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Engineering surface of perovskite $La_{0.5}Sr_{0.5}MnO_3$ for catalytic activity of CO oxidation

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A simple treatment of $La_{0.5}Sr_{0.5}MnO_3$ with diluted HNO_3 creates more B-sites (rich) on the terminated perovskite surface and improves its catalytic activity toward CO
10 oxidation, and the perovskite catalyst possesses higher ratio of Mn^{4+}/Mn^{3+} and thus enhances O_2 adsorption capability, favourable for CO oxidation and catalytic activity.

Design of efficent catalysts providing better-controlled active sites for fundamental studies of heterogenous catalysis and
15 developing novel industrial catalysts is the ultimate goal of research on heterogeneous catalysis[1]. Generally, the size, shape, composition, and interface/surface engineering in catalytic materials are the key parameters that are usually considered in synthesis to exhibit the rule of catalyst dependence[2, 3]. Since
20 heterogeneous catalysis usually occurs on solid surfaces providing the approprite electronic and/or geometric environment, design of on surface, requires precise control on atomic scale[1, 4]. As a promising candidate for the replacement of noble metal commonly coming at the expense cost and limited
25 stability, perovskite oxides (especially $La(Sr)MnO_3$ and $La(Sr)CoO_3$) are emerging as automotive exhause catalyst[5, 6]. However, T.S. Irvine[7] reported that native perovskite surfaces are preferentially A-site (rich), not catalytically active sites[8], terminated to the detriment of the B sites, which results in the
30 true catalytic properties of many perovskites based on ideal bulk-like terminated surface might have been underestimated due to their fundamental flaw. It is still lack fundamental understanding of perovskite surface catalytic mechanism at the atomic/molecular level. To overcome these disadvantages, clean
35 procedure to create more B-site (rich) terminated perovskite

surface and related catalytic property investigations are greatly in need.

Acid/base treatment of catalysts was regarded as one of the most widely accepted method to improve specific
40 performance in porous TiO_2[9], zeolites[10], layered perovskites[11] and carbon materials[12]. Treatment with H_2O_2 and NH_4OH for modification surface electronic and magnetic properies in perovskite films was also reported[13]. However, to date no work on the wet-etch treatment of perovskite catalysts was
45 reported for activating the perovskite.

Herein, we developed a method to modulate the perovskite surface of $La_{0.5}Sr_{0.5}MnO_3$ samples, e.g., treatments of dilute HNO_3 solutions with controlled time followed by the evaluation of the corresponding catalytic activity for CO
50 oxidation. Our finding demonstrates that the simple surface treatment shows importance of B-site (rich) terminated perovsktie surface control in harnessing the true catalytic potential of perovsktie oxides and opens up strategies for the development of the activity for other perovskite transition-
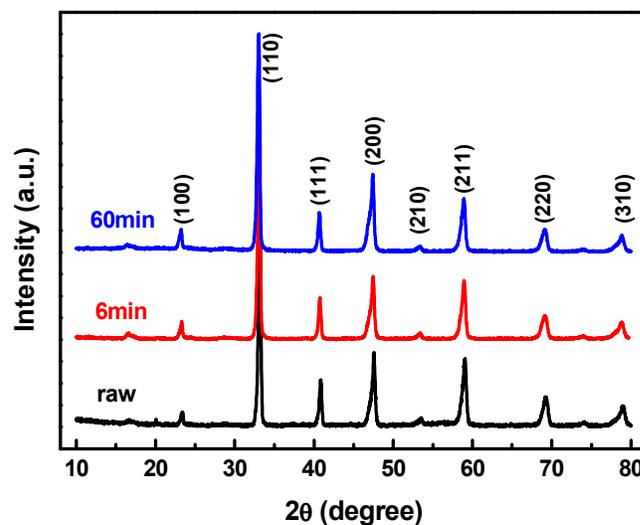55 metal oxides.

