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ARTICLE TYPE

Pt-porous ZnO nanoribbon hybrid materials with enhanced catalytic performance

Zhiqiang Cheng,[1, 2] Mingyue Yu,*[3] Guixia Yang[1] and Lijuan Kang*[1]

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We demonstrated a low-cost, fast and facile seeded growth method to synthesize ultra-fine Pt-porous ZnO nanoribbon hybrid materials with remarkable enhanced catalytic performance. The experimental result has confirmed that the bio-molecule L-lysine is very important in the synthesis. Fist, it modifies the ZnO's surface be with positive electricity; second, it is found that L-lysine also plays a role of structure directing agent to induce the formation of 1D ZnO nanoribbons. In the following catalytic test of CO oxidation and photo-degradation of organic dye, such Pt-ZnO hybrid nanoribbons exhibited remarkable enhanced catalytic properties compared with the classic rod-like Pt-ZnO hybrids.

Noble metal-transition metal oxide hybrid nanomaterials have received continuous attention owing to their highly increased chemical and physical properties compared with the single-component noble metals or metal oxides. To date, a series of such hybrid nanomaterials have been fabricated successfully, such as Au-TiO_2,[1] Au-Cu_2O,[2] Pd-Cu_2O,[3] Pt-CeO_2,[4] Ag-CeO_2,[5] Au-ZnO,[6] Pt-SnO_2[7] and et al. Generally speaking, there are two important methods which have been widely used to realize the goal of efficient hybridization of noble metals and the metal oxides: one-pot strategy and multi-step seeded grwoth process. For instance, the previous works have been reported that a one-pot auto-redox reaction could be triggered between noble metal salts and $Ce(OH)_3$, as results, M (M = Ag and Pt)-CeO_2 hybrid nanomaterials have been prepared.[8,9] However, although such one-pot strategy is indeed facile and highly simplified the post-treatment, there is an important problem to be unavoidable: both of the shapes and sizes of the noble metals and the metal oxides are uncontrollable. As a result, the noble metals are always big and irregular, which has limited the further optimization of the catalytic performance. On the opposite, seeded growth method can make sure the noble metal seeds be with uniform sizes and shapes, and the morphologies of the metal oxides can also be well under control. This provides an opportunity to study the relationship between the size, shape or hybrid nanostructure and the catalytic properties in-depth.

Consideration of the large lattice mismatch degree between the noble metals and metal oxides, appropriate surface modification treatment is very necessary. The previous works have confirmed that the noble metal's surface is always electronegative. so that it is easy to think of the most important thing is to make the transition metal oxide's surface be electropositive. Very recently, Xia's group has developed a new method to realized the goal of successful hybridization of Pt and CeO_2 by surface modification of CeO_2 be with electropositive.[10] In addition, Zhang's group has done a great deal of work on the surface-modification of metal oxide. They found that bio-molecule L-lysine could change the surface state of CeO_2 efficiently.[11,12] L-lysine is one of the specific molecules, that it has functional groups (-NH_2 and -COOH) and water-soluble but with long carbon chain. All these features make the L-lysine to be widely used in the fabrication of noble-metal-metal oxide hybrid nanostructures.

ZnO, as a n-type semiconductor, has been extensively studied for various device applications. Due to its unique crystal habit, various morphologies of ZnO have been synthesized, including one-dimensional nanorods[13] and nanowires[14], two dimensional nanobelts[15] and nanosheet[16], and three-dimensional hierarchical architectures[17] and porous hollow spheres[18]. Furthermore, the recent research interests have been paid to contract the ZnO-supported noble metal nanomaterials and to study their unique optical, electrical and catalytic peformances. Zhang et al. developed a PVP-assisted method for attaching Pd nanoparticles onto ZnO nanowires and the as-obtained hybrid material showed enhanced sensing performances towards detecting H_2S gas.[19] A more recent report from Ho and coworkers demonstrated the synthesis of noble metal decorated ZnO nanostructures with highly increased photo-catalytic properties.[20]

Be much different from the above mentioned representative works (pre-synthesized ZnO nanocrystals followed by in-situ growth of noble metal nanoparticles), here we reported a successful seeded growth method to synthesize Pt-porous ZnO nanoribbon hybrid materials by using sub 3 nm Pt nanoparticles as seeds. In a typical synthesis of Pt-porous ZnO nanoribbon, the pre-synthesized Pt colloid solution, $Zn(oAc)_2$, urea, L-lysine powder and water are mixed together and stirring at room temperature until the formation of clear and transparent solution. The resulting mixture is hydrothermal treated at 140 °C for 12 hours. Finally, the colloidal products are separated from the reaction solution by centrifugation and washed with water and ethanol for three times (experimental details are shown in ESI).

