Au-TiO₂ Nanoscale Heterodimers Synthesis from an Ambient Spark Discharge for Efficient Photocatalytic and Photothermal Activity

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Supporting Information

ABSTRACT: Ultrathin Au particles incorporating TiO₂ heterodimers were synthesized using an ambient heterogeneous spark discharge and the resultant materials were employed both in oxidizing photocatalytically CO gas and killing photothermally cancerous cells. Ti–Au spark configuration was employed to vaporize Ti and Au components into an airflow and finally ultrathin Au particles (∼2 nm in lateral dimension) were incorporated with TiO₂ nanoparticles in the form of Au-TiO₂ heterodimers (∼38 nm in lateral dimension) with enhanced photocatalytic (in CO oxidation) and photothermal activity (in cancerous cell killing) under visible light. We propose that the localized surface plasmon resonance of ultrathin Au particles on TiO₂ supports, induced by the visible light, would promote the adsorption-oxidation of CO and photothermal killing of HeLa cells. The present strategy may be suitable to fabricate other Au-metal oxide nanocomposites for catalytic and biomedical applications.

KEYWORDS: Au-TiO₂ heterodimers, ambient heterogeneous spark discharge, CO oxidation, photothermal therapy

INTRODUCTION

Nanoparticles are the building blocks for the fabrication of complex architectures because, on the one hand, they exhibit different physicochemical properties compared to the corresponding bulk material, and on the other hand, the interaction between them as a consequence of the spatial arrangement can have extraordinary properties that are not produced in the single-component. Among them, metal oxide (e.g., TiO₂, ZnO, WO₃) nanoparticles have been frequently employed in environmental, energy, and display devices, as well as in biochemical sensors because of their unique band gap energy, anticorrosion property, physical sustainability, etc.

However, the ability of pure TiO₂ in photocatalysis is currently required modifications to enhance their efficiency. One of the efficient modifications is to complex the metal oxides with noble metals such as Pd, Ag, and Au has been widely prepared and investigated. Particularly, Au has received much attention for its unique catalytic and optical properties. Au nanoparticles could enhance the charge separation at the interfaces between Au and metal oxide because Au is well-known material as good electron sinks even for accumulating conditions. The photocatalytic reactions of Au-TiO₂ heterodimers (complexation of nonidentical monomers) have been studied in hydrogen generation, site-selective metal deposition, solar cell fabrication, photosensors, and information devices.

The present work introduces an ambient heterogeneous spark discharge to assemble Au-TiO₂ heterodimers for application to photocatalytic CO oxidation and photothermal cancerous cell killing. More recently, the Au-TiO₂ heterodimers have been extensively employed to enhance catalytic performance for catalytic CO conversion at low temperature conditions. Another Au-TiO₂ heterodimer has been further employed to enhance photothermal killing of cancerous cells. To the best of our knowledge, only a few studies have conducted the application of Au-TiO₂ heterodimers to biomedicine and catalysis, such as for anticancer modality, green energy, and environmental remediation applications.

Even though the heterodimers showed an enhancement in their specific applications, the multistep wet chemical steps with the use of toxic chemicals may not be suitable for their generalization. On that account, a facile approach with greener processing is strongly required for the assembly or synthesis of hybrid nanostructures. In previous studies, we reported the creation of different carbonaceous/bimetallic nanostructures by controlling the conditions of heterogeneous spark discharges. This is the first attempt to synthesize Au-TiO₂ heterodimers in a continuous gas-phase manner without using any wet chemical steps in an ambient environment. A Ti–Au spark configuration in an airflow environment was employed to produce Au-TiO₂ heterodimers, the heterodimers were collected using hydrophobic membrane filters, and finally they were detached before use both as photocatalysts to oxidize CO and as photosensitizers to kill cancerous cells (Scheme 1).

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RESULTS AND DISCUSSION

A scanning mobility particle sizer (SMPS, 3936, TSI, US) was employed to measure the total number concentration (TNC), geometric mean diameter (GMD), and geometric standard deviation (GSD) of the Au particles, and the measured data were \(1.87 \times 10^7\) particles \(\text{cm}^{-3}\), 26.1 nm, 1.51, respectively, as shown in Figure 1. Au-TiO\(_2\) heterodimers were formed near the spark channel by incorporating Ti with Au under an existing O\(_2\) environment. The incorporation of the TiO\(_2\) particles with Au nanoparticles (<4% in CO conversion at >450 nm irradiation) was attributed to the photoinduced electron-hole separation at the Au-TiO\(_2\) interface that was facilitated by the close proximity of dispersed Au particles on TiO\(_2\) supports, as is confirmed from the SPM. The ultrafine Au particles existed on TiO\(_2\) supports could thus tightly attach on the TiO\(_2\) surface, which may produce a strong metal–support interaction.

