–30 nm to over 100 nm, and the HCHO conversion activity decreased substantially, from 64 % to 8 %.

A number of factors, such as particle size and morphology, and the dielectric constant of the oxide medium, can affect the SPR absorption of gold nanoparticles and thus the activity of the gold catalyst. The absorption spectra for the gold nanoparticles in a catalyst can be obtained from the difference between the spectra of the catalyst and oxide support (see the Supporting Information, Figure 2). The irradiation energy absorbed by the gold nanoparticles is then derived from the overlap area of the absorption spectrum of the gold nanoparticles and the spectra of the irradiation tube sources (see the Supporting Information, Figure 3) as well as the irradiation energy (for instance 0.17 $W\,cm^{-2}$ for blue light). The turnover frequency per unit of the irradiation energy absorbed by gold nanoparticles of the catalysts, the normalized turnover frequency, was calculated from the data of gold content and HCHO conversion of the catalyst. The gold content, turnover frequency derived from HCHO conversion, and gold content, and normalized turnover frequency, are listed in Table 1. The absorbed energy by the gold nanoparticles on SiO_2 is lower than those particles on other oxides. This could be an important reason for the relative low activity of Au/SiO_2 sample. The activities of the catalysts on various oxides in the normalized turnover frequency are given in the Supporting Information, Figure 4.

Based on these facts, we propose a tentative reaction mechanism for the light-driven catalytic oxidation. The irradiation of incident light with a wavelength in the range of the SPR band may result in two consequences. The first is that light absorption by the gold nanoparticles[9–11] could heat these nanoparticles up quickly.[14] We calculated the energy of the light absorbed by gold nanoparticles in the experiment with Au/ZrO_2 catalysts (gold particle size 20–30 nm) under blue light (0.17 $W\,cm^{-2}$), assuming the particles are spherical, and estimated how fast such energy could heat the particles up, namely at a rate of 3–5 °C per second. This means that gold particles of this catalyst could be heated to 100 °C, at which the HCHO oxidation proceeds significantly,[22] in 2–3 min, even if the energy conversion efficiency is 10 % or below.[15] The second consequence is that the interaction between the oscillating local electromagnetic fields and polar molecules also assists in activating the molecules. The activated polar organic molecules react with oxygen in close proximity.

The fact that it is difficult to activate nonpolar molecules under the same conditions indicates that the interaction is crucial to the catalytic reaction. The oxygen adsorbed on the active supports can migrate to the gold nanoparticles, and the adsorption of oxygen on the oxide support increases the concentration of oxygen around the organic molecules on the gold nanoparticles and thus the opportunity to react with the molecules, accelerating the oxidation. The proposed reaction mechanism is distinctly different from that for the reaction catalyzed by semiconductor photocatalysts.

Table 1: Gold content, absorption of irradiation energy, and catalytic activity of the gold nanoparticles on various oxides.

	Au/ZrO_2	Au/CeO_2	Au/Fe_2O_3	Au/SiO_2
Gold content [wt %]	2.44	2.62	3.10	2.24
Absorbed energy by gold nanoparticles under blue light [$W\,cm^{-2}$]	0.168	0.159	0.124	0.108
Turnover frequency under blue light [Au-atom^{-1} s^{-1}]	1.2×10^{-3}	6.5×10^{-4}	4.6×10^{-4}	0
Normalized turnover frequency under blue light [$cm^2\,J^{-1}$ Au-atom^{-1}]	7.1×10^{-3}	4.1×10^{-3}	3.7×10^{-3}	0
Absorbed energy by gold nanoparticles under red light [$W\,cm^{-2}$]	0.135	0.153	0.149	0.077
Turnover frequency under red light [Au-atom^{-1} s^{-1}]	9.4×10^{-4}	5.6×10^{-4}	3.4×10^{-4}	2.7×10^{-4}
Normalized turnover frequency under red light [$cm^2\,J^{-1}$ Au-atom^{-1}]	7.0×10^{-3}	3.7×10^{-3}	2.3×10^{-3}	3.5×10^{-3}

In summary, compared to the situation for conventional oxidation with heating, the visible-light-driven process has a significant advantage in that visible light interacts only with the gold nanoparticles. Given that the gold content in this study is 2–4 wt% of the supports, it requires much lesser energy input to activate the reaction compared to the conventional catalytic oxidation in which both the gold particles and the support material are heated to high temperatures. The light-driven reaction can proceed at ambient temperature at reaction rate similar to those of the catalytic oxidation under heating as shown by the turnover frequency of the reaction. Such a reaction at ambient temperature provides great convenience, for example in indoor air purification.

The finding that gold nanoparticles on ZrO_2 and SiO_2 can catalyze the VOC oxidations under visible light is likely to answer unsolved questions concerning the mechanism of doping semiconductor photocatalysts with gold to narrow the band gap of the semiconductor. The gold dopant itself may be an important contributor to the visible-light absorption and activity. Further possibilities to drive other chemical reactions with sunlight at ambient temperature include, for instance, reactions currently using gold catalysts.[17] This could open up a new direction in catalysis and herald significant changes in the economy and environmental impact of chemical production.

Experimental Section

The gold nanoparticles supported on oxide powders were prepared by the impregnation method: In general, 200 mg of support powder was added into 50 mL aqueous solution of $HAuCl_4$ and trisodium citrate under stirring. The suspension was heated to and kept at 90 °C for 10 min. The solid was then separated from the solution by centrifugation and washed with distilled water and ethanol. The precipitate was washed, and dried at 80 °C for 5 h. Gold nanoparticles on oxide powders were suspended in ethanol to coat the solid onto glass slides (2.5 cm wide and 7.5 cm long), which were heated at 80 °C.

The coated slides were placed in a glass vessel of about 6 liters. The vessel is in a chamber with six light tubes (18 W/tube, Philips) as the light source. Air conditioning was applied in the chamber to maintain the temperature at 25 °C, as the light illumination could otherwise cause an increase in the temperature of the vessel. The vessel was filled with air and sealed after the coated glass slides were mounted. Formaldehyde (HCHO) or methanol (CH_3OH) was injected into the vessel. The gaseous specimens were sampled before the light was turned on and analyzed by a gas chromatograph (Shimadzu GC-2014) used specially for this experiment. The gaseous specimens were sampled during the reaction course with light on to monitor the changes in the content of injected HCHO or CH_3OH and product CO_2. TEM images were obtained using a Philips CM200 TEM or a FEI Tecnai 20 TEM with an accelerating voltage of 200 kV. The specimens were sample powders deposited onto a copper microgrid coated with a holey carbon film. The EDS experiment was carried out on a FEI Quanta 200 Environmental SEM.

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