Development of enhanced surface area LaFeO₃ perovskites using amino acids as templating agents

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ABSTRACT

In this article LaFeO₃ perovskites of enhanced specific surface area (ssa) have been developed through a soft templating path which involves amino acids as capping agents of primary particles, in order to suppress aggregating effects, and polymer P123 as a surface enhancing agent. The treatment of the primary LaFeO₃ particles took place using the amino acids β-alanine, serine, tyrosine and threonine and the final surface area increased from 18 up to 42–59 m²/g, depending on the amino acid. The obtained material showed also a remarkable red shift band gap. The main factor affecting the development of ssa seems to be the interactions between the solid particles and the amphiphilic molecules, which in turn are controlled by the Accessible surface area and the Hydropathy Index of side chain as well as the solubility of amino acid.

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1. Introduction

Perovskite type double oxides with the general form ABO_3, where A and B are metal cations, constitute a structurally quite diverse and chemically very active class of solids. They exhibit very diverse and attractive surface, electronic, magnetic, conductive and thermal properties and are promising materials for catalytic and photocatalytic applications [1–4]. Their structural, physical, chemical, physicochemical, surface and catalytic properties have been scrutinized in several collective volumes [5–9] as well as review articles and book chapters [10–15]. In the standard formula ABO_3 the A and B cations, with $r(A^{+n}) \approx 2r(B^{+m})$, may be combined in different valences like $A^I B^V O_3$, or $A^{II} B^{IV} O_3$, or $A^{III} B^{III} O_3$, with typical representatives KVO_3, $SrTiO_3$ and $LaNiO_3$ respectively. Halogenated metal perovskites ABX_6, where X is a monovalent halogen like F^-, Cl^- or I^-, do exist but have been studied little [16] compared to the oxygenated ones.

The larger A cations, usually alkaline or rare earth elements, with inert d^0 or f^0 electronic structure, act as structural stabilizers and do not offer much to the redox catalytic activity. The smaller B cations can be 3d, 4d or 5d transition metal elements and are the main catalytic sites/centers in such solids due to their ability to undergo reversed redox cycles without destruction of the structure. In the vast majority of catalytic studies 3d cations are employed due to obvious economic reasons. Nevertheless almost 95% of the elements of the Periodic Table can participate in perovskites and these many possible combinations result in a plethora of diverse, and sometimes unexpected, properties of such solids, which have been nicked named *chemical chameleons.*

Although perovskites have been synthesized using various procedures, such as sol gel procedures with various additives, co-precipitation and hydrothermal methods, the biggest problem for surface and catalytic applications remains their low specific surface area (ssa) obtained after heating such ceramic solids. In most cases the specific surface area obtained is in the range of 10–20 m²/g, and often as low as 1–5 m²/g, depending on the duration and the final firing temperature [17–20]. The crux of the problem is the thermal aggregation of the primary particles, formed during precipitation, which should be somehow avoided in order to keep the surface area as high as possible.

In an attempt to overcome such difficulties the group of Kalliaguine [21,22] followed the reactive grinding process to synthesize perovskites with high surface area. The perovskites derived from high energy milling were used at a variety of catalytic processes. Other groups have successfully attempted to synthesized mesoporous perovskites via the nanocasting method using silicate mesoporous materials MCM-41 and SBA-15 as templates [23,24]. This method results in increase of the surface area up to ~150 m²/g. Thus Li et al. [23] used four different silica supports

(SBA-15, SBA-16, MCF and nanosilica powder NSP) to prepare LaFeO$_3$-Silica composites and the higher surface area (194 m^2/g) was observed using SBA-16. Niu et al. [24] proposed a facile route for the synthesis of nano LaCoO$_3$/mesoporous silica composites using a chelating template surfactant N-hexadecyl ethylenediamine triacetic acid.

The above methodologies suffer from the fact of the additional dissolution step of silicate template with suitable solvents like NaOH and HF. So the development of a simpler and more eco-friendly method, leading to same end, i.e higher ssa, remains of interest.