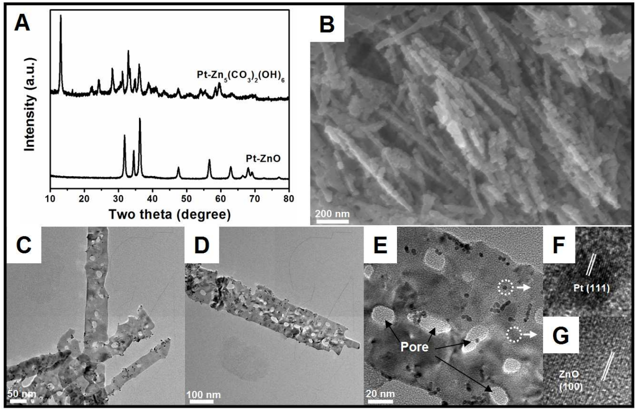

Fig. 1 (A) XRD data of Pt-ZnO hybrids before and after heat treatment; (B) SEM image; (C) to (G) TEM images of the Pt-ZnO porous nanoribbon.

Some characterization techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and powder X-ray diffraction (XRD), have been used to investigate the structure information of the products. As shown the SEM images in Figure S1, uniform 1D nanostructures have been obtained before calcination. However, the corresponding XRD data (Fig. 1A) has shown that the products are in the form of pure-phase $Zn_2(CO_3)_2(OH)_6$. No reflections of ZnO crystals could be obsered. After calcination at 450 ^oC for 2 hours, A standardized hexagonal phase ZnO reflection has been obtained. However, the signal of Pt is hard to be found, which may be caused by the much higher crystallinity of ZnO than Pt. Further SEM image in Fig. 1B illustrates that the calcined products are still in the form of 1D nanostructures. Thanks to the high content of CO_3^{2-} and OH^- groups in the precursor, a large number of micro-holes are left after calcination, which is clear to be saw in the low-resolution TEM images in Fig.C and D. Further enlarging the TEM image could help us to distinguish the presence of tiny Pt nanoparticles in the final hybrids. as shown in Fig. 1E, the Pt nanoparticles keep well their small particle sizes (about 3 nm), and load on the surface of ZnO nanoribbons uniformly. No scatted Pt nanoparticles could be found outside the ZnO nanoribbons. In Fig. 1E and F, the HRTEM images have shown that the lattice spacing (0.22 nm and 0.27 nm) correspond well with the characteristic (111) planes of Pt and (100) plnes of ZnO crystals, respectively. Such result indicats the as-prepared nanorods grow along with the 〈100〉 direction. The X-ray photoelectron spectroscopy (XPS) spectra (with the data shown in Figure S2) have also been done, the result has further identified that the presence of Zn and Pt elements in the final hybrids. The BET volume of the as-obtained Pt-ZnO porous nanoribbon has also been tested as 55.8 m^2/g (as shown in Figure S3).

In order to find out the important role of L-lysine, a control experiment has been done by no addition of L-lysine in the reaction system. The SEM images are shown in Figure S4, after the hydrothermal treatment, the as-obtained precursor is irregular nanoparticle, the original unifrom ribbon-like nanostructure are disappeared. Combination with the previous reports,[10,11] it could be confirmed that L-lysine played two important roles: (1) increasing the attractive force between ZnO and Pt by surface modification of ZnO; (2) as a structure-directing agent to induce the formation of ribbon-like precursor. In addition, we also investigate the effect of the feeding amount of urea. With the data shown in Figure S5 and S6, dereasing or increasing the feeding amount of urea has damaged the formation of ZnO nanoribbons. Poor quality ZnO nanostructures are obtained. An other control test has been taken by increasing the reaction temperature to 180 ^oC. As shown in Figure S7, the SEM image has shown that a serious agglomeration and overgrowth of ZnO have happened. In addition, decreasing the reaction temperature to 120 ^oC only makes the formation of irregular nanoparticles (Figure S8). Thus, the growth mechanism of such Pt-porous ZnO nanoribbon could be understood as: first, urea decomposed under high temperature to provide CO_3^{2-} and OH^- ions slowing. The precursor $Zn_5(CO_3)_2(OH)_6$ has begun to form. At the same time, by the help of L-lysine, Pt nanoparticles are captured by the crystallized ZnO. Then, more and more ZnO are growed along with the 〈100〉 direction. Finally, one-dimensional Pt-ZnO hybrid nanostructure has been obtained. During the further calcination process, excess CO_3^{2-} and OH^- have left the products in the form of CO_2 and H_2O, respectively, just leaving numbers of micro-holes.

