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Bimetallic alloy nanocrystals encapsulated in ZIF-8 for synergistic catalysis of ethylene oxidative degradation†

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Highly dispersed PtPd alloy nanocrystals (NCs) were firstly successfully encapsulated in microporous zeolitic imidazolate framework ZIF-8 (PtPd@ZIF-8) with tunable compositions by a “bottle around ship” approach. The PtPd@ZIF-8 catalyst showed excellent synergistic photocatalytic activity in the transformation of the adsorbed ethylene into CO₂ and H₂O at room temperature.

Recently, bimetallic alloy nanoparticles (NPs) have received much attention because they usually show a great enhancement in synergistic catalytic properties due to their interplay of electronic and lattice effects.¹ However, the metallic NPs could be dispersed on supports to prevent agglomeration to the bulk materials, which generally leads to the loss of the catalytic properties.² Therefore, suitable supports for NP catalysts are imperative.

Metal–organic frameworks (MOFs), also known as porous coordination polymers or porous coordination networks, have been emerging as supports for metal NPs due to their high surface areas, tunable pore structures and the presence of organic functional groups.^{3,4} Especially, zeolitic imidazolate framework (ZIF) ZIF-8, a subclass of MOFs, not only has high thermal and chemical stability,⁵ but also shows great potential in gas separation⁶ and catalysis as a host matrix.^{7,8c} However, to date, most of reported studies have mainly focused on MOF-immobilized monometal NPs.³ There have been only a limited number of studies on the use of MOFs as host matrices to support bimetallic NPs^{8–10} and even fewer on bimetallic alloy NPs embedded into MOFs for heterogeneous catalysis.^{8a–c–10} Recently, Xu successfully prepared AuNi alloy NPs immobilized on MIL-101 by using the double solvent method (DSM).^{8b} By using the MOCVD (metal–organic chemical vapor deposition) method, Kempe introduced PdNi alloy NPs into the cavities of MIL-101, which exhibited synergistic catalytic effects in the hydrogenation of

dialkyl ketones.^{9a} AuPd alloy NPs dispersed on the MIL-101 have been prepared *via* a colloidal method followed by reduction with NaBH₄.^{10a} However, the incorporation of bimetallic alloy NPs into MOFs host matrices still remains a great challenge because a mixture of monometal NPs is often obtained by using traditional approaches.^{3a} Moreover, the NPs usually do not occupy the MOF cavities, but are supported on the external surfaces of MOFs.¹⁰

Ethylene is a very important industrial material that produces polyethylene. However, ethylene released from flowers, fruits, and vegetables can accelerate aging and spoilage of the plants, which is not conducive to long-term storage. Consequently, in order to maintain freshness in some special environments, such as fruit storage areas, the removal of trace amounts of ethylene is necessary.¹¹ The catalytic oxidation degradation of ethylene into CO₂ and H₂O is an effective method to remove low concentrations of ethylene. Ultrafine powdered TiO₂ photocatalysts have been used to degrade ethylene.¹² Hao have made attempts to develop gold catalysts supported on mesoporous Co₃O₄ for the removal of ethylene.¹³ Recently, Fukuoka found that Pt NPs supported on mesoporous silica MCM-41 show high activity for ethylene oxidation under low-temperature conditions.¹⁴ However, Au and Pt are very expensive metals. Therefore, the bimetallic alloys incorporating less expensive metals such as Pd could increase the economic value and accelerate the practical applications of these catalysts.

Herein, we report a general encapsulation strategy for the full incorporation of PtPd alloy nanocrystals (NCs) into ZIF-8. The presynthesized PtPd alloy NCs were completely encapsulated in ZIF-8 crystals by the crystallization process of ZIF-8 in methanol at room temperature. To the best of our knowledge, up to now, there are no reports of using a “*bottle around ship*” approach to embed bimetallic alloy NPs into MOFs.¹⁵

The cubic Pt_mPd_n alloy NCs (with an average edge length of 6.5 nm, Fig. S1, ESI†) with different compositions, were prepared using a solvothermal method.¹⁶ The obtained alloy NCs can be easily encapsulated in the crystals of ZIF-8 through the assembly process. The samples were denoted as Pt_mPd_n@ZIF-8, and *m/n* is the atomic ratio of Pt and Pd. For comparison purposes, the monometallic NC catalysts, Pt@ZIF-8 and Pd@ZIF-8, were also easily prepared using