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Electronic supplementary information (ESI) available: sample preparation, characterization details, catalytic performance evaluation process, and N_2 adsorption-desorption, valence state of Mn and O 1s spectra, Arrhenius activation energy data. See DOI: 10.1039/ b000000x

Fig.1 X-ray diffraction patterns of $La_{0.5}Sr_{0.5}MnO_3$ for raw sample without treatment (#1), and samples treated with dilute nitric acid solution for 6 min (#2) and 60 min (#3).
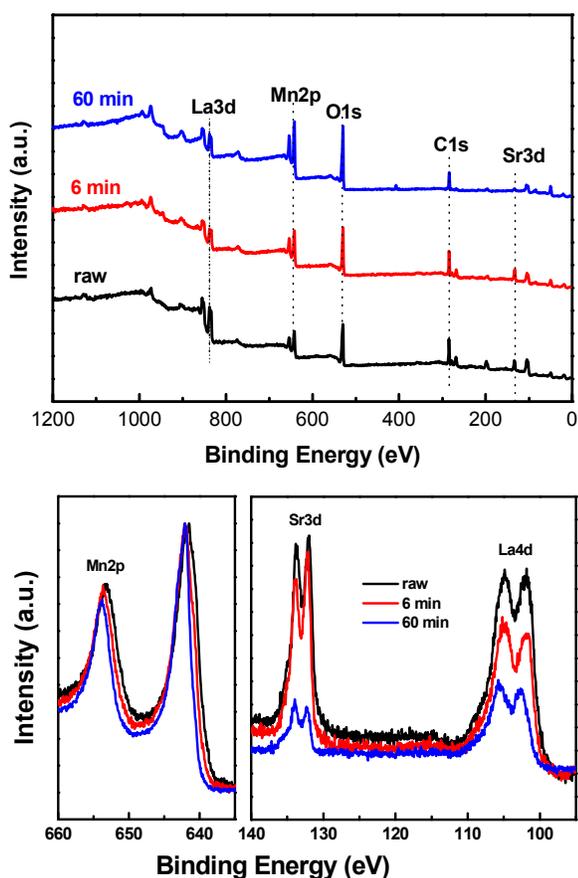
Fig.2 XPS survey and Mn2p, Sr3d and La4d spectra for the three samples #1, #2 and #3. (Intensity of Sr3d and La4d were adjusted to the normalized Mn2p)

Raw sample was synthesized *via* a hydrothermal route adapted from previous report with minor modification[14, 15]. The details of sample preparation and acid activation process are given in Supporting Information. By increasing treatment time, the crystal structure keeps the same as the raw sample, which can be indexed to a primitive cubic unit cell (in Fig.1 space group Pm3m, a= 3.841 Å). Inductively coupled plasma elemental analysis for the raw sample confirmed the energy dispersive spectrometry (EDS) result (inset of Fig. 3a) and indicated that its bulk composition is $La_{0.5}Sr_{0.5}MnO_3$. Usually, the yielded raw $La_{0.5}Sr_{0.5}MnO_3$ particles are La,Sr-enriched on the surface and this phenomenon of A-enriched in other perovskite systems often appears[7, 16 - 18]. The surface composition change from La, Sr-rich to Mn-rich by the modification of simple treatment by dilute HNO_3 solutions. Surface composition was evaluated by X-ray photoemission spectroscopy (XPS) which are surface sensitive technique in probing the surface composition and electronic structure.

According to XPS quantitative analysis, the surface composition of the raw synthesized $La_{0.5}Sr_{0.5}MnO_3$ is 39.0 atom% of Mn/(La+Sr+Mn) (Fig. 2), which means La, Sr-enrichment on surfaces, in terms of ideal 50 atom% in EDS data. Change of La, Sr and Mn atomic ratio can be easily observed from the intensity variation in XPS survey spectra and detailed narrow scan core-level spectra of normalized Mn 2p and related La 4d and Sr 3d electrons. XPS quantitative result indicated the surface is 46.8 and 67.5 atom % Mn for samples of 6 min and 60 min treatment. In contrast, the corresponding results of sample composition measurements by EDS show that the bulk Mn/(La+Sr+Mn) molar ratio (inset of Fig. 3) were 51.2%, 56.3% and 64.5% for sample #1, #2 and #3, respectively. These results indicated that the A atoms were successfully removed by wet-etch treatment, while EDS results also exhibited quite smaller decrease of A site atom compared to XPS results. It is obvious that La, Sr or Mn enrichment of $La_{0.5}Sr_{0.5}MnO_3$ particles were controlled from surface to bulk process by selective wet-etch treatment time with dilute acid at room temperature.