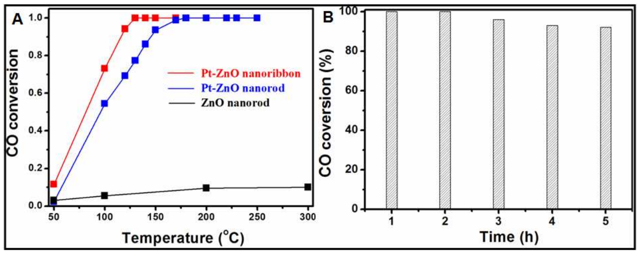

Fig. 2 (A): Catalytic oxidation of CO to CO_2 by using Pt-ZnO nanoribbon, Pt-ZnO nanorod and bare ZnO nanorod as catalysts; (B): the cycling test of Pt-ZnO nanoribbon, working at 130 ^oC for 5 hours.

Catalytic CO oxidation into CO_2 has been chosen as a model reaction to study the catalytic performance of Pt-ZnO porous nanoribbon. As a reference, the typical ZnO nanorods are synthesized according to the previous reports[13, 21] (with the TEM images shown in Figure S9) and used them as supports to load sub-3 nm Pt nanoparticles. CO conversion curves in Figure 2 show that that bare ZnO nanorods only exhibit very limited catalytic activity. It can only converse about 10 % CO to CO_2 at a relative high temperature of 300 ^oC. After the formation of Pt-ZnO nanorods, the catalytic performance is largely increased. It could convert over 54 % CO at related low temperature 100 ^oC and reached about 100 % conversion at 180 ^oC. Very excitingly, the Pt-ZnO porous nanoribbon prepared in this work exhibit the highest catalytic performance. The 100 % conversion temperature has been decreased to only about 130 ^oC, indicating a strong synergistic effect exist between Pt and ZnO porous nanoribbon. Further cycling test has been done to study the catalytic stability of this sample by continuously working at 130 °C for 5 hours. With the data shown in Fig. 2B, it can maintain over 92 % conversion of CO to CO_2, indicating its excellent catalytic performance under long-term high-temperature catalytic conditions.

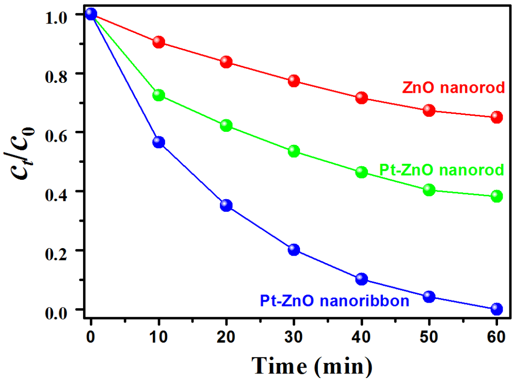

Fig. 3 Photocatalytic degradation of MO by using the as-prepared Pt-ZnO porous nanoribbon (blue line), Pt-ZnO nanorod (green line) and bare ZnO (red line).

Next, the photocatalytic-performance of Pt-ZnO porous nanoribbon has also been evaluated for organic dyes degradation under ultraviolet light. The typical photodegradation methyl orange (MO) curves of the as-prepared Pt-ZnO porous nanoribbon, Pt-ZnO nanorod and bare ZnO nanorod are shown in Fig. 3. it is found that the intensity of major absorption peaks at 595 nm decreases step by step. Fig. 3 shows time profiles of [C/C_0], here C is the concentration of MO at the irradiation time t and C_0 is the initial concentration. When the photodegradation reaction is proceeded past 60 min, almost 100 % MO has been degraded. However, when using Pt-ZnO nanorod or bare ZnO instead of Pt-ZnO nanoribbon, there are only about 60 % and 35 % degradation of MO for Pt-ZnO nanorod and bare ZnO, respectively. Based on these results, it can be seen that the recombination of Pt and ZnO could largely enhance the photocatalytic activity. The mechanism of the increased photocatalytic property is discussed as, once small Pt nanoparticles (NPs) loaded on ZnO' surface, the excited electrons are easy to be transported from ZnO to Pt, which could efficiently avoid the recombination of the photo-generated electrons and holes. In addition, the nanocatalysts exhibite a shape-dependent catalytic performances. The better catalytic activity of Pt-ZnO nanoribbon than Pt-ZnO nanorod could be understood as the porous nanostructure provides higher specific surface area and more active centers for the photo-catalytic reaction happening. Furthermore, a cycling test has been done in order to test the catalytic stability of the as-obtained Pt-ZnO nanoribbons. As shown in Figure S10, even after four successful cycles, over 90 % MO has been degraded, that indicates the high stability of Pt-ZnO nanoribbons.

