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Synthesis, characterization and application of lanthanum-impregnated activated alumina for F removal

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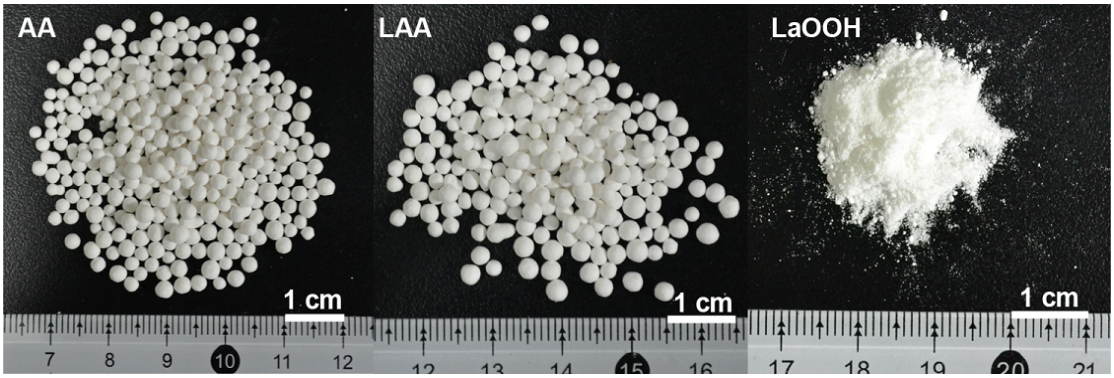

Fig. S1 Photos of AA,LAA and LaOOH.

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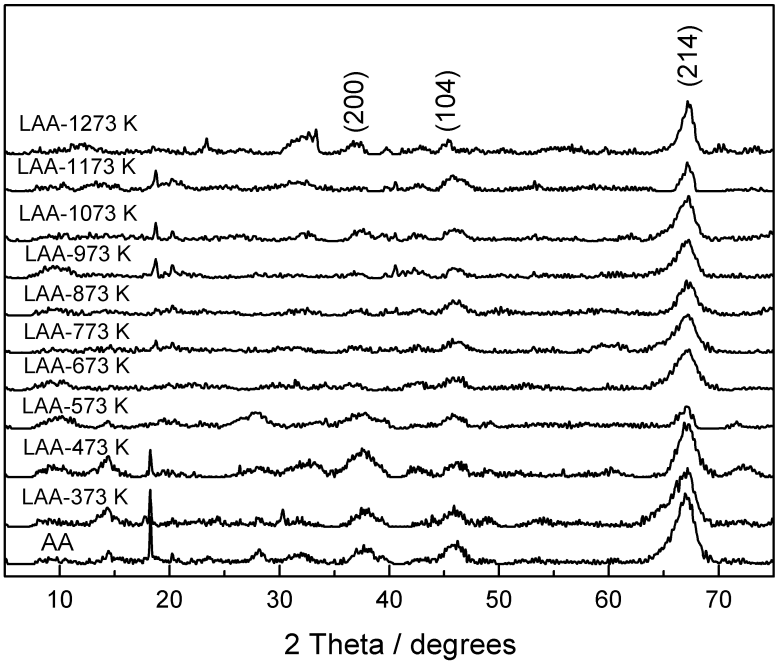

Fig. S2 XRD patterns of various LAAs synthesized at different calcination temperatures (χ-Al_2O_3PDF No. 13-0373).

The XRD results suggested that there were no new crystals in LAA compared with AA. The results indicated that LaOOH supported on LAA were amorphous. This result is inline with our previous work[1]. The characterization peaks of Al_2O_3 were weaker upon LaOOH impregnation, indicating that Al_2O_3 was covered by LaOOH.

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Table S1. Pore volume and diameter of AA and LAA.

	Pore volume ($mL\ g^{-1}$)	**Pore diameter of micropore (nm)**	**Pore diameter of mesopore (nm)**
AA	0.4485	0.588	3.94
LAA	0.3038	0.488	3.706

