

Preparation of LaSrCuO₄ nanowires by carbon nanotubes and their catalytic and chemiluminescence properties for CO oxidation

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Abstract

LaSrCuO₄ nanowires were synthesized using carbon nanotubes (CNTs) in the presence of citrate; LaSrCuO₄ nanoparticles were also prepared by a conventional citrate route in order to compare with the nanowires. The samples were characterized by transmission electron microscopy (TEM), high-resolution electron microscopy (HRTEM), frontier-transformed electron diffraction (FT-ED), X-ray diffraction (XRD), N₂ adsorption isotherm and CO-TPD (temperature-programmed desorption) methods. The catalytic and chemiluminescence (CL) properties for CO oxidation over LaSrCuO₄ catalysts with different morphologies were investigated further. The results revealed that CNTs and citrate played the key roles in controlling the morphology, crystallization and phase compositions of LaSrCuO₄ catalyst; a high thermal stability of LaSrCuO₄ nanowires against calcination was observed, and a high activity for CO oxidation was maintained.

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Keywords: Carbon nanotubes; Citrate; LaSrCuO₄; Nanowires; CO oxidation; Chemiluminescence

1. Introduction

Carbon monoxide, hydrocarbons and nitrogen oxides are the main contaminations released from motor vehicles, so society needs us to develop the low-cost catalysts with high activities. Currently, A₂BO₄ oxides of K₂NiF₄ structure, consisting of alternating layers of ABO₃ perovskite and AO rock salt, have attracted much attention due to their low-cost and high catalytic activity [1]. Many researches have been done to improve the catalytic properties of A₂BO₄ catalysts by the substitution of A-site ions [2], but little work has been performed on morphology control of LaSrCuO₄. The catalysts obtained by a conventional citrate method are usually composed of the particle-shaped nanocrystals, which are easy to sinter upon calcination at high temperatures or long-duration applications. The improvement of thermal stability of the catalyst is still a challenge to researchers.

Since the discovery of carbon nanotubes (CNTs) [3], CNTs have been the subject of an increasing research effort due to their unique mechanical and physical properties [4]. It is

expected that the peculiar tubular morphology of CNTs could give rise to a new kind of nanostructured materials [5,6], which could not easily be synthesized by conventional methods. The synthesis of V₂O₅ fibers using CNTs as templates was first reported by Ajayan et al. [7] Afterwards, a variety of nanowires have been fabricated using CNTs as templates, such as metals, hydroxides and oxides [4,8–16]. Nevertheless, only limited researches have been performed on the fabrication of technologically important binary metal oxides by CNTs, including MgAl₂O₄, CoFe₂O₄, β-zeolite, MnWO₄ and CdWO₄ [16–22]. To the best of our knowledge, the synthesis of LaSrCuO₄ nanowires has not been reported up to now. Due to the differences in the interaction between different ions and CNTs, the phase separation can easily occur upon drying and subsequent calcining. As a result, single-phase LaSrCuO₄ catalyst is not easy to acquire. Therefore, developing an approach to prepare the single-phase LaSrCuO₄ nanowires is still a challenge to researchers.

Herein, we report, for the first time, the mild synthesis of single-phase LaSrCuO₄ nanowires in the presence of both carbon nanotubes and citrate. During the process, the metals nitrates were employed as the starting chemicals to impregnate the functionalized CNTs; citric acid was added to control the molar ratios of La/Sr/Cu and to reduce the crystallization

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temperature of LaSrCuO₄ catalyst. The catalytic activity for CO oxidation and thermal stability of LaSrCuO₄ nanowires were researched. Our research is expected to improve the performances of the catalyst by controlling the morphology [23]. It is thus significant for us to research the relationships between the morphology and properties of LaSrCuO₄ catalyst.

2. Experimental

2.1. Chemicals

Carbon nanotubes (CNTs) were supplied by Department of Chemical Engineering (Tsinghua University); all the other chemicals, including La(NO₃)₃·6H₂O (A.R.), Sr(NO₃)₂ (A.R.), Cu(NO₃)₂·3H₂O (A.R.), HNO₃ (A.R. 68 wt.%) and Citric acid (CA) (A.R. C₆H₈O₇·H₂O, MW = 210), were purchased from Beijing Chemicals Company of China and used as received.