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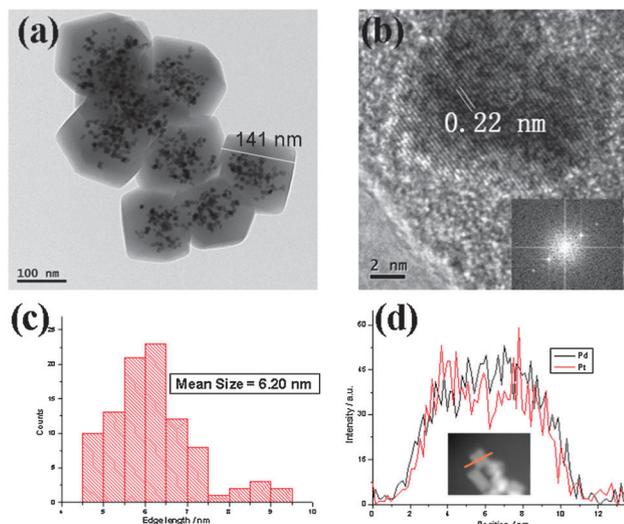


Fig. 1 (a) Representative TEM and HRTEM (b) images of $\text{Pt}_5\text{Pd}_5@ZIF-8$; (c) edge length distribution of $\text{Pt}_5\text{Pd}_5@ZIF-8$; (d) line-scanning profile across a cubic Pt_5Pd_5 NCs encapsulated in ZIF-8, which is indicated in the inset of (d). Inset in (b) is the FFT pattern of an individual Pt_5Pd_5 NC.

the same approach. Transmission electron microscopy (TEM) images show that the well dispersed Pt_mPd_n alloy NCs were fully encapsulated in ZIF-8 nanocrystals (about 140 nm) with a rhombic dodecahedral shape (Fig. 1a, Fig. S4, ESI[†]). Interestingly, no particles were observed on the outside surfaces of each ZIF-8 crystal. The mean size of the alloys is about 6.2 nm (Fig. 1c), which is similar to that of Pt_mPd_n alloy NCs before encapsulation (Fig. S1, ESI[†]). This proves that the PtPd alloy NCs were stable after the process of encapsulation, and did not agglomerate to the bulk. A high-resolution TEM (HRTEM) image shows that it is a single crystal with well-defined fringes (Fig. 1b). It has a typical face-centered cubic (fcc) Pd structure, which corresponds to a Pd(111) interplanar spacing of 0.22 nm. However, the lattice spacing of the nanocube before encapsulation is 0.19 nm, consistent with the {200} lattice spacing of the face-centered cubic (fcc) Pt or Pd (Fig. S1, ESI[†]).¹⁶ It is obvious that there is a homogeneous distribution of Pt/Pd elements in the compositional scanning line profile of Pd and Pt across an single nanocube encapsulated in the crystals of ZIF-8, suggesting the formation of an alloy structure.¹⁶

The powder X-ray diffraction (PXRD) patterns of the $\text{Pt}_5\text{Pd}_5@ZIF-8$ samples show two sets of peaks (Fig. 2). One set of peaks in the 2θ range of 5–38 degree is identical with that of ZIF-8,^{5–7} which indicates that the frameworks of ZIF-8 are stable after the encapsulation process. The other four strong characteristic peaks at $2\theta = 40.0^\circ$, 46.5° , 67.8° , and 81.6° can be assigned to the (111), (200), (220) and (311) crystalline planes of PtPd alloy NPs with a face-centered-cubic (fcc) phase structure, respectively. The four diffraction peaks are located between the corresponding peak positions of Pt@ZIF-8 and Pd@ZIF-8 (Fig. 2), which strongly proves the formation of a PtPd alloy.^{16,17} The X-ray photoelectron spectroscopy (XPS) spectra (Fig. S8, ESI[†]) of the $\text{Pt}_5\text{Pd}_5@ZIF-8$ show the binding energies of Pt(0) (73.7 eV and 70.5 eV, $4f_{5/2}$ and $4f_{7/2}$, respectively) and Pd(0) (340.6 eV and 335.3 eV, $3d_{3/2}$ and $3d_{5/2}$, respectively). No obvious peaks of Pt^{2+} and Pd^{2+} are observed, which indicates that the PtPd NCs are stable after the encapsulation procedure. The PVP protected Pt_mPd_n NCs

