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Sub-10 nm Au–Pt–Pd alloy trimetallic nanoparticles with a high oxidation-resistant property as efficient and durable VOC oxidation catalysts[†]

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Sub-10 nm AuPtPd alloy trimetallic nanoparticles (TMNPs) with a high oxidation-resistant property were prepared by photo-deposition followed by a high temperature (700–900 °C) air annealing process.

Trimetallic nanoparticles (TMNPs) have received considerable attention due to their unique catalytic, electrical, magnetic and optical properties, which are very different from those of the monometallic or bimetallic ones due to synergistic effects between multiple metal elements.^{1,2} Many methods have been developed to prepare TMNPs, and most of them need complex multi-step procedures and are in unsupported forms.³⁻⁵ The coexistence of trimetallic precursors complicates the deposition or decomposition kinetics and thus makes it more difficult to rationally design the growth process of nanocrystals. In addition, during the subsequent thermal treatment performed to get metal nanoparticles, the particles must have enough mobility to migrate on the support, interact with each other, and form trimetallic particles. However, phase separation and sintering are two common problems, especially when the metal ratio falls in the miscibility gap, or if the intended composition is not thermodynamically stable.^{6,7} Hence, the ability to synthesize supported trimetallic nanoparticles where there is a tighter control over the composition from particle-to-particle, while preserving the mean particle size below 10 nm, still remains a significant synthetic challenge.

On the other hand, catalytic studies of colloidal nanoparticles have shown that the thermal and chemical stabilities of MNP catalysts are crucial. Many industrially important catalytic processes, including CO oxidation, partial oxidation and cracking of hydrocarbons and combustion reactions, are operated at temperatures above 300 °C. The challenge of preparing highly active nanocatalysts based on sub-10 nm MNPs that have long-term stability at high reaction temperatures is in high demand.⁸⁻¹⁰

Here, we report a successful synthesis of sub-10 nm AuPtPd TMNPs by photo-deposition within ordered, extra-large mesoporous TiO_2 (EP-TiO_2) followed by a high temperature (700–900 °C) air annealing process. With respect to other Pd-containing BMNPs, the Pd species in the TMNPs display a high oxidation-resistant property, showing a high content of the Pd⁰ oxidation state (>90%) after thermal aging (up to 900 °C) and significantly enhanced activity for volatile organic compound (VOC) oxidation.

The synthetic procedure is described in Scheme 1. The mesoporous support (EP-TiO₂) has a well-defined three-dimensional cubic mesoporous structure (face-centered cubic) with a cage size of 26.4 nm and a window size of 7.9 nm.¹¹ To prepare AuPtPd TMNPs (noted as $Au_xPt_yPd_z$ /EP-TiO₂, where *x*, *y*, and *z* represent a nominal metal molar ratio of Au, Pt, and Pd, respectively), 10 mL of methanol solution containing 100 mg of EP-TiO₂ and desired amounts of metal precursors (H₂PtCl₆, HAuCl₄, and PdCl₂) was dispersed in a Pyrex glass reactor. After removal of oxygen, the mixture was subjected to the UV light irradiation for 2 h. By consecutive washing–centrifugation cycles, the product was isolated and dried at room temperature (RT). Thermal annealing at designed temperature is applied to prepare trimetallic alloy nanoparticles. The detailed synthesis and material characterization are given in the ESI.[†]

Fig. 1a shows the HAADF-STEM image of the $Au_{25}Pt_{25}Pd_{50}$ TMNPs after the photo-deposition step. The efficiency of the



 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme1} & \mbox{Scheme1}$



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Fig. 1 HAADF-STEM images and particle size distribution, typical HAADF-STEM images, corresponding EDS mappings and cross-sectional line-scanning profiles of $Au_{25}Pt_{25}Pd_{50}/EP-TiO_2$ after the photo-deposition (a–d) and after annealing at 800 °C (e–h). The inset in (e) shows the typical HR-TEM image of $Au_{25}Pt_{25}Pd_{50}/EP-TiO_2$ after annealing at 800 °C.