2.2. Pretreatment of CNTs

The original CNTs were purified and oxidized by nitric acid. Typically, 0.5 g of CNTs was dispersed in 30 mL 68 wt.% HNO₃ solution, and then the mixture was fluxed at 100 °C for 24 h; thereafter, the solid was separated by centrifuging, washed with water and dried in an oven at 80 °C for 24 h. The amount of introduced carboxyl groups was determined with the well-known Boehm titration method. A measured amount of CNTs was dispersed in deionized water. The pH value of the system was adjusted to 11 using 0.01 mol L⁻¹ NaOH solution, followed by titration using 0.01 mol L⁻¹ HCl solution. The determined concentration of the carboxyl groups (–COOH) on CNTs was 0.25 mmol mg⁻¹.

2.3. Preparation of LaSrCuO₄ nanowires

Stoichiometric La(NO₃)₃, Sr(NO₃)₂, Cu(NO₃)₂ and citric acid (CA) were dissolved in deionized water to form the solution, in which the molar ratios of CA/La/Cu/Sr were kept at 3/1/1/1. Under ultrasonic condition, 0.25 g of CNTs treated by HNO₃ was dispersed in the solution of nitrates. After being sonicated for 30 min, the mixture was magnetically stirred for 24 h. The solid was separated by centrifuging, washed with deionized water for 3–4 times, and dried at 80 °C for 24 h. Finally, the solid was calcined at 600 °C for 5 h in air to remove the template. To investigate the thermal stability of LaSrCuO₄ catalyst, we calcined the catalyst further at 750 °C for 48 h in air. To investigate the effect of citric acid on the formation of the catalyst, we also carried out the preparation without adding citric acid, and this sample was calcined at 700 °C for 5 h in air to obtain the catalyst.

2.4. Characterization

The samples were characterized by X-ray diffraction (XRD) on a Rigaku D/MAX-RB X-ray powder diffractometer, using graphite monochromatized Cu K α radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50 mA. The patterns were scanned from

10° to 70° (2 θ) at a scanning rate of 5° min⁻¹. A nitrogen adsorption isotherm was performed at 77 K on a Micromeritics ASAP2010 gas adsorption analyzer. Before the measurement, the catalyst was degassed at 200 °C for 5 h. Surface areas of the catalysts were calculated by the BET (Brunauer–Emmett–Teller) method. The morphology of the catalyst was characterized by TEM (JEOL 200CX) with the accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010) was used to determine the structure of the catalyst. The powder was dispersed in ethanol ultrasonically, and then a drop of liquid was deposited on a thin amorphous carbon film supported by the copper grids.

CO-TPD (temperature-programmed desorption) measurements were performed on a conventional CO-TPD instrument. In order to remove the pollutants adsorbed on the catalyst, 0.1 g of catalyst was loaded in a quartz reactor and heated in the He flow at 280 °C for 2 h; under the flowing He gas (40 mL min⁻¹), the system was cooled naturally to room temperature. The catalyst was then saturated with CO at room temperature for 0.5 h, and the excess of adsorbates was removed by allowing the sample to remain in a He flow until no significant amount of adsorbates can be detected. The temperature was ramped to 800 °C at a heating rate of 20 °C min⁻¹. Mass spectra (MS) were used to monitor the variations of the *m/e* ratio of CO (28) to CO₂ (44).

2.5. Chemiluminescence (CL) properties of the catalysts

Each CL signal was measured at a wavelength of 425 nm by a photon-counting method with a flow injection ultraweak chemiluminescence analyzer (BPCL, made by the Biophysics Institute of the Chinese Academy of Sciences). The CL intensities were measured through the bottom of the cell with a photomultiplier tube (PMT) window (the cell and the PMT were enclosed in a light-tight box). The PMT was operated in the current mode. The CL-based sensor was made by sintering a 0.5-mm-thick layer of powder on a cylindrical ceramic heater of 5 mm in diameter. The sensor was set in a quartz tube of 12-mm (i.d.) through which a gas mixture of CO (200 μ g mL⁻¹) and air flowed at a constant rate of 200 mL min⁻¹ at atmospheric pressure, and a digital temperature controller was used to adjust the temperature of the ceramic heater. The gases can flow only through the outside of the ceramic heater. At the beginning of the experiments, the sensor was heated at 450 °C for 60 min in air to remove the pollutants adsorbed on the catalyst.

