Supporting Information

A new reductive DL-mandelic acid loading approach for moisture-stable Mn^{4+} doped fluorides

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Experimental Section

1. *Synthesis*.

1.1 Synthesis of K_2GeF_6:Mn^{4+} (KGFM)

According to the previous report,[1] three-step chemical co-precipitation strategy was used to synthesize KGFM red phosphors.

The first step is to synthesize K_2MnF_6: starting materials of $KMnO_4$ (99.5%) and KHF_2 (99.5%) with mass ratio of 1:20 were dissolved in 49% HF aqueous solution. After stirring and cooling for 30 min, 30% H_2O_2 was dropping very slowly in the mixed solution. When the solution changing from purple to brown, the yellow K_2MnF_6 powder was precipitated. By fast filtering and washing using acetone, the yellow powder was then oven-dried at 80 °C for 2 h.

The second step is to synthesize K_2GeF_6: GeO_2 (1.39 g, 5N) and KF (2.33 g, AR) were dissolved in 7.5 mL 49% HF aqueous solution at room temperature to obtain GeO_2/HF and KF/HF solution, respectively. Then the KF/HF solution was added dropwise to the GeO_2/HF mixed solution to precipitate K_2GeF_6. The product was collected by centrifugation and washed by acetone several times. After drying in vacuum at 50 °C for 24 h, white K_2GeF_6 was ready for the next experiments.

The third step is to precipitate KGFM: First, 0.05 g (0.20 mmol) K_2MnF_6 and 0.53 g (2.00 mmol) K_2GeF_6 were added into 5 mL 49% HF in succession, and then a yellow transparent solution was formed soon under stirring (500 rpm). Next, pouring 5 mL ethanol into the yellow solution caused immediate crystallization of lots of yellow crystals. After precipitating for 5 min, the supernatant was discarded and the as-precipitated yellow powders were collected by centrifugation and washed 3 times with acetone, and finally dried at 50 °C for 5 h.

1.2 Synthesis of reference K_2SiF_6:Mn^{4+} (KSFM) and K_2TiF_6:Mn^{4+} (KTFM)

KSFM and KTFM were prepared referring to 1.1 strategy where raw K_2GeF_6 in the third step was replaced by K_2SiF_6 (99.999%) and K_2TiF_6 (99.5%), respectively.

1.3 Synthesis of mandelic acid loading KGFM (KGFM@MA) / KSFM (KSFM@MA) / KTFM (KTFM@MA)

4 g DL-mandelic acid (99.0%, AR) was dissolved in 5 mL ethanol (AR) and continuously stirring at room temperature for 3 hours to generate uniform solution. Then 0.3 g of the as-prepared KGFM / KSFM /KTFM was added in the MA solution under stirring (500 rpm). After continuously stirring for 2 hours, the treated yellow powders were collected by centrifugation and washed by 5 mL ethanol, and finally dried at 80 °C for 5h.

2. *Analysis and Characterization*.

The solid products were characterized by using X-Ray powder diffraction (XRD) studies on D8 ADVANCE powder diffractometer (Bruker AXS, Germany) with Cu-Kα radiation (λ = 1.54059 Å) at room temperature in the range of 10 °< 2θ < 70 °. The morphologies of the as-prepared products were