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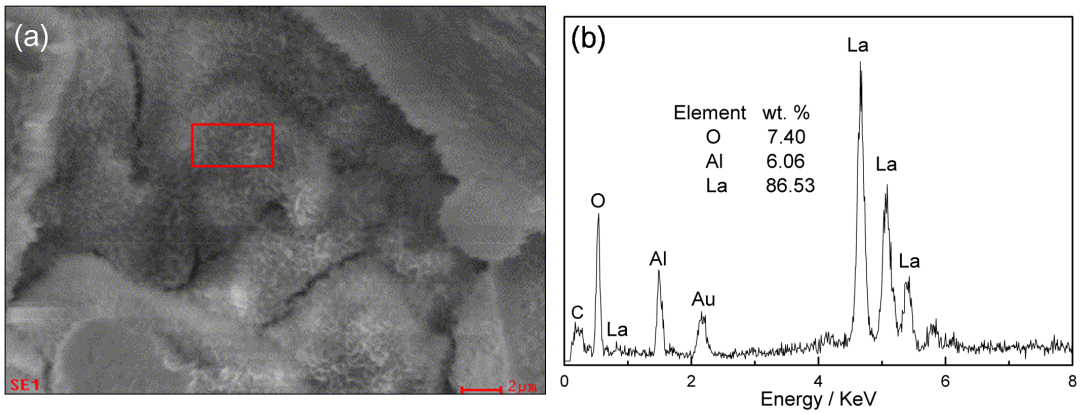

Fig. S3 EDS of flake structures on LAA.

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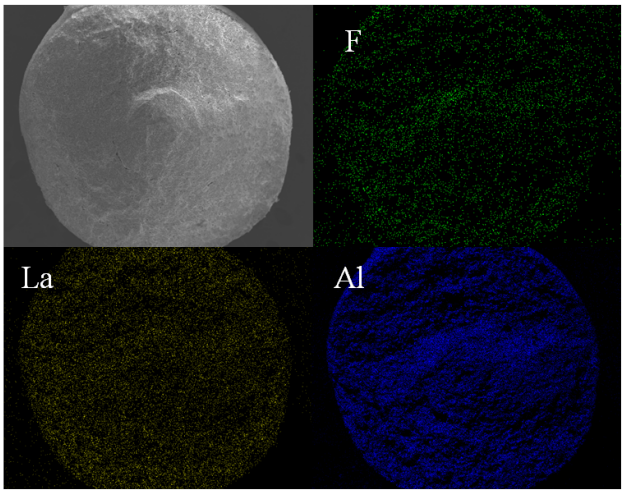

Fig. S4 EDS elemental mapping of F, La, and Al on LAA adsorbed with F.

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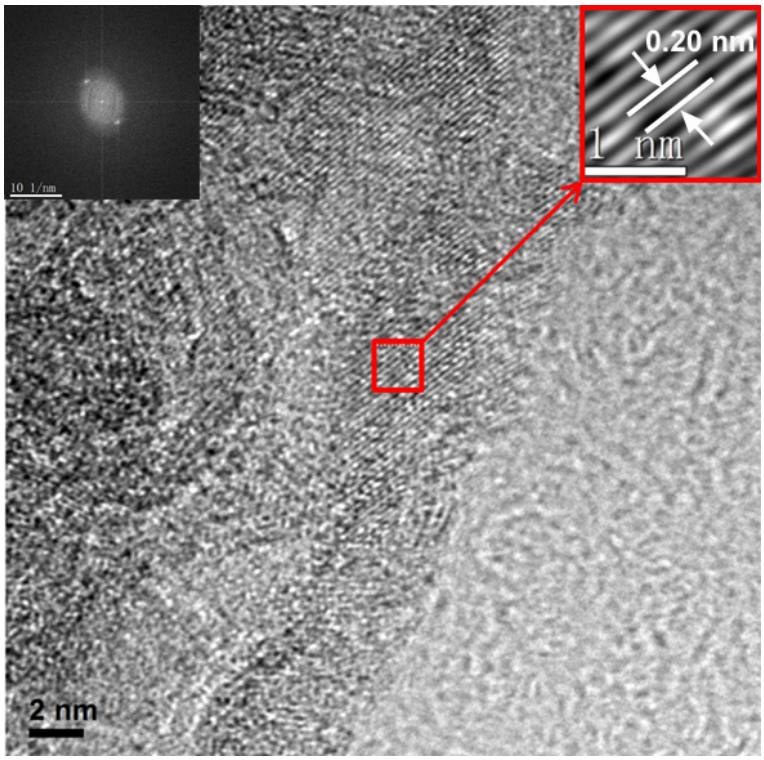

Fig. S5 High resolution transmission electron microscope HRTEM of LAA.

As shown in Fig. S4, the only interplanar distance we found in LAA is1.98 Å (≈ 0.20 nm), corresponding to χ-Al_2O_3 (1 0 4) (PDF No. 13-0373) in our XRD results.