metal photo-deposition is more than 85% (Au, Pt, Pd), and the actual composition $(Au_{23}Pt_{29}Pd_{48})$ and metal loading concentration of the $Au_{25}Pt_{25}Pd_{50}/EP$ -TiO₂ are very close to its nominal composition and the calculated loading content as determined by ICP-AES analysis (Table S1, ESI[†]) and EDS (Fig. S1, ESI[†]). After photo-deposition, the $Au_{25}Pt_{25}Pd_{50}$ TMNPs are uniformly dispersed throughout mesoporous EP-TiO₂, with an average particle size of 6.8 ± 1.7 nm. The EDS mappings and cross-sectional line-scanning profiles of several individual $Au_{25}Pt_{25}Pd_{50}$ TMNPs show that the Au signal only locates in the core of the nanoparticle with a spherical distribution, while Pt and Pd occupy the same spatial area with an irregular shape, indicating that the Au@PtPd core-shell structure is obtained (Fig. 1b–d, Fig. S1, ESI[†]).

More importantly, the EDS analysis of individual Au@PtPd particles reveals that the actual particle-to-particle composition $(Au_{22}Pt_{27}Pd_{51})$ is also close to their nominal composition.

The corresponding XRD pattern of $Au_{25}Pt_{25}Pd_{50}$ TMNPs formed after the photo-deposition shows two distinct diffraction peaks at 38.6° and 39.6°, respectively, which could be assigned to Au and PtPd alloys (Fig. 2a). The core–shell structure of Au@PtPd TMNPs suggests that the Au species were first reduced into spherical



Fig. 2 (a) XRD patterns of $Au_{25}Pt_{25}Pd_{50}/EP-TiO_2$ annealed at different temperatures. For comparison, the XRD patterns of pure Au, Pt, Pd and PdO from the JCPDS are presented. (b) Normalized XPS spectra of Pd 3d peaks for different Pd-containing samples after air annealing at 800 °C. The marked contents of Pd⁰ are determined by XPS data.

nanoparticles and then served as "seeds" for the growth of PtPd alloys on their surface. This fact is directly related to the faster deposition kinetics of Au as compared to Pt and Pd precursors, which has been reported in other synthetic system.^{4,12}

Thermal annealing at temperatures up to 900 °C is applied to prepare Au₂₅Pt₂₅Pd₅₀ alloy TMNPs. Fig. 2a shows the XRD patterns of Au25Pt25Pd50 TMNPs annealed at different temperatures. Low-temperature annealing (350-700 °C) leads to the formation of PdO and AuPt alloys.5 When the annealing temperature increases to 700 °C, the original AuPt(111) peak shifts to a higher angle (39.5°) towards the Pd(111) peak (40.1°), which is in agreement with the shrinkage of the lattice parameter due to the smaller unit cell parameter of Pd, indicating that the AuPtPd alloy is formed. Meanwhile, the intensity of the PdO peak signal is significantly reduced. When the annealing temperature is as high as 800 °C, the PdO signal almost disappears and AuPtPd diffraction peak continuously shifts to a high angle (39.7°) as a result of the reduced lattice distance due to incorporation of more Pd content. The lattice fringes of 0.228 nm and 0.197 nm for individual Au₂₅Pt₂₅Pd₅₀ TMNPs are assigned to the (111) and (200) planes of AuPtPd alloy nanoparticles, respectively, in good agreement with the XRD result (Fig. 1e inset, Fig. S2, ESI⁺).¹³

The alloy structure of $Au_{25}Pt_{25}Pd_{50}$ TMNPs formed by hightemperature annealing is further confirmed by HAADF-STEM and EDS analysis. The EDS mappings and cross-sectional linescanning profiles of several individual $Au_{25}Pt_{25}Pd_{50}$ TMNPs show that Au, Pt and Pd occupy the same spatial area with a spherical shape after air annealing (Fig. 1f–h, Fig. S3a, ESI†). The EDS analysis of individual AuPtPd alloy TMNPs reveals that the actual particle-to-particle composition ($Au_{28}Pt_{27}Pd_{45}$) is also close to their nominal composition, suggesting that the high-temperature air annealing does not change the composition of the TMNPs. Combined with HAADF-STEM analysis and the corresponding EDS mappings of a broad area (Fig. S3b, ESI†), supported Au–Pt–Pd alloy TMNPs, where there is a tighter control over the composition from particle-to-particle, have been successfully prepared.