2.6. Evaluation of activity for CO oxidation

The oxidation reaction of CO was carried out in a conventional flow system under atmospheric pressure. The catalyst (0.1 g) was loaded in a quartz reactor (inner diameter: 5 mm), with quartz beads packed at both ends of the catalyst bed. The catalyst was pretreated in N₂ flow at 450 °C for 1 h. A mixture gas of 2 vol.% CO and 98 vol.% air was fed into the catalyst bed at a gas hourly space velocity (GHSV) of 12 000 h⁻¹. The inlet and outlet gas compositions were

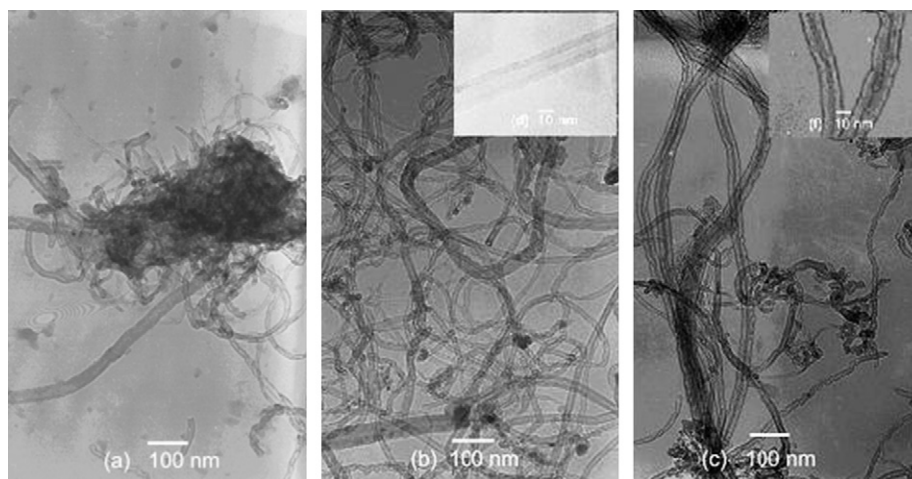


Fig. 1. TEM micrographs of carbon nanotubes (CNTs) and the impregnated CNTs with metals nitrates: (a) before treatment with HNO_3 ; (b) after treatment with HNO_3 , the insert (d) at high magnification; (c) after impregnation with metal nitrates, the insert (f) at high magnification.

analyzed by on-line gas chromatography with a GDX-403 GC-column ($1.5 \text{ m} \times 4 \text{ mm}$, 100°C) and a flame ionization detector (FID).

3. Results and discussion

3.1. Formation of LaSrCuO_4 nanowires

Fig. 1a and b give the typical TEM images of the CNTs before and after treatment with HNO_3 , respectively. Before treatment with HNO_3 , the original CNTs contained a significant amount of amorphous carbonous impurities, and they tangled up (Fig. 1a). After treatment, most of the carbon impurities have been removed, and the CNTs were clean and almost open. Their inner and outer diameters are in the range of 5–10 nm and of 20–50 nm, respectively (the insert of Fig. 1b). During the process, the surfaces of CNTs would be oxidized by HNO_3 [24–26]. Such oxidation would give rise to a large amount of oxygen-containing functional groups on the surfaces of CNTs, such as carboxylate and/or hydroxyl groups ($-\text{COOH}$, $-\text{OH}$). The generation of these functional groups has been confirmed by other researchers [27,28]. In this work, the determined concentration of the carboxylate groups ($-\text{COOH}$) on CNTs was $0.25 \text{ mmol mg}^{-1}$.

Then, the CNTs pretreated with HNO_3 were impregnated with the aqueous solution of citric acid (CA) and nitrates. Fig. 1c shows the images of the CNTs after impregnation. It can be observed clearly that the filling of matters into the inner cavities of CNTs has occurred. Although we can not observed from TEM images whether the out sides of the CNTs was used or not probably due to the much thin coating, we could believe the out side of CNTs may be also used because the generated functional groups on the surface of CNTs could complex the metals ions. Therefore, one can believe that the surface coating and the inner filling took place simultaneously during the impregnation process. It is easy to understand that the oxygen-containing groups on the surfaces of CNTs may act as the anchoring sites for the metallic precursors [27]. The strong interaction between the metals ions and the surface of CNTs is