The XRD and HRTEM results showed that there is no crystalline form of La_2O_3, LaOOH or $LaAlO_3$ in LAA, suggesting that the lanthanum oxides supported on LAA are amorphous. This result is in agreement with our previous work[1].

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EXAFS Data collection

The La LIII-edge spectra were collected at beamline 14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The spectra were taken under standard SSRF operation conditions (2.8 GeV and 150-280 mA) with a double-crystal Si (111) monochromator. The spectra were collected with a fluorescence detector positioned at a 90° angle to the incident beam at room temperature. Three scans were collected from each sample, inspected for overall quality and averaged to improve the signal/noise ratio.

EXAFS data analysis was performed using the ATHENA and AETEMIS program in the IFEFFIT computer package.[2,3] The analysis procedure was similar to our previous studies.[4, 5] The raw data measured in intensities were converted to μ(E), and averaged spectra were used in the analysis. The EXAFS signal $\chi(k)$ was extracted from the measured data using the AUTOBK algorithm[6] where k is the photoelectron wave number. The primary quantity for EXAFS is then χ(k), the oscillations as a function of photoelectron wave number. χ(k) was weighted by k^2 to account for the dampening of oscillations with increasing k. The different frequencies in the oscillations in χ(k) correspond to different near neighbor coordination shells which can be described and modeled according to the EXAFS equation

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

where f(k) and δ(k) represent the photoelectron backscattering amplitude and phase shift, respectively, N is the number of neighboring atoms, R is the distance to the neighboring atom, and the σ^2 is the Debye-Waller factor representing the disorder in the neighbor distance. The k^2 weighted EXAFS in k-space ($Å^{-1}$) was Fourier transformed (FT) in R-space (Å). The experimental spectra were fitted with single-scattering theoretical phase-shift and amplitude functions calculated with the *ab initio* computer code FEFF6[7] using atomic clusters generated from the crystal structure of α-La_2O_3 and SrLa (AlO_4). The many-body amplitude reduction factor (S_0^2) was established as 0.78 by isolating and fitting the first-shell La-O of LaOOH spectrum. The spectrum was fit by first isolating and fitting the first-shell La-O to estimate ΔE_0, the difference in threshold energy between theory and experiment. Then ΔE_0 was fixed to the best fit value from first-shell fitting and kept the same for all interatomic shells in a given spectrum. In addition, the ΔE0 value was allowed to float by no more than ±10 eV. The parameters such as interatomic distance (R), coordination number (CN), and Debye-Waller factor (σ^2) were first established with reasonable guesses and were fitted in R-space. The error in the overall fits was determined using R-factor, the goodness-of-fit parameter: R-factor = $\Sigma(\chi_{data}-\chi_{fit})^2/\Sigma(\chi_{data})^2$. Good fits occur for R-factor < 0.05.

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Table S2 Structure parameters derived from La L_{III}-edge EXAFS analysis.

Sample	shell	CN [a]	R (Å) [b]	σ^2 (Å^2) [c]	ΔE_0 (eV)[d]	R-factor[e]
LaOOH	La-O	7.6 ± 2.2	2.58 ± 0.04	0.010 ± 0.008	6.75	0.028
	La-O	1.0 ± 0.2	3.56 ± 0.34	0.016 ± 0.007		
	La-La	3.3 ± 1.4	4.22 ± 0.07	0.031 ± 0.012		
LAA	La-O	7.7 ± 1.4	2.56 ± 0.06	0.007 ± 0.003	2.36	0.012
	La-Al	3.7 ± 1.2	3.19 ± 0.12	0.018 ± 0.010		
	La-La	3.5 ± 1.5	3.43 ± 0.16	0.028 ± 0.013		
	La-La	4.3 ± 1.4	4.12 ± 0.18	0.033 ± 0.015		

[a] coordination number. [b]interatomic distance. [c]Debye-Waller factor. [d] threshold energy shift. [e] goodness-of-fit parameter: R-factor = $\Sigma(\chi_{data} - \chi_{fit})^2/\Sigma(\chi_{data})^2$

