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Iridium ultrasmall nanoparticles, worm-like chain nanowires, and porous nanodendrites: One-pot solvothermal synthesis and catalytic CO oxidation activity

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ABSTRACT

We report a facile one-pot solvothermal synthesis of monodisperse iridium (Ir) ultrasmall (1.5–2.5 nm in diameter) nanoparticles (NPs), worm-like chain nanowires (NWs), and porous nanodendrites (NDs), for which CO oxidation reaction has been employed as a probe reaction to investigate the effects of nanoparticle size and surface-capping organics on the catalytic activities. Time-dependent experiments revealed that an oriented attachment mechanism induced by the strong adsorption of halide anions (Br⁻ and I⁻) on specific facet of Ir nanoclusters or by decreasing the reduction rate of Ir precursors with changing their concentrations during the synthesis was responsible for the formation of Ir NWs and NDs. Annealing tests indicated that an O_2 -H₂ atmosphere treatment turned out to be an effective measure to clean up the surface-capping organics of Ir NPs supported on commercial SiO₂. Catalytic CO oxidation reaction illustrated that a significant improvement in the catalytic activity of CO oxidation reaction was achieved together with the changing of activation energies after such atmosphere treatment for the supported catalysts of the ultrasmall Ir NPs. It is noteworthy that this enhancement in catalytic activity could be ascribed to the changes in the surface status (including populations of Ir species in metallic and oxidized states, removal of surface capping organics, the variety of active sites, and total effective active site number) for the supported nanocatalysts during the atmosphere treatment.

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1. Introduction

Nanocatalysts of Pt-group metals (i.e., Pt, Pd, Rh, Ru, and Ir) have been widely used as a class of industrially important heterogeneous catalysts due to their excellent catalytic properties induced by their specific electronic structures [1]. In fundamental investigation of heterogeneous catalysis, CO oxidation on Pt-group metals has been employed as a benchmark probe reaction to understand the basic catalytic properties of these metals since many fundamental catalytic steps, such as molecular adsorption and desorption, surface reaction, and surface poisoning, are involved in this typical reaction correlated to the nature of the catalysts [2–4].

In typical colloidal synthesis of Pt-group metal nanoparticles (NPs), capping agents such as polyvinylpyrrolidone (PVP), oleic acid (OA), and cetyltrimethylammonium bromide (CTAB), have been utilized to inhibit overgrowth and aggregation of the NPs and to control the morphology of nanocrystals [5]. However, the presence of capping agents can seriously affect the catalytic activity and stability of Pt-group metal catalysts so that plenty of work has been developed for effective

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http://dx.doi.org/10.1016/j.susc.2015.10.007 0039-6028/© 2015 Elsevier B.V. All rights reserved. and nondestructive removing of capping agents on the nanoparticle surfaces [5–7].

Among the Pt-group metals, iridium has the highest chemisorption heat of CO at low surface coverage which exhibits high activity for CO oxidation reaction [8,9]. It has been considered nanoscale metal particles to be effective catalysts with high surface area and rich active sites. In last decade, material scientists have been attempting to synthesize size and morphology controlled Ir nanocatalysts via various synthesis methods, e.g., thermal decomposition [10], ionic liquids [11,12], solvothermal treatment [13], microwave, or UV irradiation [12,14]; however, to realize the controlled synthesis of Ir, NPs for the synthetic chemists still have a long way to go. The difficulties in the synthetic manipulation over Ir nanostructures are often attributed to the high surface energies and strong metal-metal bond of Ir metal. More recently, Xia et al. recognized that a low barrier between homogeneous nucleation and heterogeneous nucleation in the synthesis process perhaps made the Ir precursors tend to nucleate distinctly and consequently resulted in the formation of small-sized Ir NPs at low dispersion. Such small particles usually exhibit irregular morphologies, so that it makes their catalytic properties highly dependent on the size and morphology in some heterogeneous reactions [15]. Moreover, the effective control in size, shape, and dispersion of basic 0-dimensional (0-D) nanoparticles of Pt-group metals can provide ideal building blocks for constructing

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one-, two-, and three-dimensional (1-, 2-, and 3-D) model metal nanostructures [16–19]. However, since the complexity of controlled synthesis and diversely changeable surface states of Ir nanoparticles, compared with the cases of the other Pt-group metals, the size and morphology control of multi-dimensional Ir nanostructures for practical use as promising metal nanocatalysts is still a significant but challenging issue to be addressed.