Figure 4a shows the CO conversion results of the Au-TiO\(_2\) heterodimers following the morphology on a flat substrate was observed using a scanning probe microscope (SPM, IIIa, NanoScope, U.S.). The overlapped/protruded particles of bright contrast in Figure 3 may be identified with the presence of dispersed Au particles on TiO\(_2\) supports, as is confirmed from the SPM. The ultrafine Au particles existed on TiO\(_2\) supports could thus tightly attach on the TiO\(_2\) surface, which may produce a strong metal–support interaction.

Table 1. Details of the Size Distributions of Spark-Produced Individual Au and Ti Particles Their Incorporated Nanostructures (Au–Ti) under Air Flow Environment

<table>
<thead>
<tr>
<th>case</th>
<th>GMD (nm)</th>
<th>GSD ((\times 10^7) particles (\text{cm}^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au@air “Au”</td>
<td>26.1 ± 1.8</td>
<td>1.51</td>
</tr>
<tr>
<td>Ti@air “TiO(_2)”</td>
<td>43.3 ± 1.6</td>
<td>1.55</td>
</tr>
<tr>
<td>Au–Ti@air “Au-TiO(_2)”</td>
<td>35.3 ± 2.9</td>
<td>1.58</td>
</tr>
</tbody>
</table>

The analogous data for TiO\(_2\) were 1.49. Table 1 shows the details of measurements of the Au, TiO\(_2\), and Au-TiO\(_2\) cases. The TNC, GMD, and GSD of the Au-TiO\(_2\) case were 1.46 \(\times 10^7\) particles \(\text{cm}^{-3}\), 35.3 nm, and 1.58, respectively. The analogous data for TiO\(_2\) were 1.49. The size distribution of the Au-TiO\(_2\) was between the Au and TiO\(_2\) particles, and there were no additional peaks in the distribution, verifying that the nearly all Au was attached on the TiO\(_2\) to form Au-TiO\(_2\) heterodimers. In addition, the changes in size distribution through alternation of operation gas (N\(_2\) to air) exhibited that there is a significant shift to larger sizes for the Au–Ti spark configuration (see Figure S1c in the Supporting Information) because of bindings between Ti and O atoms (see Figure S1a in the Supporting Information), whereas there is no size distribution shift in Au spark discharges (see Figure S1b in the Supporting Information).

Transmission electron microscope (TEM, JEM-3010, JEOL, Japan) images with low- and high-magnifications show the architecture of Au, TiO\(_2\), and Au-TiO\(_2\) samples. As shown in Figure 2, the TEM results confirm that both the Au (\(\sim 24\) nm in lateral dimension) and TiO\(_2\) (\(\sim 39\) nm in lateral dimension) particles were agglomerates of primary particles, which is well agreement with the SMPS data noted in Table 1. As shown in the insets of Au and TiO\(_2\), about 0.23 and 0.35 nm of the lattice fringes of Au and TiO\(_2\) are observed, respectively, which can be respectively indexed as the (111) and (101) planes of the Au and TiO\(_2\) structures. In addition, TEM measurements (see Figure S2 in the Supporting Information) showed that the resulting Au and Ti nanoparticles exhibited lattice fringes which were respectively consistent with the (111) and (100) diffraction planes of face-centered cubic Au (0.23 nm) and hexagonal close-packed Ti (0.26 nm),

In particular, the crystalline structure of Au was sustainable although the operation gas for their production was changed from N\(_2\) to air. The Au-TiO\(_2\) heterodimers essentially consisted of two kinds of particles. A darker contrast exhibits a diameter of ca. 2 nm and is assigned to Au nanoparticles, whereas a lighter-contrast one as a support, with a diameter of about 40 nm, is matched to the TiO\(_2\) nanoparticles. This suggests that the heterogeneous spark discharge can be used to highly disperse Au particles on the surface of TiO\(_2\). High-resolution TEM images show that the Au-TiO\(_2\) heterodimers had both 0.23 [Au(111)] and 0.35 [TiO\(_2\)(101)] nm in the lattice fringe.