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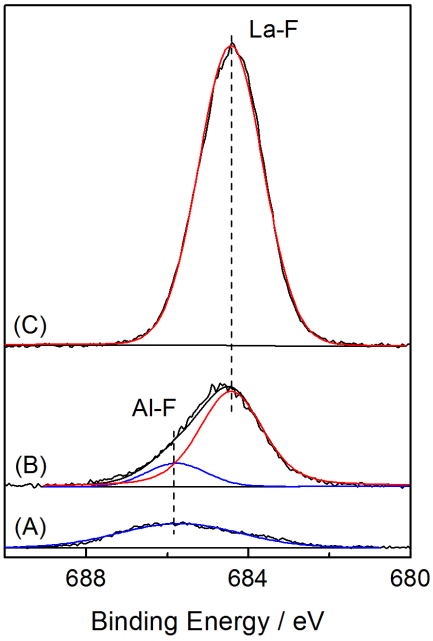

Fig. S6 High resolution XPS surveys of F 1s for spent AA (A), LAA (B), and LaOOH (C) Vertical lines indicate Al-F (blue) and La-F (red) at 685.7 ± 0.1 eV and 684.4 ± 0.1 eV, respectively.

The high resolution XPS surveys of F 1s for spent AA, LAA and LaOOH were used to explore the F adsorption on the adsorbents. The F 1s spectra were simulated by considering two peaks from Al-F and La-F.[8, 9] The peak position of Al-F at 685.7 eV was observed in AA and LAA. Moreover, the peak of La-F at 684.4 eV was resolved in LaOOH and LAA.

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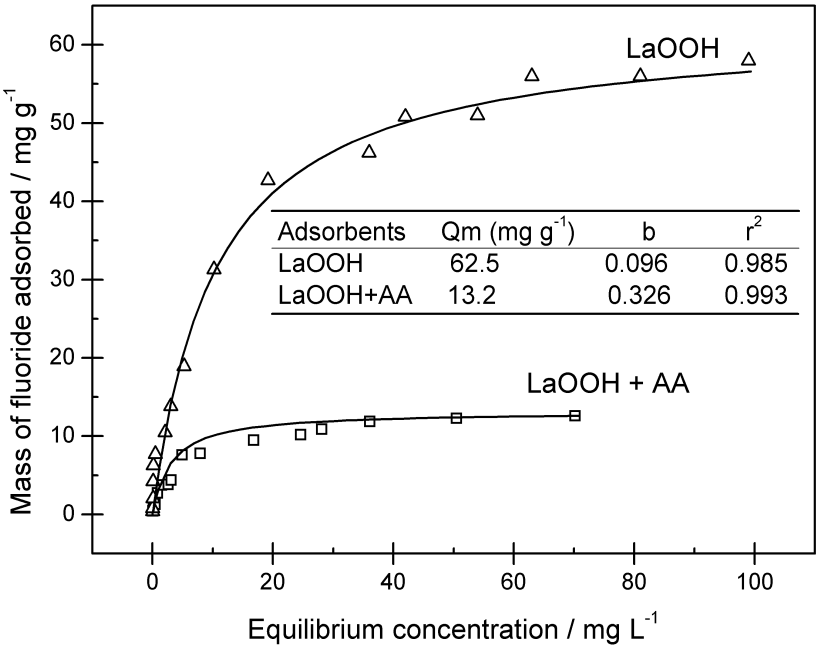

Adsorbents	Qm (mg g^{-1})	b	r^2
LaOOH	62.5	0.096	0.985
LaOOH+AA	13.2	0.326	0.993

Fig. S7 F dsorption isotherms on LaOOH and the mixture of AA and LaOOH (with 20 wt.% La). Adsorbent = 1 g L^{-1}, pH = 7, Temperature = 298 ± 2 K. Inset Table: Langmuir parameters: Qm is the maximum adsorption amount (mg g^{-1}), b is Langmuir constant (L mol^{-1}), and r^2 is the correlation coefficient.

As shown in Fig. S7, the F adsorption capacity of the mixture of AA and LaOOH (13.2 mg g^{-1}) is no better than that of LAA (16.9 mg g^{-1}, Figure 9). In this experiment, the weight percentage of La in the mixture was the same as that in LAA (Fig. 2). The results indicate that LAA takes the advantage of porous AA to anchor the LaOOH flakes, which resulted in uniformly distributed LaOOH for F adsorption. Conversely, the LaOOH powder may aggregate in the solution and less active sites are available for effective F adsorption.

In addition, the average particle size of LaOOH was 702.0 ~742.1 nm as determined using a Zetasizer Nano ZS (Malvern Instrument, UK). This small particle size indicates that the LaOOH should have difficulties in the solid/liquid separation and recovery from the treated water. In contrast, LAA was synthesized based on a commercial AA granule with a diameter of 1~3 mm (Fig. S1). This granule is suitable for column water treatment in the large scale.