Herein, we report the synthesis of monodisperse Ir nanostructures with tunable size and dimensionality, i.e., 0-D ultrasmall NPs (1.5–2.5 nm in diameter), 1-D worm-like chain nanowires (NWs), and 3-D nanodendrites (NDs), through a facile one-pot solvothermal method, by regulating the variety of Ir precursors and solvents as well as the addition of capping agents. In order to test the effects of particle size and surface capping agent on the catalytic activity for the as-synthesized Ir nanomaterials, CO oxidation reaction was utilized as a model reaction, with using silica supported iridium ultrasmall NPs as the representative catalysts. Further, effects of annealing treatment conditions in altered atmospheres on the size and surface reconstruction correlated to the catalytic properties of the Ir ultrasmall NPs are discussed.

2. Materials and methods

2.1. Synthesis of Ir nanomaterials

Monodisperse iridium nanomaterials with different sizes and multi-dimensional nanostructures were synthesized via a one-pot solvothermal method employing specific iridium precursors and polyvinylpyrrolidone (PVP) as the surface-capping stabilizer. In a typical synthesis of 1.5 nm Ir NPs, 0.06 mmol of IrCl₃ · xH_2O (M.W.: 298.57, TCI) and 100 mg of PVP (M.W.: ~29000, Sigma-Aldrich) were dissolved in 15 mL of ethylene glycol (99.0%, Sinopharm Chemical Reagent Co., Ltd) upon stirring for 1 h. The solution was then transferred to a 25 mL Teflon-lined stainless autoclave and heated at 200 °C for 24 h. After the autoclave was cooled down, the black products were centrifuged with 40 mL of acetone and 3 mL of cyclohexane and then washed by a mix of ethanol/cyclohexane for three times. A total of 2.5 nm Ir NPs were synthesized by using nearly the same above procedure and conditions except for changing the precursor from IrCl₃ into Ir(acac)₃ (M.W.: 489.54, TCI).

In a typical synthesis of 1-D Ir NWs, 0.06 mmol of IrCl₃ \cdot xH₂O, 70 mg of KBr (Sinopharm Chemical Reagent Co. Ltd), 2 mg of KI (Beijing Chemical Works), and 100 mg of PVP were dissolved in 15 mL of ultra-pure water upon stirring for 24 h. About 0.06 mmol of HCl was also added to accelerate the dissolving process of IrCl₃. The homogeneous black solution was transferred to a 25 mL Teflon-lined stainless autoclave and heated at 180 °C for 48 h before it was cooled down to room temperature. The black products were centrifuged with 20 mL of acetone and 3 mL of cyclohexane and then washed by a mix of ethanol/cyclohexane for three times.

Three-dimensional Ir NDs were synthesized with ethylene glycol based solvothermal method; 0.06 mmol of $IrCl_3 \cdot xH_2O$ and 100 mg of PVP were mixed in 15 mL of ethylene glycol without stirring. The solution was transferred to a 25 mL Teflon-lined stainless autoclave and heated at 180 °C for 24 h. After the autoclave was cooled down, the black products were centrifuged with 20 mL of acetone and 3 mL of cyclohexane and then washed by a mix of ethanol/cyclohexane for three times.

Ir/SiO₂ catalysts were prepared under sonication. Two hundred milligrams of SiO₂ (silicon oxide, Alfa Aesar) was added into 20 mL of ethanol dispersion of Ir NPs with the concentration of 0.5 mg \cdot mL⁻¹. The mixture was treated under sonication for 18 h before centrifugation and washed by 40 mL of ethanol for three times. Dark gray powder was obtained after drying in an oven at 100 °C for 12 h.