due to the presence of surface function groups ($-\text{COOH}$ and $-\text{OH}$). The homogeneous complexes of $\text{CA}-(\text{La}, \text{Sr}, \text{Cu})-\text{OOC}-\text{CNT}$ may form through the chelating reactions between $\text{CNTs}-\text{COO}^-$ and the ions (La , Sr and Cu) [29]. It has been reported that the elements or compounds with a surface tension lower than 200 mN m^{-1} can effectively fill the CNTs [30–32]. Ugarte et al. have reported that the open CNTs could be filled with molten silver nitrate through a capillary force; and they further reported that only the carbon nanotubes with inner diameters of 4 nanometers or more could be filled [28]. Therefore, the use of water as solvent, which has a low surface tension of 72 mN m^{-1} , could explain the filling into the inner volumes of the CNTs.

The final step was the oxidation in air to remove the template. The oxidation temperature was carefully selected to be high enough to oxidize the CNTs and to form the perovskite crystals. Fig. 2 gives the XRD patterns of LaSrCuO_4 samples prepared at different conditions. In the presence of citric acid,

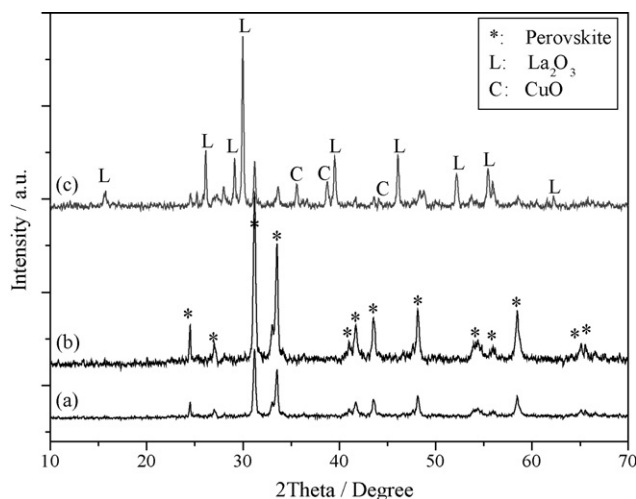


Fig. 2. XRD patterns of LaSrCuO_4 samples prepared by carbon nanotubes at different conditions: (a) adding citric acid, calcined at 600°C for 5 h; (b) Sample (a) calcined at 750°C for 48 h; (c) without adding citric acid, calcined at 700°C for 5 h.

single-phase LaSrCuO_4 with K_2NiF_4 -typed structure formed after calcination at 600°C for 5 h (Fig. 2a). The low formation temperature of LaSrCuO_4 crystals can be ascribed to the formation of the homogeneous precursor at atomic level [33]. Upon calcining at 750°C for 48 h, the diffraction peaks of LaSrCuO_4 sample become sharper, indicating that LaSrCuO_4 crystals have grown larger to some extent (Fig. 2b). The contrast experiment showed that LaSrCuO_4 crystals formed at a high temperature (700°C) without adding citric acid; at the same time, the impurities phases (La_2O_3 and CuO) were always present (Fig. 2c). This indicates that citric acid played an important role in reducing the crystallization temperature of LaSrCuO_4 crystals and in maintaining the stoichiometric ratios of La, Sr and Cu. It is well known that the pure CNTs can be completely oxidized into CO_2 in air only above 700°C [34]. It is interesting that the temperature for the removal of CNTs is significantly lower (600°C) in our work. The low oxidation temperature could be related closely to a catalyzing effect of La-Sr-Cu oxides on the graphitic decomposition, because LaSrCuO_4 is an excellent oxidation catalyst. Eder et al. have

also observed such a catalytic effect while they prepared TiO_2 by CNTs [34].

Further, the morphologies of LaSrCuO_4 catalysts were observed by TEM and HRTEM, as shown in Fig. 3. After being calcined at 600°C for 5 h, the resulting LaSrCuO_4 crystals exhibit interesting wire-like nanostructures, which have the diameters in the range of about 50 nm and the lengths of 1.5–2 μm (with an aspect ratio of about 40) (Fig. 3a). However, the diameters of LaSrCuO_4 nanowires are generally larger but their lengths are shorter than those of the CNTs. It is possible that LaSrCuO_4 nanocrystals in neighboring CNTs and/or in the same CNT coalesced or fused together to form the wire-like nanostructures. HRTEM micrographs of single nanowire clearly present several grains with distinct diffraction contrast, which is consistent with being a polycrystalline material (Fig. 3b); Frontier-transformed electron diffraction (FT-ED) patterns show multiple diffraction spots clustered around each main area of diffracted intensity (the insert of Fig. 3b). This type of diffraction pattern is also characteristic of a polycrystalline material. It is most interesting that after being