The scanning electronic microscope images revealed morphological evolution in acidic environment, which improves the surface region from smooth in grinded raw material surface to a bit rough and fully rumpled surface, showing the possible reorganization of surface structure (Fig. 3). The reason of selective removal of A-site atoms is because the longer distance of La-O and Sr-O bonds than Mn-O bonds and relatively higher surface energy of A-O bond. The surface electronic structure after treatment was improved, and the content of Mn^{3+} decreased and Mn^{4+} increased on the surface of Mn-rich particles. The ratios of $Mn^{4+}/(Mn^{3+}+ Mn^{4+})$ are 40.2%, 62.8%, and 63.7% for samples #1, #2 and #3, respectively, as shown in Supporting Information Fig. S3. The additional Mn^{4+} promoted the formation of the surface oxygen vacancies. The production of Mn^{4+} at relatively high temperatures is important for the improvement of CO oxidation[19, 20].
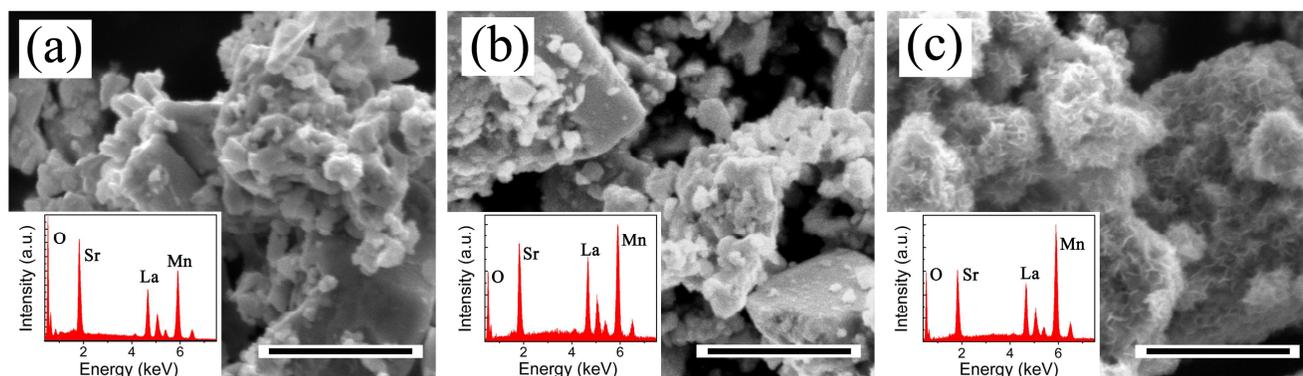
Fig.3 SEM and EDS (inset) of $La_{0.5}Sr_{0.5}MnO_3$ (a) without treatment (1#), treated for (b) 6 min (2#) and (c) 60 min (3#). All scale bars are 1 μm.

The catalytic CO oxidation over as-obtained sampales were evaluated in $CO/O_2/N_2$ stream. As shown in Fig. 4, for the conversion of CO into CO_2, T_{10} (the temperature of the conversion 10%) for sample #1, #2, #3 are 245, 169 and 158 °C and T_{50} (the half conversion temperature) are 340, 245 and 230 °C, respectively. To illustrate the relations between enhanced catalytic behavior and the surface electronic structure, we schematically proposed the surface composition change which indicate the elemental compositions, terminated layers on surfaces, the corresponding surface evolution (Fig. 4). This means that the treated samples exhibited much higher activity, which might be attributed to the more presence of active sites for creating B-site (rich) terminated perovsktie surface.