2.2. Characterization method and catalytic activity measurement

Transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) was conducted on an FEG-TEM (JEM-2100 F, JEOL, Japan) operated at 200 kV. The TEM samples were made from drying a drop of nanoparticle dispersion in ethanol on carbon-coated copper grids. Powder X-ray diffraction (PXRD) analysis was performed on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2° at a 2 θ scanning speed of 4° \cdot min⁻¹ under Cu_{K\alpha} radiation ($\lambda = 1.5406$ Å). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was conducted on a Profile Spec ICP-AES spectrometer (Leeman, USA). X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra Imaging Photoelectron Spectrometer (Kratos Analytical Ltd., UK) with a monochromatic Al K α (1486.7 eV) X-ray source operated at 225 W with 15 kV acceleration voltage. The C 1s line at 284.8 eV was used to calibrate the binding energies (B.E.). Thermogravimetry (TG) measurement was performed on a Q600 SDT TGA-DSC-DTA instrument (TA Instrument, USA) in air with temperature programming (5 °C \cdot min⁻¹ from RT to 600 °C).

Atmosphere treatments and CO oxidation tests were implemented by a homemade flow reactor system including a quartz tube. In a typical CO oxidation experiment, 20 mg of each supported iridium sample and 1 g of quartz sand were mixed as the catalyst, and the experiment was carried out under a flow of reactant gas mixture (1 vol% CO, 5 vol% O₂, and balance He) at a rate of 40 mL \cdot min⁻¹. The effluent gas compositions were analyzed by an online gas chromatograph (Agilent 7890A, USA) with a carbon molecular sieve column (Carboxen 1000, Supelco, USA) and a thermoconductivity detector (TCD). Atmosphere treatments were conducted before CO oxidation tests including oxidation treatment (10 vol% O₂ and balance He) at 400 °C for 2 h and reduction treatment (10 vol% H₂ and balance He) at 400 °C for 1 h successively.

In situ IR spectra were measured on a TENSOR 27 spectrometer (Bruker, German) in diffuse reflectance mode (DRIFTS). The samples were placed in the Praying Mantis DRIFTS cell and exposed to flowing gas mixture (40 mL \cdot min⁻¹; 1 vol% CO, 5 vol% O₂, and balance He).

3. Results and discussion

3.1. Characterization of multi-dimensional Ir nanostructures

A facile solvothermal method was exploited in the present synthesis of uniform Ir nanostructures including 0-D ultrasmall NPs (1.5–2.5 nm in size), 1-D worm-like chain NWs, and 3-D NDs. All the synthesis conditions were collected in Table 1, and the synthetic approaches toward these Ir nanostructures were concisely described in Scheme 1.

Possibly due to the specific chemical properties of Ir, such as high surface energies and strong metal-metal bond, we found that it was not easy to alter the particle size of Ir NPs through simply controlling the precursor concentration and reaction temperature in the synthesis. Instead, simply changing the variety of the Ir precursor was demonstrated as an effective way to alter the size of monodisperse Ir NPs in the size region below 3 nm, by which two kinds of ultrasmall Ir NPs in different sizes were prepared (Tables 1 and 2, Fig. 1a,b, and Scheme 1). According to the TEM images shown in panels of Fig. 1a and 1b, the size distributions of the two samples were (1.5 ± 0.2) nm (NP-1) and (2.5 ± 0.3) nm (NP-2), respectively. The Ir NPs exhibited polyhedral shape with narrow size distributions, which were mainly enclosed by the (111) facets (the insert of Fig. 1a,b). The size differences appeared to be related to the change in reduction rate of the two precursors in the solvothermal synthesis. In this approach, it seemed that the Ir precursor of Ir(acac)₃ was more difficult to be reduced than that of IrCl₃ did with ethylene glycol as the solvent since acetylacetonate has stronger coordination with iridium ion than chloride ion does. Therefore, in the former case, a slower reduction and growth procedure occurred, leading to the formation of fewer nuclei and the production of larger Ir nanoparticles in the size of 2.5 nm.

