SPECIAL ISSUE: Emerging Investigators of Nanomaterials

In situ redox strategy for large-scale fabrication of surfactant-free M-Fe₂O₃ (M = Pt, Pd, Au) hybrid nanospheres

Wang Li¹, Xilan Feng¹, Dapeng Liu^{1*} and Yu Zhang^{1,2*}

ABSTRACT A facile *in situ* redox strategy has been developed to fabricate surfactant-free M-Fe₂O₃ (M = Pt, Pd, Au) hybrid nanospheres. In this process, noble metal salts were directly reduced by the pre-prepared Fe₃O₄ components in an alkaline aqueous solution without using organic reductants and surfactants. During the redox reaction, Fe₃O₄ was oxidized into Fe₂O₃, and the reductates of noble metal nanoparticles were deposited on the surface of the Fe₂O₃ nanospheres. Then the characterizations were discussed in detail to study the formation of M-Fe₂O₃ hybrids. At last, catalytic CO oxidation was selected as a model reaction to evaluate the catalytic performance of these samples. It demonstrates that Pt-Fe₂O₃ nanospheres can catalyze 100 % conversion of CO into CO₂ at 90°C, indicating superior activity relative to Pd-Fe₂O₃ and Au-Fe₂O₃.

Keywords: noble metal, iron oxides, hybrid, CO oxidation, nanospheres

INTRODUCTION

Noble metal nanostructures have received continuous attention due to their unique physicochemical properties for numerous catalytic applications [1–15]. However, noble metals are extremely rare in nature, resulting in their high price level. In order to lower down the overall cost to meet the increasing demands in industry for noble metals, it seems urgent to improve their catalytic efficiency. Research shows that if noble metals are supported on substrates like metal oxides [16,17], metal sulfides [18–21], zeolites [22], metal organic frameworks (MOFs) [23–27] or carbon materials [28–30], the as-obtained hybrids could show much better catalytic performance than noble metals themselves. An appropriate substrate can effectively disperse and protect the active centers, and moreover by utilizing substrate

effects the catalytic activities, stabilities and selectivity of noble metals can be further optimized [31–33]. Among the substrates, magnetic oxides are more attractive on accounts of their excellent magnetic response [34–40]. Once noble metals are loaded on the magnetic oxide substrates to form stable hybrids, the fast separation of catalysts can be easily achieved from the reaction systems, which will favor simplifying the post-treatment to improve the recyclability.

In previous reports, four main kinds of iron oxides supported noble metal nanostructures have been successfully fabricated. One is the simple Fe₃O₄/noble metal hybrids, in which noble metal components were evenly dispersed in the Fe₃O₄ structures [41,42]. The second is the Janus nanostructure. The representative research were done by Sun's group that they realized the synthesis of colloidal dumb-bell-like noble metal-Fe₃O₄ hybrids in an oil phase via the classic seeding growth method [34–38]. The third is in a more complex core@shell nanostructure. Yin *et al.* [39] presented a water-phase strategy to prepare Fe₃O₄@SiO₂@Au@SiO₂ multi-layered core@shell nanostructure. For the last, noble metal salts and organometallic precursors were reduced at the same time to form noble metal/Fe alloys, and further oxidizing process resulted in the iron oxides coated noble metals nanostructures. Such obtained four kinds of hybrids are of high quality, however the oil-phase synthesis makes the post-treatment a little onerous, and some indispensable expensive ligands increase the overall cost [43,44].

Ideally, a promising method should be green and suitable for mass production of noble metal catalysts under mild conditions. Moreover, it should decrease and even deny the usage of toxic organic solvents and surfactants. Compared

¹ Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing 100191, China

² International Research Institute for Multidisciplinary Science, Beihang University, Beijing 100191, China

* Corresponding authors (emails: liudp@buaa.edu.cn (Liu D); jade@buaa.edu.cn (Zhang Y))