To further investigate the origin of different catalytic activity behaviors, temperature programmed reduction (TPR) of H_2 was tested to unedstand the relative reducibility closely related to its catalytic performance (Fig. S1). For the raw samples (#1) , the peak in the range of 700-800 °C most likely corresponded to the reduction of the remaining Mn^{3+} to Mn^{2+}, meanwhile, the peak at about 507 °C can be attributed to the reduction of Mn^{4+} to Mn^{3+}. The peak shifted to lower temperature, which may resulted from a single-electron reduction of Mn^{3+} located in coordination-unsaturated microenvironment[19]. For sample treated with dilute nitric acid solution for 6 (#2) and 60 min (#3), this situation may be favorable the reduction of Mn^{4+} to Mn^{3+} at lower temperature as a result of the surface electronic structure changed on the surface Mn-rich particles.The peak at about 282 °C can be assigned to removal of nonstoichimetric excess oxygen accommodated within the lattice[15]. It is obvious that the position shifted to lower temperatures for the treated samples, indicating the better reducibility. The TPR results suggest[21] that high reducibility was achieved after the treatment with acid in this work, which has been generally accepted that good redox property leads to excellent catalytic reactivity[22].

O1s XPS was measured to investigate the oxygen species on the surface or lattice of catalysts. Free oxygen vacancy was produced during whole reactivity[23], which can serve as active sites and can increase the oxygen exchange rate, favoring the interaction with CO. The corresponding concentrations of O_{ad} (adsorbed oxygen species)/$O_{lattice}$ (lattice oxygen species) were obviously elevated (Fig. S3), which was in good accordance with the observed catalytic activities and H_2-TPR results.

In this work the method of acid treatment create B-site (rich) terminated perovskite surface to overcome their fundamental flaw for catalytic activity, meanwhile, leading to an increased surface area (Fig. S2). In order to eliminate the surface area effect, the apparent activation energy (E_a) of CO oxidation was calibrated (as shown in Supporting Information Fig. S4). By comparing the E_a values of catalysts, one can evaluate their catalytic performance. The lower the E_a value is, the easier is the complete oxidation of CO^{24}. The results clearly revealed that CO oxidation over three samples exhibits a surface-dependence catalytic activity similar to high-index planes dependence in some binary oxides systems (e.g.$Co_3O_4^{25}$ and Cu_2O^{26}), which are supposed to provide more active sites in either environments. However, the facets control for ternary perovskite oxides is much more difficult[27]. Therefore, this method applied here may give an alternative choice for enhancing surface dependent catalytic activities.
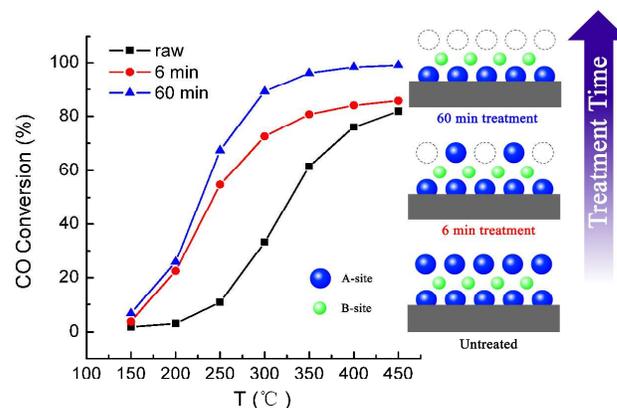

Fig.4 Activity profiles of CO oxidation over the samples without treatment (raw), and treated with dilute nitric acid solution for 6 min and 60 min.

In summary, we have developed a reliable and ready method to create B-site (rich) terminated perovsktie surface for controllable selective wet-etching of perovskite-type oxides. Our wet-etching method can be applied to other perovskite-type oxides. We thus provide the fundamental engineering on metal oxide surfaces, if properly controlled, one can radically enhance the catalytic activity.

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