One surprising positive feature of the prepared AuPtPd alloy TMNPs is their sub-10 nm size even after such a hard thermal treatment, which is very important for their catalytic applications. The high-temperature annealing (800 $^{\circ}$ C) only leads to slight

growth of the size from 6.8 \pm 1.7 to 8.1 \pm 2.3 nm (Fig. 1a and e). Both trimetallic alloy composition and the unique nanostructure of EP-TiO₂ are responsible for its excellent thermal stability. In the case of monometallic and bimetallic nanoparticles of Au, Pt, and Pd, serious sintering phenomena were observed (Fig. S4, ESI[†]). The average sizes of Au₅₀Pt₅₀, Au₃₃Pd₆₇ and Pt₃₃Pd₆₇ calculated by the Debye-Scherrer equation are 30.3 nm, 14.3 nm and 12.4 nm, respectively, much larger than Au25Pt25Pd50 TMNPs. Besides, in stark contrast to the situation using EP-TiO₂ as the support, the AuPtPd TMNPs supported on commercial TiO₂ nanocrystals (anatase) grow into large TMNPs (~ 20 nm), possibly through the uncontrolled particle-migration process (Fig. S5, ESI⁺).¹⁴ However, the TMNPs can be fixed on the internal surface of the cage-like mesoporous supports due to the significantly reduced particle-migration probability, which greatly enhances thermal stability of AuPtPd TMNPs within EP-TiO₂.¹⁵

Another important feature of the supported AuPtPd alloy TMNPs is the high oxidation-resistant property of the Pd species. Many studies of Pd-based catalysts have confirmed that reduced Pd⁰ is far more active than PdO in VOC oxidation.⁷ However, it is well known that Pd⁰ tends to be oxidized under oxidation conditions when temperature is above the threshold 200 °C.¹⁶ From the XRD data, Au₂₅Pt₂₅Pd₅₀ alloy TMNPs show the lowest PdO signal as compared to those for Pd, PtPd and AuPd samples after the same thermal treatment in air (Fig. S4, ESI[†]). XPS analysis is performed to quantitatively evaluate the Pd⁰ content of the TMNPs. It shows that the Pd⁰ content is as high as 73% for Au₂₅Pt₂₅Pd₅₀ alloy TMNPs, while almost all the Pd species of pure Pd and Pt₃₃Pd₆₇ are in the PdO form (Fig. 2b, Fig. S6, ESI[†]). This difference implies that the presence of the Au composite is very important to stabilize the Pd⁰ oxidation state. It has been reported that Au can be helpful in the PdO decomposition at high temperature (~ 800 °C), resulting in the formation of AuPd and Pd⁰,¹ which has been also confirmed by XPS analysis in this study (Fig. 2b). Based on the bulk Au-Pt-Pd phase diagram (Fig. 3a), the high Pd content (>50%) is the miscible region to form AuPtPd alloys.² The formation of AuPtPd alloy TMNPs stabilizes the Pd⁰ composite and suppresses its re-oxidation during the cooling process.¹⁷ The stable and high Pd⁰ content of AuPtPd alloy TMNPs manifests the unique synergistic effects between multiple metal elements and distinguishes them from monometallic or bimetallic systems.

We have also successfully prepared the AuPtPd alloy TMNPs that fall in the miscibility gap of the bulk AuPtPd system using the same method. Fig. 3b shows the XRD patterns of the supported $Au_{50}Pt_{y}Pd_{z}$ TMNPs after air annealing at 800 °C. Only $Au_{50}Pt_5Pd_{45}$ falls in the miscibility region based on the bulk Au-Pt-Pd phase diagram, and its corresponding XRD pattern shows a single XRD diffraction peak at 39.1°, indicating that an alloy structure is formed. It is surprising to find that both $Au_{50}Pt_{15}Pd_{35}$ and $Au_{50}Pt_{25}Pd_{25}$ also formed thermally stable alloy structures, which were not miscible at temperatures below 900 °C and 1000 °C, respectively. Continuously reducing the Pd content leads to the formation of Au-rich and Pt-rich AuPtPd phases. This observation suggests that thermodynamically stable miscibility of the sub-10 nm AuPtPd system is different from that of the bulk