with these classical oil-phase routes, some water-phase synthesis seems more economic and promising, despite its multi-step layer-by-layer coating technology and surface modifications make the synthesis rather complicated for a large scale. Not far from recently, an interesting clean synthesis of surfactant-free noble metal catalysts has become a hot spot owing to its fast and facile synthetic process and especially the avoidable post-treatment [45–49]. The synthesis was conducted by utilizing the redox relationship either between noble metal salts and reductive supports or between noble metal salts and low-valence transition metal precursors. For instance, through an *in situ* redox between the reductive $\text{WO}_{2.72}$ substrate and the oxidative noble metal salt precursors [45], a series of noble metal/ WO_3 nanocomposites with uniform metal dispersion, tunable metal particle size, and narrow metal particle size distribution were obtained in the absence of reducing agent or surfactants. This clean synthesis route has also been developed to the Ag– CeO_2 system [48,49] by triggering the autocatalyzed reaction between $\text{Ce}(\text{OH})_3$ and $\text{Ag}(\text{NH}_3)_2^+$ to form the final rice-ball like hybrid nanostructures. Besides, we focused on this subject and successfully developed a new non-organic synthetic method to fabricate pomegranate-like $\text{Pt}@\text{CeO}_2$ multi-core@shell high-temperature-stable catalysts [50]. And the similar strategy was then applied to the fabrication of $\text{Pd}@\text{CeO}_2$ and $\text{Au}@\text{CeO}_2$ systems [51,52].

Due to rich valence states, complex redox reactions could happen among transition metals as well. For example, Cu^{2+} can be reduced by Ce^{3+} in the alkali condition to form self-assembled $\text{Cu}_2\text{O}/\text{CeO}_2$ nanostructures [53]. Be-

sides, Fe_3O_4 that has reductive Fe^{2+} can react with Ce^{4+} to prepare hydrophilic Ce atoms doped Fe_2O_3 nanoparticles. In light of the possible redox relationship, it is believed that an appropriate reaction condition might trigger the redox between Fe_3O_4 and the noble metal salts. Moreover the pre-formed Fe_3O_4 could play the role of support to avoid the independent nucleation of noble metal nanoparticles, and meanwhile provide effective interface with noble metals to promote synergistic effects.

In this paper, we report a facile *in situ* redox strategy under hydrothermal condition to induce the reaction of noble metal salts and Fe_3O_4 nanospheres to form surfactant-free hybrids. The schematic synthesis is described in Scheme 1. Compared with the oil-phase methods, this process was conducted without addition of organic solvents and surfactants. By varying the kinds of noble metal salts, M- Fe_2O_3 (M = Pt, Pd, Au) hybrid nanospheres can be easily synthesized in a large scale. Moreover, the products could be fast separated by a magnetic field. Detailed characterizations were carried out to study the structural information of the final products. And the following catalytic tests show that the Pt- Fe_2O_3 nanospheres can catalyze 100 % conversion of CO into CO_2 at a temperature of 90°C , and more active than Pd- Fe_2O_3 and Au- Fe_2O_3 .

EXPERIMENTAL SECTION

Synthesis of Fe_3O_4 nanospheres

The synthesis was conducted according to the previous literature [54]. The as-obtained products were washed with

Scheme 1 Synthesis of M- Fe_2O_3 hybrid nanospheres.

HCl and water for several times in advance to clean the surface of Fe_3O_4 completely.

Synthesis of noble metal- Fe_2O_3 hybrid nanospheres

80 mg of Fe_3O_4 nanospheres were dispersed in 10 mL water by ultrasound-treatment for 5 min. Then 1 mL KOH (0.2 mol L^{-1}) and 1 mL noble metal salts (20 mmol L^{-1}) (K_2PtCl_4 for Pt; K_2PdCl_4 for Pd and HAuCl_4 for Au) were added in turn. After further ultrasound-treatment for 2 min, the mixture was transferred into a 15 mL Teflon-lined stainless steel autoclave, followed by heating at 120°C for 90 min. After cooled down to room temperature, the product was collected by magnetic separation and washed for three times.

Synthesis of Fe_3O_4 nanoparticles

1 mmol FeCl_2 and 2 mmol FeCl_3 were dissolved in 20 mL water, followed by addition of 0.8 mL $\text{NH}_3\cdot\text{H}_2\text{O}$. After stirring for 30 min, the products were washed and purified by magnetic separation and then dried at 60°C overnight.

Synthesis of Pt- Fe_2O_3 hybrid nanoparticles

The synthesis was similar with that of noble metal- Fe_2O_3 hybrid nanospheres except for the usage of Fe_3O_4 nanoparticles instead of Fe_3O_4 nanospheres.

