Electronic Supplementary Information

Ionic liquid–mediated synthesis of meso-scale porous lanthanum transition metal perovskites with high CO oxidation performance

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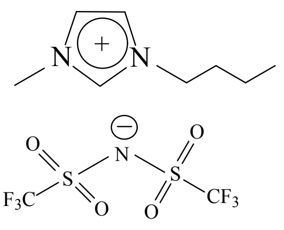
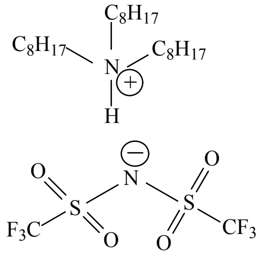
Experimental:

In a typical synthesis of mesoporous $LaMnO_3$ perovskites oxides, 8.65 g of lanthanum methoxyethoxide (10–12% in methoxyethoxide, Gesta), 0.62 g $Mn(OOCCH_3)_2 \cdot 6H_2O$ (98 %, Aldrich), and 1.0 g of ionic liquid (the chemical structures of the ionic liquids in the current investigation are shown in the following diagrams) were dissolved in 5.0 ml of ethanol. The solution was stirred at room temperature for 1–2 h until the $Mn(OOCCH_3)_2 \cdot 6H_2O$ completely dissolved. Then 5.0 ml of ethanol and a small amount of water were added slowly with stirring. The mixed solution was gelled in an open petri dish at 50°C for 24 h and aged at 200°C for 2 h, and a solid film was obtained. The ionic liquid was extracted by refluxing the sample with acetonitrile in a Soxhlet extractor for 10 h. The as-made sample was directly heated at 400, 600, and 700°C for 2 h. The $LaFeO_3$, $LaCoO_3$, and $LaNiO_3$ perovskites were prepared by the same process and calcined at 650°C.



$[Bmim]^+ Tf_2N^-$



$[N_{8,8,8,H}]^+ Tf_2N^-$

The bulk R-$LaMO_3$ perovskites (R-$LaMnO_3$ and R-$LaCoO_3$) were prepared by the citrate sol-gel method. Metal nitrate and citric acid were used as starting materials. An aqueous solution was prepared with the cation ratio La: Mn: citric acid of 1:1:2. The solution was dried at 110°C for 24 h. Then as-made $LaMnO_3$ and $LaCoO_3$ were heated at 700 and 650°C, respectively, for 2h.

The materials were characterized by N_2 adsorption (TriStar, Micromeritics), powder x-ray diffraction (Panalytical Empyrean diffractometer with Cu Ka radiation k = 1.5418 A° operating at 45 kV and 40 mA), thermogravimetric analysis (TGA 2950, TA Instruments), Fourier-transform infrared spectrum (PerkinElmer Frontier FTIR spectrometer), transmission electron microscopy and scanning transmission electron microscope (HD-2000, STEM operated at 200 kV transmission), H_2 temperature programmed reduction (Auto chem II, Micromeritics).

Catalytic CO oxidation was carried out in a fixed-bed reactor (U-type quartz tube with inner diameter of 4 mm at atmospheric pressure. A 30 mg catalyst supported by quartz wool was loaded in the reactor. The feed gas of 1% CO balanced with dry air passed though the catalyst bed at a flow rate of 10 mL/min, corresponding to a gas hourly space velocity (GHSV) of 20,000 mL (h gcat)$^{-1}$.

Table S1

Table S1. Texture characteristics of fresh and calcined LMTP samples

LMTP	Ionic liquid	Synthesized La-M nanocomposites			Calcinated La-M samples [a]		
		Surface area / m ^{2}/g	Pore Size[b] / nm	Pore Volume / cm^3/g	Surface area / m ^{2}/g	Pore Size[b] / nm	Pore Volume / cm^3/g
$LaMnO_3$	No IL	1.4	/	/	0.4	/	/
	$[N_{8,8,8,H}]^+ Tf_2N^-$	308	8-12	0.26	36	20-25	0.14
	$[Bmin]^+ Tf_2N^-$	382	< 2	0.16	24	10-15	0.07
$LaFeO_3$	$[Bmin]^+ Tf_2N^-$	505	2-4	0.17	20	15-25	0.07
$LaCoO_3$	$[Bmin]^+ Tf_2N^-$	278	4-6	0.26	27	8-10	0.06
$LaNiO_3$	$[Bmin]^+ Tf_2N^-$	353	4-10	0.30	21	8-10	0.05

[a] 700 °C calcination for $LaMnO_3$, and 650 °C calcination for $LaFeO_3$, $LaCoO_3$ and $LaNiO_3$. [b] BJH adsorption pore size distributions.