Fig. 3 (a) Immiscible area isotherms of the bulk Au–Pt–Pd phase diagram. (b) XRD patterns of samples 1–5 annealed at 800 °C. (c) the reaction temperatures for 50% (T_{50}) and 15% (T_{15}) conversion of *n*-hexane for samples 1–6 (1 wt%) and 7–10 (4 wt%).

system, offering a new composition regulation opportunity for the alloy TMNP catalysts. It is worthy of note that almost all the Pd species of supported $Au_{50}Pt_{25}Pd_{25}$ alloy TMNPs are in the Pd⁰ state (~92%, Fig. 2b).

One of the greatest challenges in MNP catalysis is the deactivation of catalysts under realistic process conditions.¹⁸ In some realistic industrial reactions such as the catalytic combustion widely used in the tail gas processing and the oil refining process, they can maintain the reaction at only 300–400 °C for most of the time, but sometimes the reaction temperature can reach as high as nearly 1000 °C at one moment owing to the inevitably excessive combustion or other reasons. Although it may only last for several seconds, the momentary process brings serious irreversible degradation of the catalyst. So in the preparation process of the industrial catalysts, the catalysts must be aged under harsh pretreatment conditions before use in order to make sure they are durable and stable enough.

In this study, the catalytic performance of AuPtPd TMNPs has been investigated in the oxidation of 1000 ppm *n*-hexane in air. In order to evaluate their durability in long-term operation, all samples were pre-treated by thermal aging at 800 °C in air for 5 h prior to the catalytic testing. The fresh Pt and Pd samples (4 wt% loading) show good catalytic activity towards *n*-hexane oxidation, with T_{50} less than 240 °C. However, after thermal aging at 800 °C in air, a sharp decrease of their oxidation

activity was observed, and their T_{50} increased to above 400 °C (Fig. 3c, Fig. S7, ESI†). The activation temperatures (T_{15}) of the Pt and Pd catalysts also increased to 305 °C and 260 °C, respectively, suggesting a very poor activity for *n*-hexane oxidation. Pd-based bimetallic nanoparticles (Au₃₃Pd₆₇ and Pt₃₃Pd₆₇) also displayed poor oxidation activity after the thermal aging (Fig. 3c). In contrast, all AuPtPd alloy TMNPs showed good activity even though their metal loading concentration was only one-fourth of the Pt or Pd catalyst. Among them, the Au₅₀Pt₂₅Pd₂₅ sample showed the best catalytic activity with the lowest T_{50} (286 °C) and T_{15} (203 °C), which has the highest Pd⁰ content. We believe that the sub-10 nm size and stable, high Pd⁰ oxidation state of the supported Au₅₀Pt₂₅Pd₂₅ alloy TMNPs are responsible for their excellent catalytic performance.

The photo-deposition method is crucial for the successful synthesis of $Au_{50}Pt_{25}Pd_{25}$ alloy TMNPs, whose intended metal ratio falls in the miscibility gap of the bulk Au–Pt–Pd phase diagram and displays the best catalytic performance. The attempt to prepare $Au_{50}Pt_{25}Pd_{25}$ alloy TMNPs by conventional wet impregnation or colloidal-photo deposition failed. From XRD data in Fig. S8 (ESI†), after annealing at 800 °C, a phase separation (Au-rich and Pt-rich phases) was observed and large nanoparticles (> 20 nm) were obtained. In the current synthetic system, one-step photo-deposition of Au, Pt and Pd precursors is preferred on the same active sites, resulting in the formation of Au@PtPd TMNPs.¹⁹

In conclusion, we have reported a simple preparation of supported Au–Pt–Pd trimetallic alloy nanoparticles where there is a tighter control over the composition from particle-to-particle, while preserving the uniform sub-10 nm size distribution. The crucial role of mesoporous TiO_2 and the photo-deposition strategy for the successful synthesis argue for the importance of using well-defined nanoporous structures for the design of a better metal nanoparticle catalyst operating under realistic conditions. The method may be

useful for the synthesis of hitherto unknown composite multimetallic nanoparticles structured on nanometer domains with new chemical and electronic states, which may benefit their catalytic/ other properties.

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