Synthesis of Pt@ CeO_2 nanospheres

The whole synthesis was conducted according to our previous report [50]. 1 mL of $0.1 \text{ mol L}^{-1} \text{Ce}(\text{NO}_3)_3$ was solved by 10 mL of H_2O , and then bubbled by Ar for 10 min. Then, 1 mL of $0.2 \text{ mol L}^{-1} \text{NaOH}$ was injected, followed by the rapid addition of 1 mL of $0.01 \text{ mol L}^{-1} \text{K}_2\text{PtCl}_4$. The solution was heated to 70°C and kept for 1 h. After being cooled, the solid was washed by water and purified by centrifugation. The purification process was repeated for three times.

Characterizations

The X-ray diffraction (XRD) patterns of the products were collected on a Rigaku-D/max 2500 V X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al $\text{K}\alpha$ X-ray radiation as the X-ray source for excitation. Inductively coupled plasma (ICP) analyses were performed with a Varian Liberty 200 spectrophotometer to determine the contents. The catalytic performances on CO

oxidation of the catalysts were monitored on-line by gas chromatography (GC9800).

Catalytic tests

10 mg catalysts were mixed with 20 mg SiO_2 powders. The mixture was put in a stainless steel reaction tube. The experiment was carried out under a flow of the reactant gas mixture (1% CO, 20% O_2 , balance N_2) at a rate of 30 mL min^{-1} . The composition of the gas was monitored on-line by gas chromatography.

RESULTS AND DISCUSSION

The Fe_3O_4 nanospheres were prepared according to the previous literature [54] and used as the starting materials (as shown in Fig. S1, Supplementary information). These nanospheres are in a mean size of 150–200 nm and consist of 15 nm sized nanoparticles. After reaction with noble metals salts (K_2PtCl_4 , K_2PdCl_4 or HAuCl_4), there are obvious difference in the XRD patterns of the noble metals deposited products compared with that of the Fe_3O_4 nanospheres as seen in Fig. 1. In these patterns, the characteristic peaks related to $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS No. 39-1346) clearly appear rather than Fe_3O_4 (JCPDS No. 65-3107). However as known Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ have very similar XRD patterns, so XPS characterization becomes necessary to give further evidence to support our judgement. From the XPS spectra (Figs S2–S4), it can be seen that all samples just show the signals related to Fe^{3+} rather than a mixed state of Fe^{2+} and Fe^{3+} , firmly confirming the complete oxidation of Fe_3O_4 into Fe_2O_3 by noble metal salts [55]. Moreover, despite of the disappearance of Pt and Pd signals in the XRD patterns, the characteristic XPS peaks of Pt, Pd and Au undoubtedly prove the surface deposition of noble metal

Figure 1 XRD patterns of the pure Fe_3O_4 nanospheres, Pt- Fe_2O_3 , Pd- Fe_2O_3 and Au- Fe_2O_3 .

components on these nanospheres. This conclusion can be further supported by the following TEM characterizations.

According to the initial results judged by XRD and XPS characterization, hereafter we abbreviated the as-formed products as $M\text{-Fe}_2\text{O}_3$ ($M = \text{Pt}, \text{Pd}$ and Au). The typical TEM images of $\text{Pt-Fe}_2\text{O}_3$ in Figs 2a and b show that almost no change in size and morphology occurred after the spherical Fe_3O_4 precursors oxidized into Fe_2O_3 . Due to evident contrast compared with Fe_2O_3 , Pt nanoparticles can be easily distinguished in the images. Numerous Pt nanoparticles with a size of 2 nm evenly distributed on the surface of each Fe_2O_3 nanosphere. The ultra-small size of Pt should be responsible for its relatively weak XRD signals. The high-resolution TEM (HRTEM) image shows that the lattice spacings of 0.24 nm correspond well with the char-

acteristic (111) planes of Pt (Fig. 2c, inset). The STEM (Fig. 2d) and mapping analysis (Figs 2e and f) also demonstrate the clear element distribution of Fe and Pt in $\text{Pt-Fe}_2\text{O}_3$. The mass production of $\text{Pt-Fe}_2\text{O}_3$ can be easily realized into gram scale due to the facile synthesis process and simple post-treatment as seen in Fig. 2g. The as-prepared $\text{Pt-Fe}_2\text{O}_3$ nanospheres exhibit high colloidal stability in polarity solvents like water, ethanol and DMF (Fig. 2h), and they response well under external magnetic fields that facilitates their separation from solutions (Fig. 2i).