Figure S1

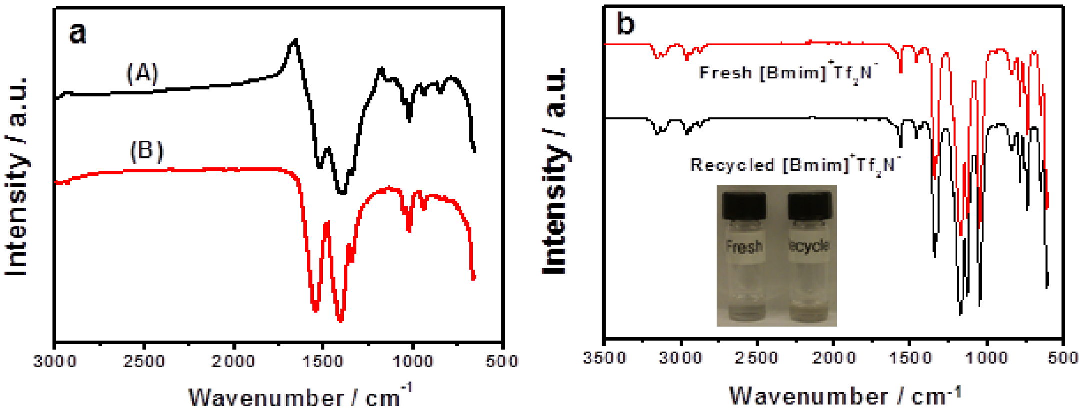


Figure S1. FTIR spectrums of (a) La-Mn nanocomposite (A. mesoporous La-Mn nanocomposite after ionic liquid extraction; B. bulk La-Mn nanocomposite synthesized wihout ionic liquid); (b) refreshed and recovered $[Bmim]^+Tf_2N^-$ ionic liquid.

It can be seen from Figure S1(a) that the mesoporous La-M nanocomposite after ionic liquid extraction shows no infrared adsorbed peaks of the ionic liquid $([Bmim]^+Tf_2N)^-$. Its structure is similar to that of bulk La-M nanocomposite synthesized without ionic liquid, which means the ionic liquid can be completely extracted by acetonitrile. Figure S1(b) shows FTIR spectrums of refreshed and recovered $[Bmim]^+Tf_2N$; they have exactly the same infrared adsorbed peaks, which means the recovered $[Bmim]^+Tf_2N$ can be recycled in the new preparation process.