In summary, a deeded growth method has been developed by using sub 3 nm Pt nanoparticles as seeds followed by a hydrothermal treatment to produce Pt-$Zn_5(CO_3)_2(OH)_5$ precursors. After calcination at 450 °C, porous hybrid nanostructures are obtained. Bio-molecule L-lysine is very important in our synthesis. It can be not only as an adhesion agent to hybridize Pt and ZnO together, but also as a structure directing agent to induce the formation of one-dimensional ribbon-like nanostructures. In the following catalytic applications, the as-obtained Pt-ZnO porous nanoribbon exhibits remarkable increased catalytic performance compared with the classic Pt-ZnO nanorod and bare ZnO nanorod. It can converse 100 % CO to CO_2 at a relative low temperature of 130 °C. Furthermore, in the reaction of photocatalytic degradation of MO, Pt-ZnO porous nanoribbon can accomplish the reaction within 60 min. These results have firmly confirmed that the efficient hybridization of Pt nanoparticle and ZnO nanoribbon is beneficial to the catalytic applications. It is believed that such bio-molecule assisted seeded growth method and the as-produced Pt-ZnO porous nanoribbon could enlighten more generally the potential application of noble-metal-metal oxide hybrid nanomaterials in future.

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Supporting Information Available: Experimental details, SEM image of Pt-$Zn_5(CO_3)_2(OH)_6$ precursor, XPS spectra of Pt-ZnO nanoribbon, SEM images of the precursors obtained by changing the reaction conditions, such as increasing the reaction temperature, changing the feeding amount of urea and without the addition of L-lysine in the reaction solution, and the TEM image of Pt-ZnO nanoribbon after the catalytic reaction of CO oxidation.

Author information

1 College of Resources and Environment, Jilin Agricultural University, Changchun, 130118, P.R China.
2. School of Aerospace Engineering, Tsinghua University, Beijing, 100000, P.R China.
3 Changchun University of Science and Technology, Changchun, 130118, P.R China.
E-mail: mingyue141210@126.com; kanglijuan61@126.com.

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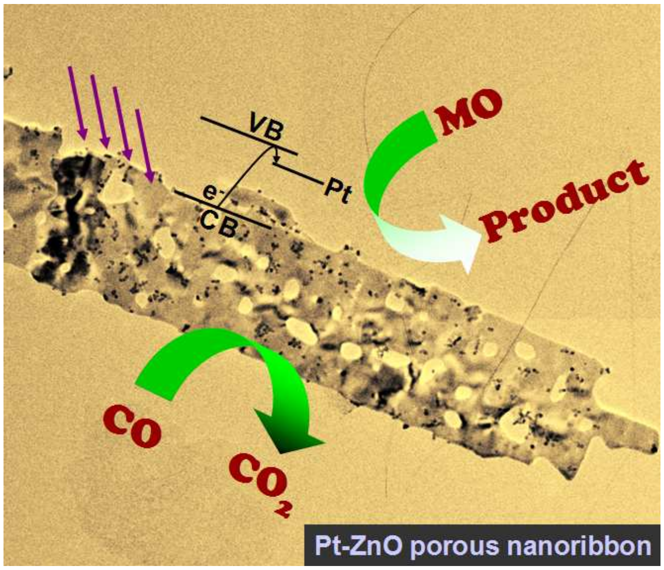

By the help of bio-molecule L-lysine, a seeded growth method has been developed and Pt-ZnO porous nanoribbon is obtained successfully. In the following catalytic applications of CO oxidation and photocatalytic degradation of MO, such hybrid nanomaterial exhibites remarkable enhanced catalytic properties which could be attributed to the efficient hybridization of Pt and ZnO, and the unique 1-D porous nanostructure.