A typical globular surface texture of the spark-produced Au-TiO\(_2\) heterodimers following the morphology on a flat substrate was observed using a scanning probe microscope (SPM, IIIa, NanoScope, U.S.). The overlapped/protruded particles of bright contrast in Figure 3 may be identified with the presence of dispersed Au particles on TiO\(_2\) supports, as is confirmed from the SPM. The ultrafine Au particles existed on TiO\(_2\) supports could thus tightly attach on the TiO\(_2\) surface, which may produce a strong metal–support interaction.

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of the ultrafine Au particles. The adsorbed O2 molecules on the surface of the heterodimers can trap the photoinduced electrons to generate the radicals for CO conversion. On the other hand, it is found that the >600 nm irradiation did not significantly promote the conversion of CO, which implies that the TiO2 support cannot catalytically oxidize CO under visible light irradiation. N2 adsorption measurements (via a Micromeritics ASAP 2010 apparatus) were employed to determine the textural property of the Au-TiO2 heterodimers and to verify the production of interconnected pores in the heterodimers (inset of Figure 4a). The measured isotherm of the Au-TiO2 heterodimers indicates its meso- and macro-porous characteristics. The uptakes at >0.85 and <0.85 of P/P0 may originate from the void spaces between agglomerated Au-TiO2 and between Au and TiO2, respectively.15 The pores within Au-TiO2 heterodimers could show an appropriate structure for adsorbing CO, which eventually led to enhanced photocatalytic performances in CO oxidation. Figure 4b shows Fourier transform infrared spectra (IFS 66/S, Bruker Optics, Germany) of Au-TiO2 samples before and after CO oxidation. As compared to the spectrum of Au-TiO2 without adsorbing CO, a feature at ~2180 cm−1, with another shoulder at ~2160 cm−1, that appeared on the sample was caused by CO adsorption on Au-TiO2. CO adsorbed on Au-TiO2 heterodimers is consumed by reaction with O2 at the interface. Moreover, a shifted peak at a lower frequency (~2080 cm−1) was also introduced because of another correspondence of the CO adsorption with photocatalysis.16 The IR spectrum also shows the existence of TiO2 particles, other bands at around 850 cm−1 assigned to Ti–O and TiO2 stretching,17 verifying that TiO2 nanocrystals exist within the heterodimers. This incorporation may be of value to transfer carriers and induce a synergistic effect to enhance the photocatalytic activity.

We further tested the efficiency of the heterodimers to transfect HeLa cells using plasmid DNA (pDNA) that contain the luciferase and EGFP gene. In order to give positive surface polarity of the Au-TiO2 heterodimers (inset of Figure 5a), poly-l-lysine (PLL) was directly incorporated on the heterodimers through Byeon–Roberts method.18 Zeta potential of Au-TiO2@PLL nanocomposites was ~14 mV by controlling PLL concentration. The transfection efficiency of nanocomposites-pDNA complexes in the cell line was greater than that of individual pDNA (Figure 5a). The ability for the nanocomposites was the greatest, even greater than those of polyethylenimine (PEI) and chitosan. Another inset in Figure 4a shows Fourier transform infrared spectra (IFS 66/S, Bruker Optics, Germany) of Au-TiO2@PLL nanocomposites before and after CO oxidation. As compared to the spectrum of Au-TiO2 without adsorbing CO, a feature at ~2180 cm−1, with another shoulder at ~2160 cm−1, that appeared on the sample was caused by CO adsorption on Au-TiO2. CO adsorbed on Au-TiO2 heterodimers is consumed by reaction with O2 at the interface. Moreover, a shifted peak at a lower frequency (~2080 cm−1) was also introduced because of another correspondence of the CO adsorption with photocatalysis.16 The IR spectrum also shows the existence of TiO2 particles, other bands at around 850 cm−1 assigned to Ti–O and TiO2 stretching,17 verifying that TiO2 nanocrystals exist within the heterodimers. This incorporation may be of value to transfer carriers and induce a synergistic effect to enhance the photocatalytic activity.

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The authors declare no competing financial interest.

ASSOCIATED CONTENT

# Supporting Information

The experimental procedure and size distributions and TEM images of Au, Ti and Au−Ti nanoparticles under N2 gas flow environment. UV−vis spectra of Au, TiO2, and Au-TiO2 samples, and XRD and XPS spectra of the Au-TiO2 heterodimers. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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REFERENCES