Figure S2

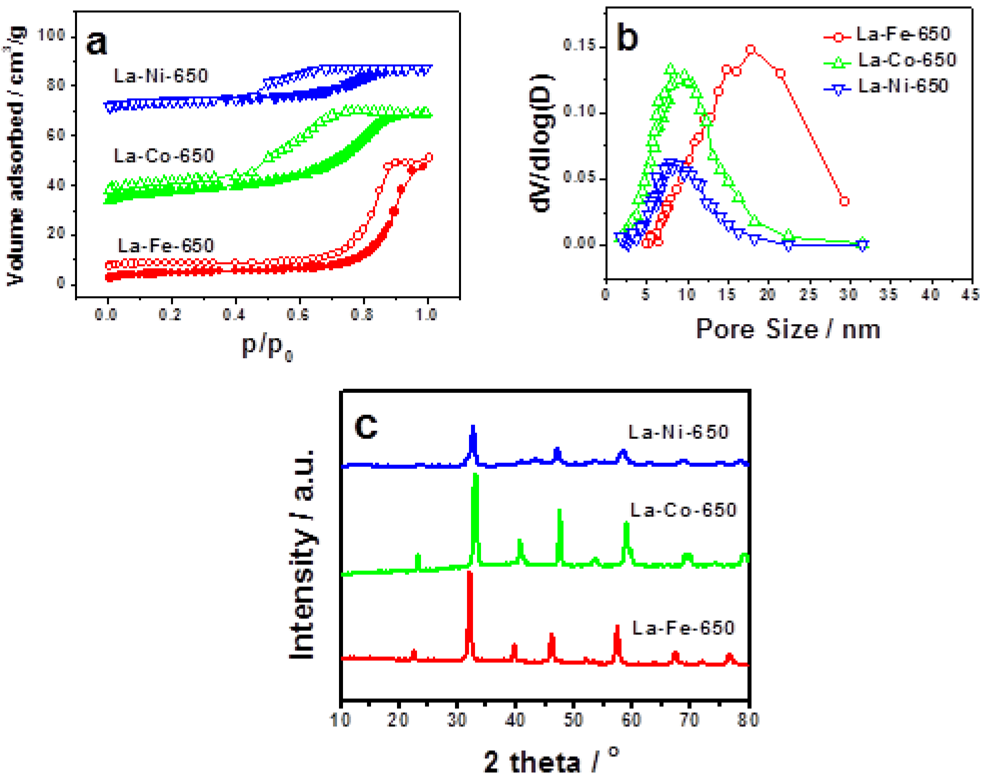


Figure S2. Characterizations of La-Fe, La-Co and La-Ni nanocomposites calcinated at 650 °C. **(a-b)** N_2 sorption isotherms and BJH adsorption pore size distributions of La-Fe-650 (●), La-Co-650 (▲, shift up for 30 cm^3/g), and La-Ni-650(▼, shift up for 70 cm^3/g) calcinated at 650°C; **(c)** XRD patterns of La-Fe-650, La-Co-650 and La-Ni-650 calcinated at 650°C.

Figure S3

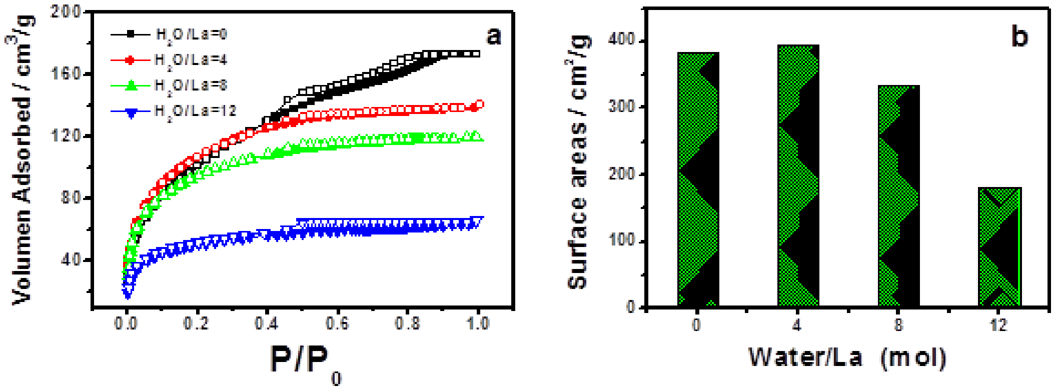


Figure S3. Effect of H_2O/La (mol) on texture properties of La-Mn nanocomposites prepared by $[Bmim]^+ Tf_2 N^-$. (a) N_2 adsorption isothermal and (b) surface areas of as-made La-Mn nanocomposites.