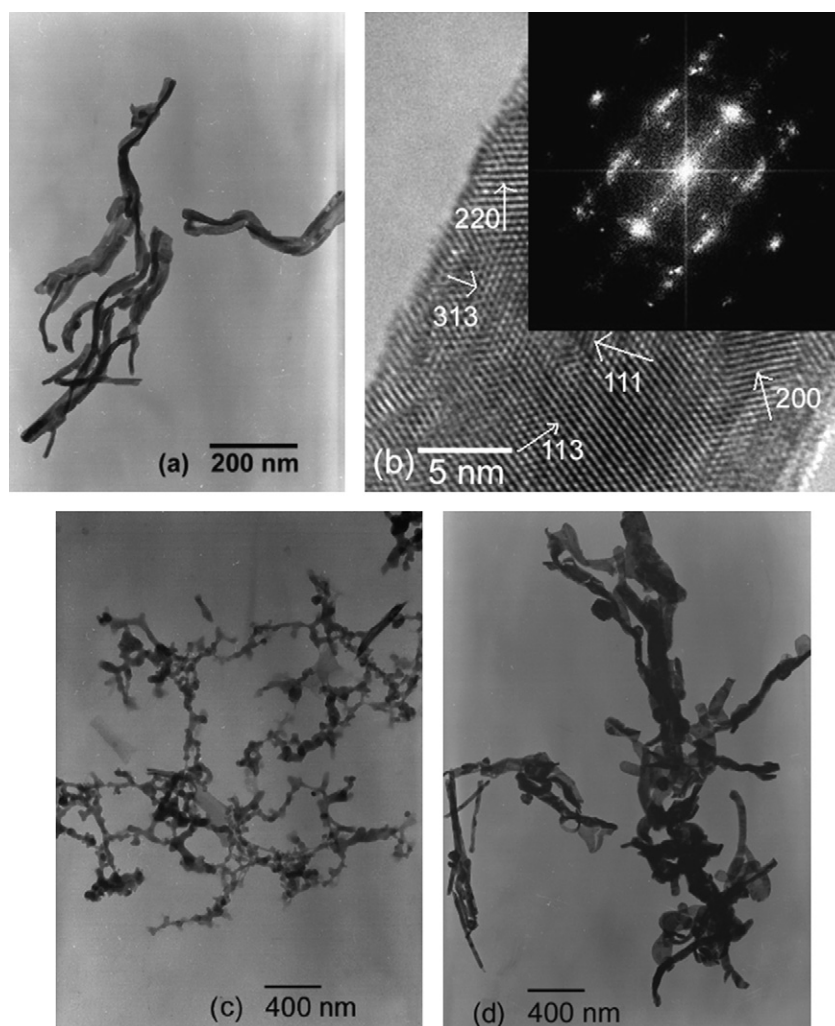


Fig. 3. TEM and HRTEM (the insert of FT-ED patterns) images of LaSrCuO_4 samples: (a and b) by CNTs in presence of citrate, calcined at 600°C for 5 h; (c) Sample (a) calcined at 750°C for 48 h; (d) by CNTs without adding citrate, calcined at 700°C for 5 h.

calcined at 750 °C for 48 h, LaSrCuO₄ maintained the wire morphology, and a net of continuous nanowires was formed (Fig. 3c). On the other hand, without adding citric acid, the obtained sample showed an irregular wire morphology with 100–200 nm in diameters and 1–2 μm in lengths (Fig. 3d); this sample consisted of LaSrCuO₄ and the impurities' phases (i.e. La₂O₃ and CuO) (Fig. 2c). It is clear that the tubular structure of CNTs has controlled the formation of LaSrCuO₄ nanowires. These findings are interesting, since the LaSrCuO₄ catalysts generally obtained by a citrate route consist of nanoparticles.