XRD patterns of the as-synthesized Ir NPs agreed well with the standard card JCPDS 06-0598 for bulk iridium (Fig. 2). The considerably broadened contours of the peaks were resulted from the ultrasmall

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Table 1

Synt	hesis	cond	itions	of I	r nanos	tructu	ires b	y th	e emp	loyed	SO	vot	hermal	meth	bc
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Sample	Precursor	Solvent	Capping agent	Temperature/°C	Time/h	Stirring
1.5 nm NPs	IrCl ₃	EG	Only PVP	200	24	Yes
2.5 nm NPs	Ir(acac) ₃	EG	Only PVP	200	24	Yes
NWs	IrCl ₃	Water	PVP, Br ⁻ , I ⁻	180	48	Yes
NDs	IrCl ₃	EG	Only PVP	180	24	No

grain sizes of Ir NPs, while the enhanced relative intensity of the (111) peak to the (110) and (100) peak for Ir NPs confirmed that Ir NPs were mainly surrounded by the (111) planes, as also revealed by TEM images shown in the insets of Fig. 1a and 1b. Meanwhile, the positive shift of the (111) peak appeared within both two kinds of ultrasmall NPs demonstrated that the lattice compression could not be neglected inside the ultrasmall NPs, which was probably because of the high surface energy of the (111) surface for iridium compared with other noble metals [20,21]. Lattice compression occurred along with the reducing of surface area and slightly increasing of lattice strain, which resulted in the decreasing in total energy of Ir NPs.

Previously, Pt-group metal 1-D NWs have been obtained via a variety of chemical methods, and the growth of 1-D NWs are often considered to be a complex reorganization process [13,14]. In our work, worm-like chain 1-D Ir NWs were synthesized via a hydrothermal method in the co-existence of KBr and KI at 180 °C (see Scheme 1). Fig. 1c presents a typical TEM image of the worm-like chain NWs with a cross-sectional diameter of (2.1 ± 0.3) nm. As observed from the HRTEM image shown in Fig. 1d, Ir NWs showed a polycrystalline structure, which was constructed by the aggregation of ultrasmall Ir NPs (ca. 2 nm in diameter) with showing blurring twin boundaries. As distinguished in this figure, the lattice fringe spacing of 2.24 Å was corresponding to the (111) crystal planes of iridium.

During the synthesis process, halogen ions – Br⁻ and I⁻ – seemed to play an important role in the crystallization and orientated attachment of the ultrasmall Ir NPs. The major function of Br⁻ ions was supposed to improve the crystallinity of the Ir NWs structure, which could be observed from the XRD patterns as shown in Fig. 2. From the XRD patterns, there was no difficulty to find out not only (111), but also (200) and (220) peaks obviously appeared for Ir NWs, quite different from those for other Ir nanostructures. Generally, Br⁻ ions were regarded as a kind of facet-specific capping agents preferentially binding {100} facets of noble metals [22-24]. However, possibly due to the great surface energy difference between (111) and other crystal planes [20,21], metal nanostructures exposed {100} facets were hardly obtained via such synthesis method. It had been realized that I⁻ ions could act as the same character with Br⁻ ions or an etching reagent in the synthesis of concave and hollow alloy nanostructures [22,23]. In this synthesis, I⁻ ions seemed to play dual roles as both facet-selective and nanowiredirecting agents. It might be because of the adsorption and desorption of I⁻ ions from the surface of Ir NPs that leaded to the oriented



Scheme 1. Schematic illustration for the solvothermal synthesis of Ir nanoparticles, nanowires, and nanodendrites.

attachment of small NPs into worm-like chain NWs. TEM images from time-dependent experiments also agreed with the oriented attachment mechanism responsible for the formation of Ir NWs (Fig. 3). At the beginning of the reaction, only about 2 nm Ir NPs could be found in 4 h reaction. Along with the time elapsing, small aggregation parts with forming short nanochains took place and grew longer slowly. After 48 h reaction, worm-like chain Ir NWs were obtained. To further reveal the effect of both two kinds of halide ions, control experiments were carried out with the presence of only Br⁻ or I⁻ in the system (Fig. S1). Irregular Ir NPs were acquired under both different conditions, which indicated a combined effect of Br⁻ or I⁻ during the formation of Ir NWs. The surface adsorption of Br⁻ seemed to mainly improve the crystallinity of Ir NPs while the surface adsorption of I⁻ led to the oriented aggregation of Ir NPs.