After careful consideration, there are still doubts needed to be clearly eliminated on the redox reactions between noble metals salts and Fe_3O_4 . To give clear illustration, three control experiments were carried out. First, we tried to repeat the synthetic process in the absence of Fe_3O_4 nano-

Figure 2 TEM images of $\text{Pt-Fe}_2\text{O}_3$ (a–c) and their corresponding STEM images (d–f); production of $\text{Pt-Fe}_2\text{O}_3$ in one pot (g); photos of the $\text{Pt-Fe}_2\text{O}_3$ nanospheres in water, ethanol and DMF (h), and that of $\text{Pt-Fe}_2\text{O}_3$ powders under a magnet (i).

spheres. After hydrothermal treatment for 90 min, it left only a clear colorless solution. No successful nucleation of Pt could be observed indicating that Fe_3O_4 nanospheres in the synthetic process played an important role as reductant. The second control was conducted by directly hydrothermal treatment of Fe_3O_4 nanospheres and K_2PtCl_4 without addition of KOH. As expected, there was no Pt found on the surface of Fe_2O_3 suggesting necessity of the alkaline condition. The third control was taken by replacing Fe_3O_4 nanospheres by Fe_3O_4 nanoparticles prepared by the classical co-precipitation method to determine the influence of Fe_3O_4 precursors on the final products. In Fig. S5, it can be seen that after the reaction in the same condition, Pt nanoparticles grew up to 5 nm on the Fe_3O_4 nanoparticles, indicating that three-dimensional Fe_3O_4 nanospheres show better template effect than zero-dimensional Fe_3O_4 nanoparticles to stabilize Pt components and restrict their growth.

Similar to K_2PtCl_4 , the oxidation potential of K_2PdCl_4 is higher than Fe^{2+} , so the synthetic process is then employed to the Pd- Fe_2O_3 system. As shown in Figs 3a and b, when K_2PdCl_4 is used as the oxidant, Pd- Fe_2O_3 hybrid nanospheres with the similar structure of Pt- Fe_2O_3 are formed. Sub-4 nm sized Pd nanoparticles are evenly distributed on the surface of Fe_2O_3 nanospheres. The lattice spacing

of 0.23 nm corresponds well with the characteristic (111) planes of Pd (Fig. 3c, inset). And the mapping analysis (Figs 3d–f) present the clear element distributions of Fe and Pd.

In comparison with Pt- Fe_2O_3 and Pd- Fe_2O_3 , the as-prepared Au- Fe_2O_3 demonstrated a quite different hybrid structure. In Figs 4a–c, on the surface of every single Fe_2O_3 nanosphere there exists one Au nanoparticle with a size of sub-35 nm, forming an typical one-to-one Janus structure. The components of Fe_2O_3 and Au could be easily distinguished by their obvious contrast. The STEM image and mapping analysis in Figs 4d–f further confirm the elemental distributions of Fe and Au. The much bigger size of Au than Pt and Pd means its faster growth rate in the similar reaction conditions. In other words, Fe_2O_3 surface could stabilize Pt and Pd more effectively than Au, resulting in their ultrasmall particle sizes.

The magnetization curves in Fig. 5 demonstrate that the as-obtained hybrids are superparamagnetic. The saturation magnetization is about 65.7, 59.5 and 55.1 emu g^{-1} for Pd- Fe_2O_3 , Pt- Fe_2O_3 and Au- Fe_2O_3 , respectively, which are a little lower than the value of the Fe_3O_4 precursor (81.5 emu g^{-1}). The decreased saturation magnetization is another proof of the oxidation of Fe_3O_4 into Fe_2O_3 .

Iron oxides are good supports for noble metal catalysts. The formation of hybrid structures of iron oxides and no-

Figure 3 TEM (a–c) and STEM (d–f) images of Pd- Fe_2O_3 .

Figure 4 TEM (a–c) and STEM (d–f) images of Au-Fe₂O₃.

Figure 5 Magnetization curves at 300 K of pure Fe₃O₄, Pt-Fe₂O₃, Pd-Fe₂O₃ and Au-Fe₂O₃.

ble metals can not only possess quick magnetic response, but also show strong synergistic effects that favour enhancing catalytic performance. In the following, the as-prepared M-Fe₂O₃ samples were tested by the model reaction of CO oxidation to evaluate their catalytic activity and stability. T_{100} , the temperature of conversion of CO into CO₂, was used to compare the catalytic activities of the three samples of Pt-Fe₂O₃, Pd-Fe₂O₃ and Au-Fe₂O₃. From Fig. 6, it is seen

that the values of T_{100} follow such a sequence that Pt-Fe₂O₃ (90°C) < Pd-Fe₂O₃ (125°C) < Au-Fe₂O₃ (250°C, only about 50 % conversion). Obviously Pt-Fe₂O₃ exhibits the highest catalytic activity among the three samples, and even better than previously reported pomegranate-like Pt@CeO₂ multi-core@shell catalysts (145°C) and the typical Pt-CeO₂ catalysts (144°C) [56]. The cycling test was then conducted to study the stability of Pt-Fe₂O₃. After ten successful cycles, Pt-Fe₂O₃ sample still maintained 100 % conversion of CO into CO₂ at 90°C, indicating its good catalytic stability.