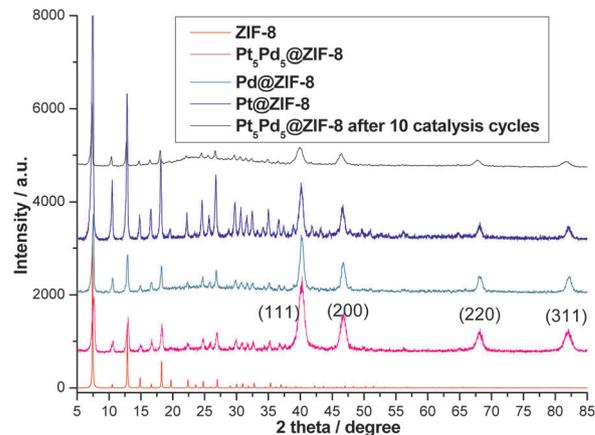


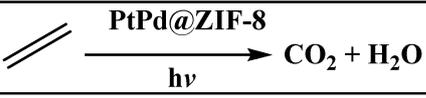
Fig. 2 PXRD patterns of ZIF-8, $\text{Pt}_5\text{Pd}_5@ZIF-8$, Pt@ZIF-8, Pd@ZIF-8, and $\text{Pt}_5\text{Pd}_5@ZIF-8$ after ten runs of catalysis.

stabilized by imidazole may play an important role in the assembly process.^{7b} Compared to the standard binding energy peak values of Pt(0) and Pd(0), the values are shifted to lower binding energies, suggesting a modification of the electronic structure of the surface Pt and Pd atoms, which could further be indicative of the formation of bimetallic alloys.^{10a}

Compared with pure ZIF-8 ($1023.5 \text{ cm}^2 \text{ g}^{-1}$), $\text{Pt}_5\text{Pd}_5@ZIF-8$ ($712.9 \text{ cm}^2 \text{ g}^{-1}$) shows decreased Brunauer–Emmett–Teller (BET) surface areas (Fig. S9, ESI[†]), which may be attributed to the non-porous bimetallic NCs and traces of PVP located at the surfaces.^{7a,b} However, the incorporation of bimetallic NCs does not alter the pore-size distribution of the matrix of ZIF-8 (Fig. S10, ESI[†]), because the larger size of PtPd alloy NCs (6.5 nm) cannot occupy the cavities (1.16 nm) of the framework. Therefore, the PtPd alloy NCs are not encapsulated in the cages of ZIF-8 but located in the intercrystals.^{7b}

The microporous material ZIF-8 shows good ethylene adsorption capacity (42 mg g^{-1}) at room temperature under atmospheric pressure.¹⁸ Encapsulation of Pt_mPd_n alloy NCs did not affect the adsorption uptake (Fig. S11, ESI[†]). $\text{Pt}_m\text{Pd}_n@ZIF-8$ catalyst systems were then investigated in the ethylene oxidation degradation reaction (Table 1). Although the parent material ZIF-8 showed high adsorption capture of ethylene, it could not effectively degrade the captured ethylene under the visible light (Table 1, entry 1). This can be ascribed to the fact that ZIF-8 shows ultraviolet absorptive behavior due to a wide band gap of 4.9 eV,¹⁹ although the solar light consists of $\sim 5\%$ UV (wavelength 200–400 nm).²⁰ It is no surprise that the Pt_5Pd_5 NCs showed almost no activity (Table 1, entries 2 and 3), which might be attributed to the agglomeration of the NPs without the protection of the support.¹⁴ Interestingly, the noble metal NPs remarkably promote the photocatalysis.²¹ More than 50% ethylene was converted into CO_2 and H_2O by using Pt@ZIF-8 assisted by solar light from a 300 W xenon lamp at room temperature (entry 4), which was higher than the conversion achieved using Pd@ZIF-8 almost under the same conditions (entry 5). $\text{Pt}_5\text{Pd}_5@ZIF-8$ showed only about 5% conversion of ethylene at room temperature or at 80°C under dark conditions (entries 6 and 7). Consequently, it has been excluded that heat led to the transformation of ethylene. Expectedly, the bimetallic $\text{Pt}_m\text{Pd}_n@ZIF-8$ catalyst system showed higher