Note that the roles of CNTs and citrate in the formation of LaSrCuO₄ nanowires deserve more study. Ajayan et al. have reported that a surface-tension effect can induce the growth of uniform V₂O₅ thin films on the outside of nanotubes, along with oxide fillings in the inner cavities of the CNTs [7]. The formation of LaSrCuO₄ nanowires could be divided into two stages:

Noncrystalline precursor → Nanocrystals (i)

Nanocrystals → Nanowires (ii)

It is well known that the original CNTs are hydrophobic, while the CNTs treated with HNO₃ become hydrophilic. During the impregnation process, the CA-nitrates complexes filled into the CNTs inner and/or coated on the CNTs surface; during the thermal annealing process, the precursor decomposed and crystallized to form the nanocrystals; finally, the nanocrystals grew into the nanowires due to the geometric confining effect by the template. Moreover, the phase transformation of the homogeneous precursor into the perovskite structure is expected to be helped by the surrounding tube walls and citric acid. Gogotsi et al. [32] have reported that the CNTs with an outer diameter of 100 nm could act as pressurized miniature vessels. The macroscopic pressure outside the tubes remained unchanged, while the pressure inside increased. Therefore, the CNTs acted as the nanoreactors, as in a hydrothermal process, which favored for the crystallization of LaSrCuO₄ catalyst at a low temperature (600 °C). Additionally, as shown in Figs. 2c and 3d, without adding citric acid, both LaSrCuO₄ crystals and the impurities phases (i.e. La₂O₃ and CuO) formed at a high temperature (700 °C), although the nanowires were formed. It has been reported that citrate route can favor the crystallization of perovskite structure at temperatures as low as 500–600 °C [35,36]. While citrate was added, the homogeneous CA-(La, Sr, Cu) complexes at a molecular-level coated on or/and filled into CNTs. As a result, the addition of citric acid not only favors maintaining the stoichiometric ratios of La, Sr to Cu, but also reduces the crystallization temperature of the perovskite structure.

3.2. The activity and thermal stability of LaSrCuO₄ nanowires

LaSrCuO₄ is one of the most important oxidation catalysts that are widely applied in indoor air cleaning and automotive exhaust treatment. The catalytic activity for CO oxidation over

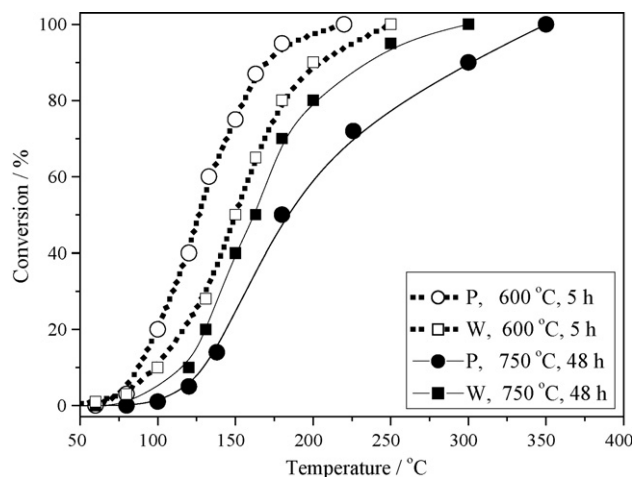


Fig. 4. The activities for CO oxidation over LaSrCuO₄ catalysts after being calcined at different temperatures and durations: W, nanowires by the CNTs; P, Nanoparticles by a citrate route.

LaSrCuO₄ nanowires was evaluated. Fig. 4 shows the activities of CO oxidation over LaSrCuO₄ nanowires (designated as W) and nanoparticles (designated as P, †see Supporting information: by a citrate route). The complete oxidations of CO over P and W (600 °C, 5 h) were achieved at 220 and 240 °C, respectively. The activity of catalyst can be influenced by various factors, e.g., crystal structure, composition, BET surface area or/and particle size, etc. Because of their same crystal structure and compositions, the influences of the BET surface area and/or particle size on the activities of the catalysts are mainly considered. After calcination at 600 °C for 5 h, LaSrCuO₄ nanoparticles have a surface area (20.56 m² g⁻¹) higher than the nanowires (15.70 m² g⁻¹) (Table 1), which could supply more active sites. Therefore, the catalytic activity of LaSrCuO₄ nanoparticles is higher than that of the nanowires.