measured by SEM (FEI Quanta 400). The absorption spectra were recorded with a Cary 5000 UV-Vis-NIR spectrophotometer (Varian) equipped with double out-of-plane Littrow monochromator. The photoluminescence excitation (PLE) and photoluminescence (PL) spectra within the temperature range 293 - 500 K were measured using an Edinburgh Instruments FSP920 Time Resolved and Steady State Fluorescence Spectrometers equipped with a 450 W Xe lamp, a 60 W μF900 microsecond flash lamp, TM300 excitation monochromator and double TM300 emission monochromators and thermo-electric cooled red-sensitive PMT. The spectral resolution of the steady measurements was about 0.05 nm in UV-Vis. The sample was mounted in an Oxford OptistatDN2 nitrogen cryostat for PLE and PL measurements above room temperature. The room temperature inner quantum yield (IQY) of the samples was measured using a barium sulfate coated integrating sphere (150 mm in diameter) attached to the FSP920. The Fourier transform infrared (FT-IR) spectra were measured with a resolution 1 cm^{-1} in the range 400 - 4000 cm^{-1} using Bruker EQUINOX 55 spectrometer. X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Fisher Scientific, USA) measurements were performed to characterize the chemical compositions of the obtained product. Thermal gravimetric (TG) analyses were performed on a Netzsch STA 449F3 instrument in flowing N_2 with a heating rate of 5 °C/min.
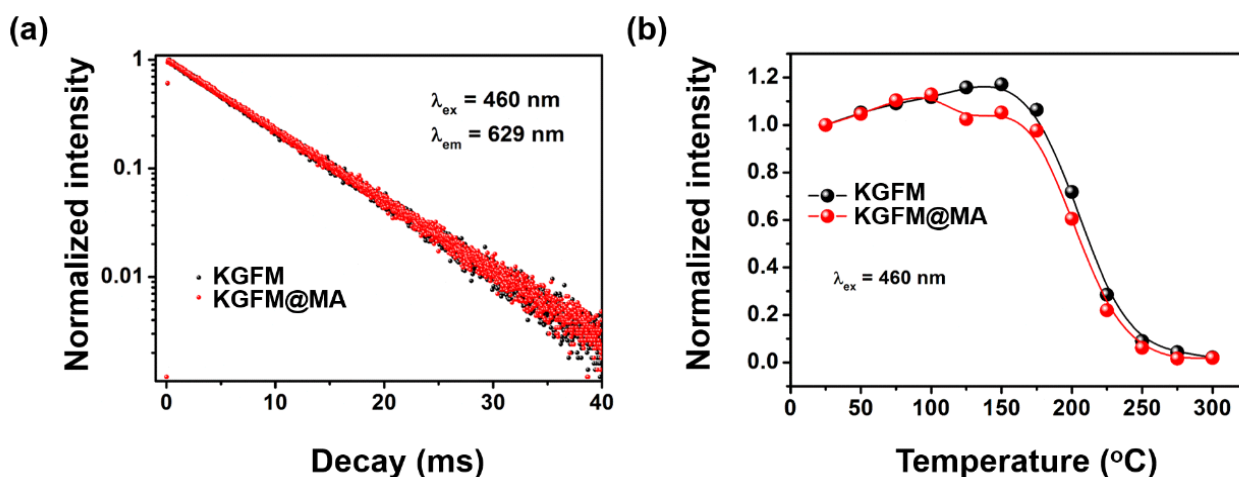
Results and Discussion

Fig. S1 (a) Decay curves and (b) thermal quenching curves of KGFM and KGFM@MA.

Table S1 Compared luminescent properties of KGFM and KGFM@MA

Sample	Normalized PL intensity (%)[a]	Decay lifetime (ms)	EQY (%)[b]	E_{abs} (%)[c]	$T_{50\%}$ (°C)[d]
KGFM	100	6.6	68.8	70.3	212
KGFM@MA	99	6.6	61.7	64.9	206

a.   PL was normalized by the integrated intensity of original KGFM.

b.   EQY is abbreviation of external quantum yield and is defined as the ratio of the number of emitted photons (I_{em}) to the number of excited photons (I_{ex}), and can be calculated by the following equation:

$$EQY = \frac{I_{em}}{I_{ex}} = \frac{\int Ls}{\int E_R}$$

Where E_R is the emission spectrum of the excitation light, recorded with the equipment blank sample in place, and collected using the sphere, and L_s is the luminescence emission spectrum of the sample.

c. E_{abs} is abbreviation of absorption efficiency.