Porous 3-D Ir NDs were obtained via a solvothermal method in ethylene glycol, without adding any other reagents except IrCl₃ and PVP (Scheme 1). TEM image displayed a cauliflower-like structure that divided into a stalk and a corolla part (Fig. 1e,f). This specific structure was quite different from other sphere-like Ir NDs that had been reported in the literatures [16,25]. HRTEM analyses demonstrated that Ir NDs were also formed by the oriented attachment of ultrasmall Ir NPs (ca. 2 nm in diameter) with blurring twin boundaries (Fig. 1f and Fig. S2). Moreover, the lattice fringe spacing was distinguishable in different parts of the Ir NDs. At the corolla part, specific lattice fringe spacing was 2.24 Å corresponding to the (111) crystal planes of iridium, while both (111) and (220) crystal planes could be observed at the stalk part of the Ir NDs. The (110) crystal planes might be generated from the beginning of the reaction due to the low concentration of IrCl₃ precursor with no stirring before, then these Ir NPs with active (110) planes became the stalks of oriented attachment to form the cauliflower like structure. Time-dependent experiments also agreed with the oriented attachment mechanism as we suggested above in accounting for the formation process of the Ir NDs (Fig. 4).

In order to determine the surface composition of as-synthesized samples, XPS analysis was carried out to measure the surface oxidation states of iridium within the samples. Fig. 5 showed the XPS spectra of Ir nanostructures in the Ir 4f region, in which Ir NPs exhibited two energy bands from 61.6 to 67.7 eV and from 58.4 to 65.0 eV, corresponding to the Ir $4f_{7/2}$ (60.8 eV for Ir and 62.2 eV for IrO_x) and Ir $4f_{5/2}$ (63.8 eV for Ir and 62.2 eV for IrO_x) and Ir $4f_{5/2}$ (63.8 eV for Ir and 65.1 eV for IrO_x) core electrons [26–28]. The fact of Ir 4f peak shifting to lower binding energies for the last three samples indicated their better crystallinity since the determined binding energies were more closed to those of Ir single crystal [27]. By the deconvolution of the peaks, the proportions of iridium in oxidation state were 37.7% for the sample of Ir NP-1, 28.4% for the sample of Ir NDs, respectively, which increased gradually with decreasing the average sizes of as-

Table 2
Average sizes of the Ir ultrasmall NPs before and after atmosphere treatment (nm).

Sample	TEM	XRD*
NP-1 (before)	1.5 ± 0.2	1.36
NP-2 (before)	2.5 ± 0.3	1.67
NP-1 (after)	5.8 ± 1.8	5.88
NP-2 (after)	5.1 ± 2.4	5.29

* Average sizes for XRD were calculated by the Scherrer equation.

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Fig. 1. TEM images of as-synthesized Ir NPs with the size of (1.5 ± 0.2) nm (a) and (2.5 ± 0.3) nm (b), TEM and HRTEM images of as-synthesized worm-like chain Ir NWs (c, d) and NDs (e, f). The inserted images are the HRTEM images for Ir NPs.

synthesized three kinds of Ir nanomaterials in dimensionality, indicating that the surface of the Ir nanostructures in smaller size tended to be more easily oxidized under the solvothermal conditions used in this work.

3.2. Loading and atmosphere treatment of the Ir/SiO₂ nanocatalysts

As we knew before, after a relatively high temperature treatment of H_2 , a strong interaction would produce between Pt-group metal catalysts and valence-variable oxide supports, which was called the strong metal-support interaction (SMSI) [29,30]. SMSI includes surface charge and substance transfer process and can seriously influence surface adsorption behaviors and catalytic properties of the supported catalysts

[30]. In this work, an inert oxide support – silica – was used to decline or eliminate the influence of SMSI on the catalytic properties of the assynthesized Ir nanomaterials.