CONCLUSIONS

To conclude, we successfully developed a facile non-organic route to synthesize noble metal-Fe₂O₃ hybrid nanospheres in a large scale. Without addition of organic reductants and surfactants, this clean redox reaction just happens between noble metal salts and Fe₃O₄ components in an alkaline aqueous solution. During the redox reaction, Fe₃O₄ was oxidized into Fe₂O₃, and the reductates of noble metal nanoparticles were deposited on the Fe₂O₃ nanospheres. However due to different redox reaction rates, Pt and Pd tend to form small sized nanoparticles with uniform dispersion, while Au grew into much bigger ones forming the typical Janus structure with Fe₂O₃ nanospheres. Catalytic tests show that Pt-Fe₂O₃ nanospheres are highly ac-

Figure 6 CO conversion curves of Pt-Fe₂O₃, Pd-Fe₂O₃ and Au-Fe₂O₃.

tive and can catalyze 100 % conversion of CO into CO₂ at 90°C. This conversion temperature is much lower than that of Pd-Fe₂O₃ and Au-Fe₂O₃. Owing to the naked surfaces, suitable particle sizes and the presence of noble metal and magnetic composites, it is believed that Pt-, Pd-, Au-Fe₂O₃ may have promising applications in catalytic, energy, and biology areas.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information TEM images of Fe_3O_4 nanospheres and nanoparticles. TEM images of $\text{Pt-Fe}_2\text{O}_3$ nanoparticles. XPS spectra of sample $\text{Pt-Fe}_2\text{O}_3$, $\text{Pd-Fe}_2\text{O}_3$, and $\text{Au-Fe}_2\text{O}_3$. The calculated component contents of sample $\text{Pt-Fe}_2\text{O}_3$, $\text{Pd-Fe}_2\text{O}_3$, and $\text{Au-Fe}_2\text{O}_3$ obtained from ICP analyses. These details are available in the online version of the paper.

Wang Li received her bachelor degree from Changzhi University in 2014. She is currently a graduate student under the supervision of Prof. Yu Zhang at the School of Chemistry and Environment, Beihang University. Her research interest is mainly focused on the synthesis of advanced inorganic materials and their applications in catalysis and lithium/sodium ion batteries.

Yu Zhang received his PhD degree in chemistry from Jilin University in 2007. Then he worked as a New Energy and Industrial Technology Development Organization (NEDO) fellow at Hiroshima University, Japan. In March 2013, he joined Beihang University as a “Zhuoyue” Program Associate Professor. Now he is a professor of the School of Chemistry and Environment, Beihang University. His interests mainly focus on advanced materials for hydrogen storage/production, lithium/sodium ion battery and fuel cells.

利用原位氧化还原策略宏量制备M-Fe₂O₃ (M = Pt, Pd, Au)杂化纳米球

李旺, 冯锡岚, 刘大鹏, 张瑜

摘要 本工作利用原位氧化还原策略, 成功制备出无表面活性剂修饰的M-Fe₂O₃ (M = Pt, Pd, Au)杂化纳米球. 在反应过程中, 以事先制备好的Fe₃O₄纳米球作为载体和还原剂, 在碱性条件下直接还原高价态的贵金属盐前驱体. 反应后, Fe₃O₄被氧化成Fe₂O₃, 而贵金属纳米粒子作为还原产物则牢牢的沉积在氧化产物Fe₂O₃表面形成M-Fe₂O₃杂化纳米球. 通过表征系统研究了所得产物的形貌、结构和催化性质. 并以CO催化氧化为模型反应对产物进行评估, 结果表明, 样品Pt-Fe₂O₃在90°C即可将CO 100%催化转化为CO₂, 相比Pd-Fe₂O₃和Au-Fe₂O₃具有更高的催化活性.