Figure S4

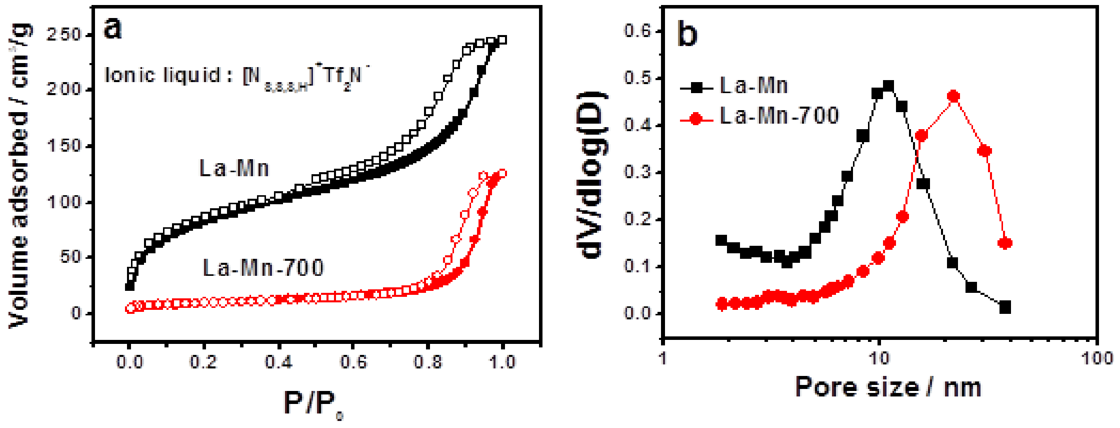


Figure S4. N_2 sorption isotherms and desorption pore size distributions of La-Mn and La-Mn-700 (calcinated at 700°C) prepared by $[N_{8,8,8,H}]^{+}Tf_2N^{-}$.

Figure S5

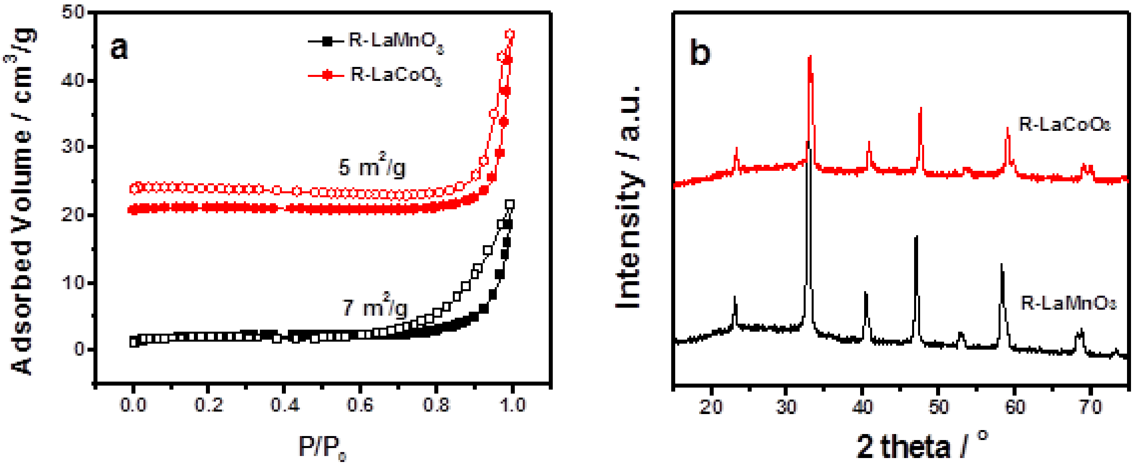


Fig S5. Characterization of R-LaMnO3 (calcinated at 700 ºC) and R-LaCoO3 (calcinated at 650 ºC). (a) N_2 sorption isotherms; (b) XRD patterns.

Figure S6

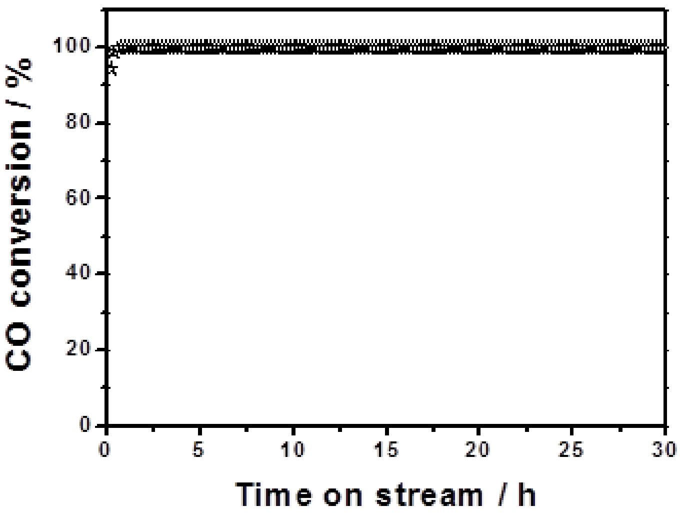


Figure S6. Long-term durability test of meso-$LaMnO_3$ for CO oxidation at 140°C under GHSV=20,000 mL (h□gcat)$^{-1}$