In order to test the catalytic properties of the as-synthesized Ir nanomaterials using CO oxidation as the probe reaction, two kinds of monodisperse ultrasmall Ir NPs with high fraction of surface Ir atoms were selected as the representative nanocatalysts to prepare silica supported Ir nanocatalysts (Ir/SiO₂) for CO oxidation reaction. They were prepared under sonication with a loading amount of 2–3 wt% of Ir NPs. As seen from the TEM images shown in Fig. 6a and 6b, the Ir NPs were uniformly dispersed on the catalyst support of SiO₂.

It has been reported that a high coverage of oxygen atoms on the surfaces of supported Pt-group metal catalysts may decrease the catalytic

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Fig. 2. XRD patterns of as-synthesized 1.5 nm and 2.5 nm Ir NPs, NWs, and NDs. Standard XRD pattern of bulk iridium (JCPDS 06-0598) is also shown in the panel for reference.

activity of CO oxidation reaction [4]. An appropriate pre-treatment would be essential to reactivate such catalysts. TG analysis result (Fig. S3) indicated that no matter which kind of Ir NPs, low boiling point, and unstable organic species occupied about 80 wt% of the sample. In this way, an atmosphere treatment should be conducted before the CO oxidation tests for these samples to improve their catalytic activity.

Atmosphere treatments were implemented by a homemade flow reactor system including a quartz tube. According to TG analysis result, 400 °C was considered to be a suitable temperature for O₂-H₂ treatment to remove the excessive PVP, the same as the literatures reported [5,31]. All the supported samples were treated with 2 h flow of 10 vol% O₂ followed by 1 h flow of 10 vol% H₂ at 400 °C. The TEM images (Fig. 6c-d) indicated that a sintering process occurred during atmosphere treatments, with decreasing the size dispersity of Ir NPs at the same time (Fig. S4). In order to find out which sectional sintering took place during the atmosphere treatment, TEM images (Fig. S5) were taken for the sample of NP-1/SiO₂ without H₂ treatment. It showed that the size of Ir NPs had grown up from 1.5-2.5 nm to 5-6 nm in sizes because of the relatively high annealing temperature (at 400 °C) and removing of surface organic species. However, the monodispersitv of Ir NPs was sustained before the H₂ treatment. This may evidence that surface organics and oxide species protected the surface unsaturated Ir atoms from the reconstruction and sintering in H₂ atmosphere. Evidenced by the disappearance of the signal of N 1s peak (ca. 398 eV) and C 1s peak (ca. 285 eV) in XPS full spectra (Fig. S6a) and a decrease of the absorption peak of C = O stretching vibration for amide (ca. 1655 cm⁻¹) in FT-IR spectra (Fig. S7) after the atmosphere treatment, this O₂-H₂ treatment was found to be very effective in removing adsorbed organic species such as PVP molecules from the Ir NPs surfaces, which have not been reported before. It was also noted that he proportions of Ir in oxidation state for NP-1/SiO₂ before and after atmosphere treatment are 37.7% and 23.9%, respectively (Fig. S6b), while those for NP-2/SiO2 are 28.4% and 20.2% respectively, indicating that the faction of surface Ir atoms in metallic state considerably increased after the O_2/H_2 atmosphere treatment at 400 °C.



Fig. 3. TEM images of time-dependent experiments for worm-like chain Ir NWs after the reactions for 4 h (a), 8 h (b), 16 h (c), and 48 h (d) at 180 °C.

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Fig. 4. TEM images of time-dependent experiments for Ir NDs after the reactions for 4 h (a), 8 h (b), 12 h (c), and 24 h (d) at 180 °C.

3.3. CO oxidation properties of the Ir/SiO₂ nanocatalysts

In recent years, it has been considered that CO oxidation reaction is structure-sensitive for small-sized noble metal NPs: the larger the particle size, the higher the turnover frequency for a series of Pt-group metals [6,32,33], but there is also counterexample on supported Pt catalysts [34]. The catalytic activity of CO oxidation reaction seemed to be a



Fig. 5. XPS Ir 4f spectra for the as-synthesized 1.5 nm and 2.5 nm Ir NPs, NWs, and NDs.

result of combined actions from a variety of factors, such as size, oxidation states, surface organics, and supports. In order to test the effects of particle size and surface capping for the as-prepared Ir/SiO₂ nanocatalysts, CO oxidation reaction was carried out with two kinds of Ir ultrasmall NPs, owing to the fact that they had uniform size, relatively large surface area, and good dispersibility on the SiO₂ support (Fig. 6a and b).