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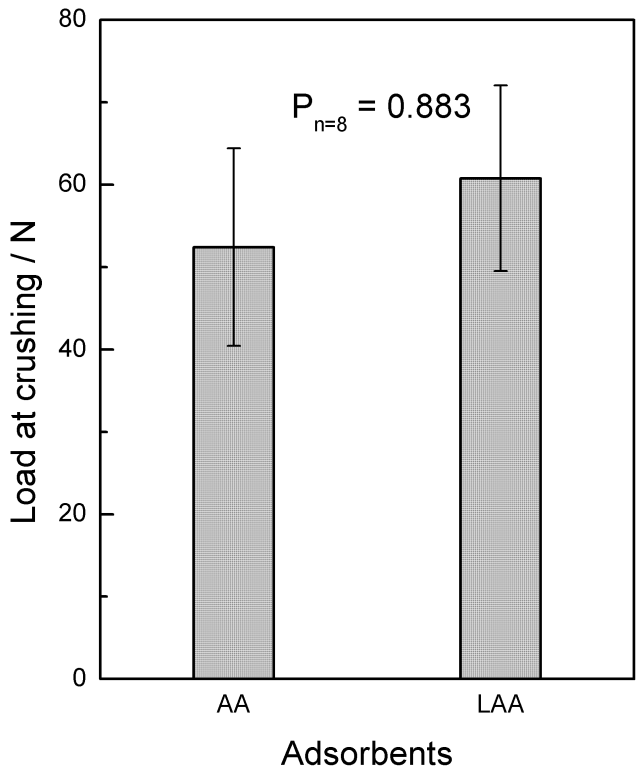

Fig. S8 Mechanical strength of AA and LAA.

The mechanical strength of AA and LAA were analyzed using a universal testing machine at a cross-head speed of 2 mm min^{-1} (Sansi Inc., China). The loads at crushing for AA and LAA were 52.4 ± 12.0 and 60.8 ± 11.3 N, respectively. No significant difference existed between AA and LAA (p=0.883, n=8, Fig. S8). The good mechanical strength implies that LAA can be used in the large scale and be easily recovered from treated water.

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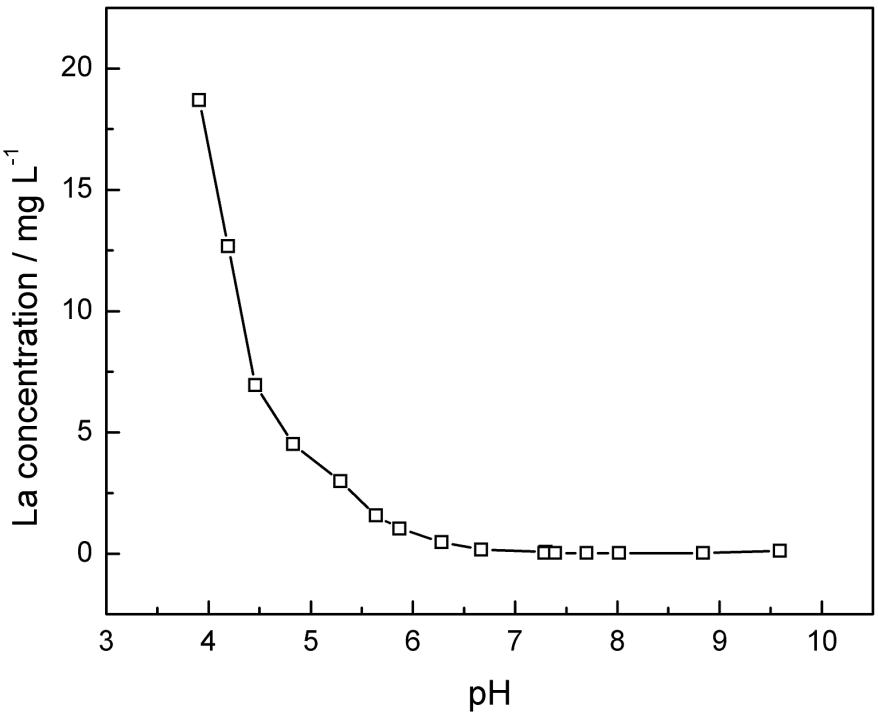

Fig. S9 La release from LAA as a function of solution pH.

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