Note that the thermal stability of a catalyst is also an important factor for the applications in practice. We further calcined the catalysts at a high temperature for a long duration in order to investigate their thermal stabilities. After calcination at 750 °C for 48 h, a high thermal stability was observed for LaSrCuO₄ nanowires. The surface area of LaSrCuO₄ nanowires decreased from 15.70 to 12.07 m² g⁻¹. This could be related closely to the unique wire morphology [34]. As a result, the activity of LaSrCuO₄ nanowires decreased to 300 °C for complete oxidation of CO. On the other hand, after calcination at 750 °C for 48 h, LaSrCuO₄ nanoparticles sintered severely

Table 1
Surface areas and activities for CO oxidation of LaSrCuO₄ catalysts prepared by different methods

Sample	Preparation	^a SA (m ² g ⁻¹)	^a T ₁₀₀ (°C)
^b W	600 °C, 5 h	15.70	240
	750 °C, 48 h	12.07	300
^b P	600 °C, 5 h	20.56	220
	750 °C, 48 h	7.57	350

^a SA, surface area by the BET method; T₁₀₀, the temperature of CO complete oxidation.

^b W, nanowires by CNTs and citrate; P, nanoparticles by a citrate route.

and the particle sizes grew larger (†see Supporting information for Fig. S1); and the surface area of this catalyst decreased significantly ($7.57 \text{ m}^2 \text{ g}^{-1}$), indicating that the active sites sintered severely for the nanoparticles. As a result, the catalytic activity for completed oxidation of CO over the particles decreased significantly to 350°C .

Concerning the catalytic mechanism, the oxidation of carbon monoxide has been considered as a so-called suprafacial catalytic process [37]. Tascon et al. proposed a mechanism of CO oxidation on LaCoO_3 [38]. It was deduced that Co^{3+} is the active center, and that the lattice oxygen is the active oxygen species. CO adsorbed on Co^{3+} and then reacted with the lattice oxygen; whereas the chemisorbed oxygen transforms into the lattice oxygen to balance the consumed lattice oxygen. The oxygen transformation in the CoO_6 octahedral is proposed [39,40].

CO-TPD (temperature-programmed desorption) profiles on these catalysts after calcination at 750°C for 48 h were recorded to explore the different active centers. A significant portion of CO desorbed as a form of CO_2 in the process, so the total adsorption amount of CO on the catalyst was consistent with the desorption amounts of CO_2 and CO. In Fig. 5, some differences can be clearly observed in the CO and CO_2 desorption profiles over the nanowires and particles. In Fig. 5a, CO_2 -TPD profiles of LaSrCuO_4 nanowires show four CO_2

desorption peaks ($140, 285, 465, 630^\circ\text{C}$); but for LaSrCuO_4 particles, three peaks ($450, 690, 755^\circ\text{C}$) are observed. In Fig. 5b, CO-TPD profiles of the nanowires present three CO_2 desorption peaks ($140, 590, 740^\circ\text{C}$); but two peaks ($140, 590^\circ\text{C}$) are observed for the particles. It is clear that the peak intensities of CO_2 (CO) desorbed from the nanowires are stronger than those from the particles, but their initial temperatures desorbed from the nanowires are lower. The quantitative analysis results showed that the total CO amount adsorbed on LaSrCuO_4 nanowires is larger than that on the particles, indicating that there may be more active centers on LaSrCuO_4 nanowires than on the latter. The results strongly support that after being calcined at 750°C for 48 h, the nanowires have higher activity for CO oxidation than the particles. It is evident that the catalytic properties of the catalyst could be improved by controlling the morphology of the particles.

While CO molecules were oxidized catalytically to form CO_2 molecules on the surface of the catalyst, a moderate amount of energy was released, which would be absorbed by some CO_2 molecules. As a result, CO_2 molecules would jump from ground state up to excited state. While the CO_2 molecules decayed from the excited state to the ground state, the weak chemiluminescence (CL) light would be emitted. The emitted CL intensity varies linearly with the produced CO_2 concentration, and the CL spectra response to CO were used to quantitatively analyze the given catalytic oxidation reaction. Fig. 6 gives the CL spectra response to CO over the LaSrCuO_4 catalysts after being calcined at 750°C for 48 h. The CL intensity response to CO over LaSrCuO_4 nanowires is higher than that of the corresponding particles, denoting that more CO molecules were oxidized into CO_2 molecules. The CL result is well consistent with the order of activity over these catalysts at 200°C . This also confirms that after being calcined at 750°C for 48 h, the nanowires have a higher activity of CO oxidation than the corresponding particles.