Before CO oxidation tests, an O_2 -H₂ atmosphere treatment was carried out not only to remove surface organics but also to reduce the surface Ir species of the nanocatalysts. According to the pretesting result (Fig. S8), NP-1/SiO₂ catalyst with such atmosphere treatment displayed better catalytic activity than that with only O₂ or without any treatment. This result indicated that this annealing treatment in O_2 -H₂ was very effective in cleaning the surface of supported Ir catalysts and thus improving the catalytic activity of the Ir/SiO₂ catalyst in CO oxidation reaction.

To test the size effects of Ir nanocatalysts, CO oxidation measurements were taken before and after atmosphere treatment on two kinds of NPs with SiO₂ as the support (Fig. 7). From Fig. 7a, a sudden increase in the activity of the catalysts separated the curves into two reaction regimes, a high-activity regime and a low-activity one, which was called an "ignition." The CO conversion would not increase after the ignition because of the 100% conversion of CO [34]. Before the atmosphere treatment, NP-2/SiO₂ displayed a higher CO oxidation activity with lower temperature of half CO conversion ($T_{1/2}$), followed by NP-1/SiO₂ although they had a similar activation energy (E_a) in the reaction at the low-activity regime (Fig. 7b, Table 3), which was calculated by Arrhenius plots at kinetic-controlled regime (i.e., CO conversion < 15%). However, NP-1/SiO₂ and NP-2/SiO₂ exhibited almost the same catalytic activity and activation energy after the O₂-H₂ atmosphere treatment (Fig. 7a). Moreover, the $T_{1/2}$ of the calcined catalysts decreased about

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Fig. 6. TEM images for SiO₂ supported Ir catalysts before (a, b) and after (c, d) atmosphere treatment. From left to right: NP-1 and NP-2.

90–100 °C compared with untreated ones, which should be mainly due to the increased total number of effective active sites from the removing of organic capping species on the Ir NPs surfaces, together with increased proportion of active Ir atoms in metallic state as shown by the XPS analysis (Fig. S6b).

The calculated activation energy of the samples from Arrhenius plots in Fig. 7b (about 60 kJ \cdot mol⁻¹) was much smaller than those of the untreated ones (about 120 kJ \cdot mol⁻¹), which probably belonged to different reaction paths, also supported the discussion above. It had been reported that the activation energies of CO oxidation reaction between bulk and nanosized Ir catalysts were comparable in most of the conditions [8]. Coincidentally, single crystal catalytic experiments had confirmed that the activation energies of CO oxidation reaction were (14 ± 2) kcal \cdot mol⁻¹ (about 60 kJ \cdot mol⁻¹) on Ir (110) surface [35] and 23–31 kcal \cdot mol⁻¹ (about 96–130 kJ \cdot mol⁻¹) on Ir (111) surface [36,37], respectively. This coincidence perhaps suggests that the observed CO oxidation activity in this work should be mainly contributed from the more active Ir sites in metallic states rather than from less active Ir sites in oxidized states [38].