Towards this end, Papadas et al. have proposed recently a facile soft templating process for increasing the ssa of ceramic oxide materials like BiFeO$_3$ [25]. The method involves the use of β-alanine, or 3-aminopropanoic acid, as a capping agent of primary BiFeO$_3$ nanocrystals and polymer-assisted self assembly aggregation using P123. The resulting material consists of a network of connected 6–7nm–sized BiFeO$_3$ nanoparticles with large internal porosity (62 m^2/g) and uniform pores (ca.6.3 nm). An extension of this work was also applied successfully to pure iron oxides but using as capping agent nitrosonium tetrafluoroborate NOBF$_4$ [26].

This work is an attempt to develop LaFeO$_3$ perovskite various aminoacids of different hydropathy, namely β-Alanine, Serine, Threonine and Tyrosine, as capping agents of the primary particles, in an attempt to scrutinize the mechanism of interaction between the solid surface and the amphiphilic species. The primary particles were developed using glycine as a fuel for their preparation. The hybridic entities LaFeO$_3$ + aminoacid were then treated with Pluronic P123 copolymer, as an enhancing agent of ssa and porosity of the materials. The structures of the used amino acids, with some of their properties, are shown in Table 1. The purpose is to examine to what extent the chemical as well as the spacial properties of aminoacids play role in the synthesis route.

2. Experimental

2.1. Synthesis of primary perovskite particles

The primary perovskite particles LaFeO$_3$, termed in the next as *LaFeO$_3$ bulk*, were synthesized using a sol gel auto-combustion method using glycine as fuel to initiate the combustion. The use of glycine was chosen because, as shown previously, because upon heating in the presence of nitrates, results in very fast ignition and the formation of small perovskite particles at relatively low temperature [27]. Namely, in a glass beaker pre-estimated amounts of La(NO$_3$)$_3$·6H$_2$O (Fluka) and Fe(NO$_3$)$_3$·9H$_2$O (Merck) were dissolved in distilled water under stirring and glycine is added in molar ratio (NO$_3^-$)/Glycine = 1. Then the solution was heated at 100 °C to evaporate the water and afterwards at 250 °C to initiate the fast ignition of glycine with the nitrates. The powdered solid obtained was then calcined at 400 °C for 6 h and termed in the next as *LaFeO$_3$-Bulk*.

2.2. Synthesis of final perovskites

The *primary perovskite particles obtained after ignition at* 250 °C were then functionalized as follows: The particles were added into deionized water and the amino acids β-Alanine, Serine, Tyrosine and Threonine were added in amounts g-mol (LaFeO$_3$)/g-mol (aminoacid) = 1. The pH was adjusted to 4.0 with 1 N HNO$_3$ and the suspension was left under gentle stirring overnight at RT. The resulted suspension was then centrifuged and dried at 60 °C. The

Table 1
Amino acids used and some of their properties.

Aminoacid	MW (Da)	MV (Å^3)	pK$_{COOH}$	Accessible surface area-ASA (Å^2)	Hydropathy Index (HI) of side chain[b]	Water solubility (mg/ml)
NH$_2$CH$_2$CH$_2$COOH β-Alanine, Ala, A	89	88.6	3.63	0[a]	− 0.4[b]	545
H$_2$N—CH—COOH ⏐ CH$_2$ ⏐ OH Serine, Ser, S	105	89.0	2.21	115	−0.8	421
H$_2$N—CH—COOH ⏐ CH−OH ⏐ CH$_3$ Threonine, Thr, T	119	116.1	2.09	140	−0.7	13.2
H$_2$N—CH—COOH ⏐ CH$_2$ ⏐ (benzene ring) ⏐ OH Tyrosin, Tyr, Y	181	193.6	2.20	230	−1.3	0.46

[a] The Accessible Surface Area of β-Alanine was taken equal to zero since it does not possess side chain.
[b] The HI of β-Alanine was taken as equal to that of Glycine NH$_2$CH$_2$COOH which does not possess any side groups. The data are from J.Kyte and R.F.Doolittle, J. Mol. Biol. 157 (1983) 105.