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Superior preferential oxidation of carbon monoxide in hydrogen-rich stream under visible light irradiation over gold loaded hedgehog-shaped titanium dioxide nanospheres: Identification of copper oxide decoration as an efficient promoter

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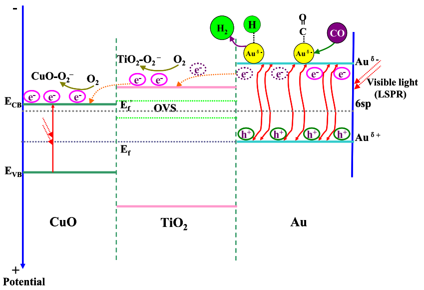
HIGHLIGHTS

- CuO modified 3D urchin-like hierarchical TiO_2 microspheres were prepared as support.
- CuO decoration promotes CO PROX over Au/TiO_2 under visible light irradiation or not.
- LSPR effect of Au nanoparticles promotes the adsorption and activation of CO.
- Confined electrons of CuO and TiO_2 is beneficial to the activation of O_2.
- CuO reinforces the electron interaction between Au and TiO_2 sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Gold nanoparticles loaded on the special three-dimensional urchin-like micro/nano hierarchical TiO_2 microspheres, with CuO layer modification, are performed for the CO preferential oxidation in H_2-rich stream at room temperature under visible light irradiation or not. It is found that the suitable outer decoration of CuO in TiO_2 microspheres can obviously improve the catalytic activity of Au/TiO_2, and adding visible light can further promote the performance. Based on the characterizations of catalysts, it is proposed that the CuO layer distributed on the shell of TiO_2 urchin-like microspheres can enhance the electron transfer among Au, TiO_2 and CuO sites to drive the increase in surface electron densities of Au and support sites induced by both the localized surface plasmon resonance of Au nanoparticles and the photo-excitation of CuO under visible light irradiation, resulting in the adsorptions and activations of CO and O_2. Therefore, as a synactic result of its unique band gap relation, its unique electron property and its morphologic effect, the novel CuO modified TiO_2 support not only enhances the microstrain itself on the stabilization of the size of Au nanoparticles, but more importantly also reinforces the electron interaction between support and Au sites.

1. Introduction

With reference to the bulk counterparts, the metal nanoparticles can display distinct properties and catalytic activities,

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which are critically dependent on the particle size [1,2]. Since Haruta [3,4] et al. have discovered that highly dispersed gold nanoparticles dispersed on metal oxide supports could exhibit surprisingly high catalytic activity to CO oxidation at low temperature, it is well established that gold catalysts supported on oxide supports have long been of considerable industrial and environmental application, such as in the proton-exchange membrane fuel cells for removing CO in a rich hydrogen atmosphere [5,6]. Due to the complex process of a heterogeneous catalysis, the nature of Au active species for oxidizing CO still remains obscure and a matter of debate [7]. Most reports show that the catalytic activity of Au nanoparticles is dependent on the size distribution of Au nanoparticles and the Au-support interface to a large extent. Other effects, e.g., the physicochemical properties and morphologies of supports, the Au-support charge transfer and the surface electron densities of Au nanoparticles, are also regarded as the fundamental importance. Therefore, to design a special Au catalyst for the CO preferential oxidation (CO PROX) with a high activity at low temperature, is always a challenge.

It is well known that TiO_2 is one of the most widely used metal oxide supports for gold nanoparticles in CO oxidation at low temperature [3,5]. Many attempts have been made to improve the catalytic activity of Au/TiO_2 at room temperature in the past years. For example, Solsona B and his group [8] reported that the doping of nitrate could increase by 1.3 fold in the catalytic activity of Au/TiO_2. Moma, J. A [9] and Mohapatra et al. [10] reported that the addition of sulfate could achieve an enhancement of more than 5-fold to Au TiO_2 for CO oxidation. Yan et al. [11] prepared a highly stable catalyst by Au loaded on the alumina thin layer coating TiO_2 support. Dai's group [12] reported that main-group, transition, and rare-earth metal oxide additives could exert the promotional effect on Au/TiO_2. Moreover, the surface defects of supports reported by Goodman et al. [13] could stabilize the high active Au nanoparticles. These results indicate that the creation of oxygen vacancies on the supports and the size effect of Au nanoparticles can play a crucial role in the CO oxidation.

However, the structure and morphology of catalysts also have a great influence on its catalytic performance [14]. It has been reported that the morphology/shape of α-Fe_2O_3 could affect the performance of gold catalyst for CO oxidation [15,16] and γ-Al_2O_3 nanofibers as support on gold catalyst were more contributive to CO oxidation than the commercial γ-Al_2O_3 [17]. Laszlo G. et al. [18] summarized that the morphological roles of promoting support oxide mainly included the crystalline or amorphous character, the type of crystalline structure (oxygen vacancies) and the shape of oxide supports. Li et al. [19] also reported that the CeO_2—TiO_2 nanorods as support made Au catalyst exhibit a much higher activity compared to the CeO_2—TiO_2 nanoparticles.