In situ IR spectra were obtained during CO oxidation reaction (Fig. 8). CO was bonded as a kind of linear adsorbed species with a frequency range of 2010–2096 cm⁻¹ for the Ir/SiO₂ catalysts [6,38,39]. Before the atmosphere treatment, the bands were divided into two parts: highfrequency bands with the peak positions at 2058 cm⁻¹ (NP-1) and 2054 cm⁻¹ (NP-2) and low-frequency bands at 2037 cm⁻¹ (NP-1) and 2033 cm⁻¹ (NP-2) respectively, which indicated the coexistence of surface Ir species in metallic state and oxidation state for these NPs, respectively [38]. Only high-frequency bands with the peak positions at 2075 cm⁻¹ (NP-1) and 2071 cm⁻¹ (NP-2) were found after the atmosphere treatment, which evidenced the change of chemical state of surface iridium species to predominately metallic states after H₂ reduction in the atmosphere treatment, as also demonstrated by the XPS results (Fig. S6b). The 4 cm^{-1} wave number difference between the two kinds of samples both before and after the atmosphere treatment could be attributed to the size differences of the as-obtained Ir NPs. However, the visible wave number shift occurred after the atmosphere treatment seemed not only because of the size effects but also because of the result from the change of surface active sites. It has been reported that for platinum and iridium, the heat of CO chemisorption increases with the metal surface density by the following order: (110) > (100) > (111) [9]. The surface state change of Ir nanocatalysts seemed playing an important role in the chemisorption behavior of CO, which turned out to alter the activity of CO oxidation reaction. The increasing activity of CO oxidation with average sizes of Ir NPs can also be attributed to the reducing of unsaturated surface active sites by removing surface capping organics on these sites and the exposing of more terrace sites due to the reconstruction of the NPs from 1.5-2.5 nm to 5–6 nm in diameter after the atmosphere treatment, which prevents a preferential poison by carbon formed from CO dissociation on unsaturated surface active sites (step-edge sites), a competing process to CO oxidation [8].

4. Conclusions

In this work, Ir ultrasmall NPs, worm-like chain NWs, and NDs were synthesized via a facile one-pot solvothermal method. One-dimensional Ir NWs and 3-D Ir NDs were formed by the oriented attachment mechanism with the help of strong adsorption of halides (Br^- and I^-) on particular facets of Ir nuclei and retarded reduction rate by changing the concentration gradient of Ir precursors. The proportion of Ir in oxidation

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Fig. 7. Change of CO conversion with temperature (a) and Arrhenius plots (b) for CO oxidation before and after atmosphere treatment for the Ir NPs/SiO₂ catalysts under a flow of reactant gas mixture (1 vol% CO, 5 vol% O₂, and balance He) at a rate of 40 mL \cdot min⁻¹.

state decreased with the increasing of average size and dimension of nanostructures due to the reducing of specific surface area. An O₂-H₂ atmosphere treatment was found to be effective to improve the catalytic activity of the ultrasmall Ir NPs, but it could broaden the size distributions of the NPs due to the sintering effect at 400 °C. Further research indicated that the O₂ treatment could clean up the surface organic species effectively along with a slight growth of Ir NPs in sizes, while the following H₂ treatment not only increased the proportion of metallic Ir sites, but also reduced the unsaturated surface active sites of the NPs, which resulted in a considerable increase in the total number of effective active sites. The increasing catalytic activity of Ir ultrasmall NPs could be attributed to both the inhibition of CO decomposition on unsaturated surface active sites caused by the average size changes of the particles and the exposing of more terrace sites via the removing of surface organic species. The difference of activation energies before and after the O₂-H₂ atmosphere treatment also evidenced possible

Table 3

8

Activation energy and half CO conversion temperature for SiO₂ supported Ir catalysts.

Catalyst	Before treatment		After treatment		
	$E_{\rm a}/{\rm kJ}\cdot{\rm mol}^{-1}$	$T_{1/2}/^{\circ}C$	$E_{\rm a}/{\rm kJ}\cdot{\rm mol}^{-1}$	$T_{1/2}/^{\circ}C$	
NP-1/SiO ₂ NP-2/SiO ₂	$\begin{array}{c} 118.4 \pm 3.6 \\ 123.1 \pm 7.4 \end{array}$	>280 258	$59.7 \pm 3.1 \\ 63.0 \pm 2.9$	172 172	



Fig. 8. In situ IR spectra of SiO₂ supported Ir catalysts before and after O_2 - H_2 atmosphere treatment during CO oxidation reaction.

changing of the surface status and reaction path for the ultrasmall Ir nanocatalysts. This work has not only offered a synthetic method in tuning the size and shape of the Ir nanocatalysts but also presented fundamental insights in understanding the structure-activity relationship of catalytic CO Oxidation for Ir nanomaterials in ultrasmall size regime. The exploration of the structure-activity relationship for other important heterogeneous reactions with the assynthesized special Ir nanostructures is still underway in our laboratory.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.susc.2015.10.007.

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