Table 1 The activity of Pt_mPd_n@ZIF-8 for ethylene oxidation degradation^a

			
Entry	Catalyst	Pt (Pd) loading (wt%)	C ₂ H ₄ conversion (%)
1	ZIF-8 ^b	0 (0)	<5
2 ^c	Pt ₅ Pd ₅	4.95 (2.70)	<5
3 ^d	Pt ₅ Pd ₅	4.95 (2.70)	<5
4	Pt@ZIF-8	5.03 (0)	53.2
5	Pd@ZIF-8	0 (2.75)	29.5
6	Pt ₅ Pd ₅ @ZIF-8 ^e	4.95 (2.70)	4.8
7	Pt ₅ Pd ₅ @ZIF-8 ^f	4.95 (2.70)	5.0
8	Pt ₃ Pd ₇ @ZIF-8	4.95 (6.31)	68.2
9	Pt ₅ Pd ₅ @ZIF-8	4.95 (2.70)	93.1
10	Pt ₇ Pd ₃ @ZIF-8	4.95 (1.16)	82.7
11	Pt@ZIF-8, Pd@ZIF-8	5.03 (0), 0 (2.75)	56.1
12	Pt ₅ Pd ₅ @ZIF-8 ^g	4.95 (2.70)	90.1
13	Pt ₅ Pd ₅ @ZIF-8 ^h	4.95 (2.70)	83.2
14 ⁱ	Pt ₅ Pd ₅ @ZIF-8	4.95 (2.70)	84.3
15 ^j	Pt ₅ Pd ₅ @ZIF-8	4.95 (2.70)	94.2

^a Conditions: 200 mg catalyst; C₂H₄: 100 ppm; O₂: 1.11 × 10⁴ ppm; N₂: balance; temperature, 25 °C; time: 2 h; Xenon lamp, 300 W. ^b 9 h. ^c 35 mg catalyst. ^d 35 mg catalyst, dark conditions. ^e Dark conditions. ^f 80 °C, dark conditions. ^g 50 mg catalyst. ^h mg catalyst. ⁱ 200 ppm C₂H₄. ^j 50 ppm C₂H₄.

conversions at 25 °C (entries 8–10). The use of a mixture of pure Pt@ZIF-8 and pure Pd@ZIF-8 in a 1 : 1 ratio (entry 11) showed a clearly lower catalytic activity than the corresponding bimetallic alloy catalyst Pt₅Pd₅@ZIF-8 (entry 9), which further indicated a synergistic catalytic effect.^{9a} Notably, over 83.2% ethylene conversion was accomplished using a very low amount of the catalyst (25 mg, entry 13) under the similar conditions. Increasing (200 ppm) or decreasing (50 ppm) the ethylene concentration also gave high conversion (entries 14 and 15). More importantly, reusability studies at ambient temperature exhibited no significant decrease in the conversion after 10 catalytic cycles (Fig. S13, ESI[†]), showing great potential applicability to warehouse storage.

In conclusion, we have demonstrated a facile synthetic strategy via a “bottle around ship” approach to prepare MOF-encapsulated PtPd alloy NCs with tunable compositions for the first time. The MOF-immobilized alloy NCs were firstly used in the synergistic catalysis of ethylene oxidation degradation. The catalytic properties are highly composition dependent with ~50% Pt showing the optimum activity. It not only reduces the amount of noble Pt used, but also enhances the catalytic activity. Our studies reveal that ZIF-8 not only serves as a support to prevent the aggregation of the alloys, but also adsorbs ethylene and promotes photodegradation of ethylene into CO₂ and H₂O.

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