Hereinto, the epitaxial multilevel structure of the urchin-like microspheres is one typical micro/nano hierarchical structure. Yin's group [20] have ever demonstrated that the urchin-like TiO_2 particle suspension exhibited a significantly different rheological property with the smooth particle suspension. So the urchin-like hierarchical TiO_2 has higher photocatalytic efficiency than P25. It is also proposed that the TiO_2 material with the unique micro/nano structure, could absorb more incidental light through multiple reflection of hierarchical microspheres, similar to the principle of integrating sphere [21]. So the well-organized three dimensional urchin-like hierarchical TiO_2 microspheres by the solvothermal synthesis [22] as support may be greatly beneficial to CO PROX. In addition, copper or copper oxide can exhibit an activity in CO oxidation [23] and the copper or copper oxide supported on TiO_2 does in CO PROX [24]. Yu et al. [24] reported that the best catalytic effect was located in the monolayer dispersion threshold of the amount of CuO and the excess loading amount of CuO was adverse. Furthermore, visible light can excite the outer electrons of CuO due to the 1.7 eV band gap of CuO, while also causes Au nanoparticles to excite electrons due to the localized surface plasmon resonance (LSPR) of Au nanoparticles [25]. These photo-excited electrons may be transferable between CuO and Au. Therefore, we think that the synergistic effect between gold and copper oxide on the activity depends not only on the size of the Au particles but also simultaneously on the electron interaction between Au and the oxide component, especially under visible light irradiation. In fact, the surface electron densities of Au species can be promoted by the localized surface plasmon resonance (LSPR) of Au nanoparticles [25]. Our previous results further [26,27] showed that visible light could promote the CO PROX in the presence of H_2 over Au/TiO_2 or the polymer polyaniline (PANI) decorated Au/TiO_2 by increasing the surface electron densities of Au sites. Moreover, the increase in the amount of negative charge on the Au core, i.e., an electron-rich environment, can be contributive to the catalytic activity of Au for aerobic oxidation [28] and selective oxidation reactions [29]. Therefore, it will be interesting to investigate the behavior of electron transfer during the process of CO PROX over the CuO decorated Au/TiO_2 catalyst under visible light irradiation.

On the basis of the above consideration and this general scenario, the objective of the present study is to investigate the CuO decorated Au/TiO_2 catalyst for CO PROX in H_2-rich stream under visible light irradiation or not. We focus on the preparation of the special morphologic support, i.e., CuO modified well-organized three dimensional urchin-like micro/nano hierarchical TiO_2 microspheres were first prepared. Then, series of different loaded CuO layers with gold (1 wt%) catalysts were evaluated in the CO PROX in the presence of H_2. The photo-response behavior (i.e., LSPR) of Au nanoparticles, the interband excitation of CuO, the electron transfer among Au, TiO_2 and CuO, and also the high surface electron densities of Au nanoparticles may be conducive to the adsorption and activation of CO. Correspondingly, the confined electrons of CuO or TiO_2 can be contributive to that of O_2. The possible electron transfer process among the interface of Au, TiO_2 and CuO over $Au/TiO_2@CuO$ under visible light irradiation is also proposed.

2. Experimental

2.1. Preparation of catalysts

All chemicals were of analytical grade and used without further purification. According to the synthetic method of Fan et al. [21], we also prepared the well-organized three dimensional urchin-like hierarchical TiO_2 microspheres. Briefly, the respective obtained 50 wt% $TiCl_4$ aqueous solution and the TBT/toluene solution formed by 4 mL of tetrabutyl titanate dissolved in 30 mL of toluene in an ice water bath under stirring were mixed dropwise into the mixture. And then after further stirring for 1 h, it was transferred into a 50 mL stainless steel autoclave lined with Teflon and held at 150 °C for 24 h. Finally, the precipitates were filtered, washed with ethanol for several times, and dried at 70 °C to obtain the TiO_2 microspheres.

$Au/TiO_2@CuO$ catalysts with different weight ratios (Cu/Ti 5/95, 10/90 and 20/80) were prepared by co-precipitation method. Typically, according to the weight of TiO_2 microspheres powder, the suitable amount of $(CH_3COO)_2Cu$, TiO_2 microspheres and $HAuCl_4 \cdot 3H_2O$ was diffused in a distilled water of 100 mL under stirring to obtain the mixture A. The corresponding amount of Na_2CO_3 was dissolved in 30 mL of water under stirring. Next, the formed Na_2CO_3 solution was added dropwise into the mixture A and the pH value of the slurry was adjusted to 10 with 1.0 mol L^{-1} NaOH aqueous solution at room temperature, and then further was stirred for 12 h. The obtained precipitates were centrifuged, washed