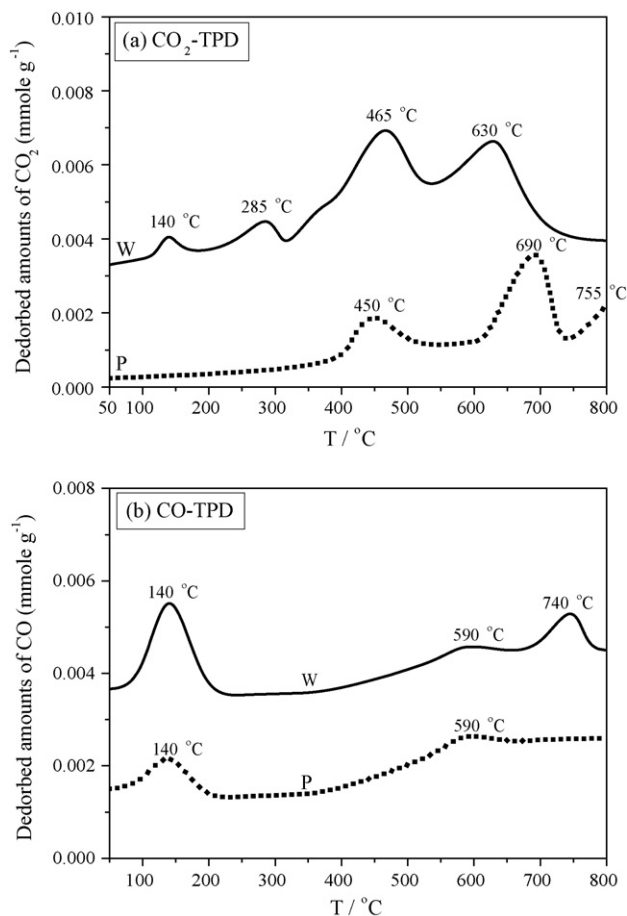


Fig. 5. CO_2 -TPD (a) and CO-TPD (b) profiles of CO adsorption on LaSrCuO_4 catalysts after calcination at 750°C for 48 h: W, nanowires; P, particles.

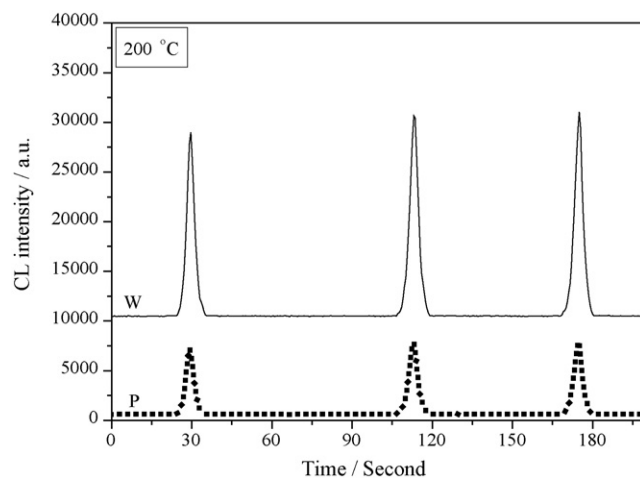


Fig. 6. The chemiluminescence (CL) response to CO of LaSrCuO_4 catalysts after calcination at 750°C for 48 h. Measurement conditions: Flow rate of the mixture gas of air and CO is 200 mL min^{-1} , $200 \mu\text{g mL}^{-1}$ CO, 200°C ; W, nanowires; P, particles.

4. Conclusions

The study shows that CNTs and citrate played the key roles in the formation of LaSrCuO₄ nanowires. The morphology of the catalyst can be effectively controlled by CNTs; the addition of citric acid not only favors maintaining the stoichiometric ratios of La, Sr to Cu, but also reduces the crystallization temperature of the catalyst. In the presence of both CNTs and citrate, single-phase LaSrCuO₄ nanowires can be prepared readily at the temperature as low as 600 °C. After being calcined at 700 °C for 48 h, LaSrCuO₄ nanowires had a higher thermal stability than the corresponding nanoparticles, and a high activity for CO oxidation was maintained for the nanowires. The combined approach would generate some useful new kinds of nanostructured materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2007.06.004.

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