d. $T_{50\%}$ is defined as the heating temperature where the PL strength drops to 50% of the original intensity at room temperature.
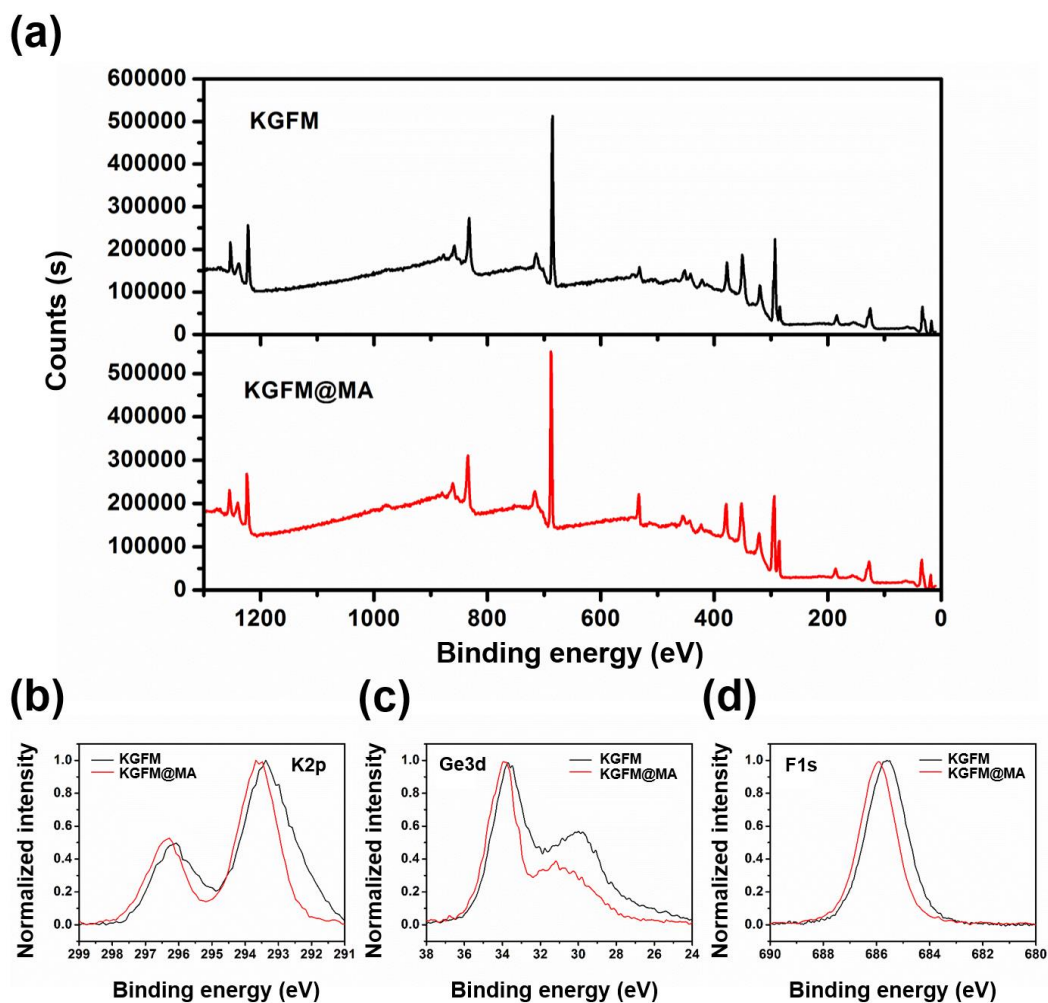
Fig. S2 (a) XPS survey and normalized spectra of (b) K2p, (c) Ge3d, and (d) F1s of KGFM and KGFM@MA.

Table S2 Atomic percentage of the surface elements of KGFM and KGFM@MA

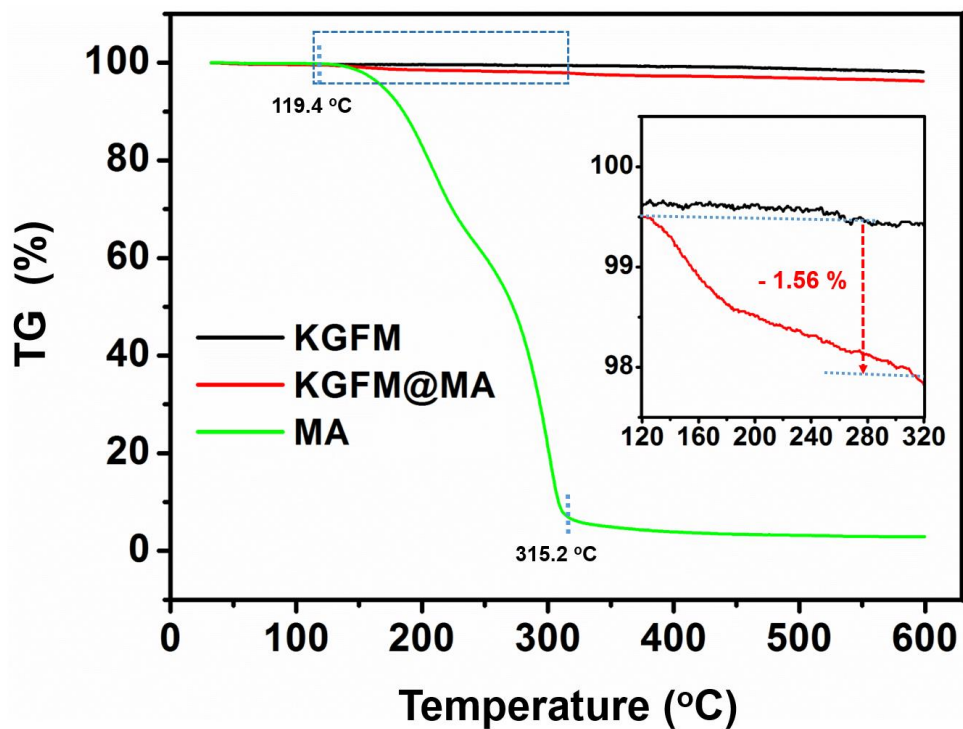| Sample	Average atomic (%)					
	C1s	O1s	K2p	Ge3d	Mn2p	F1s
KGFM	10.7	4.91	13.43	22.35	0.67	47.94
KGFM@MA	22.81	7.08	14.93	19.01	0.60	35.57

Fig. S3 TG curves of KGFM, KGFM@MA and MA, the inset is the enlarged figure of the selected area.
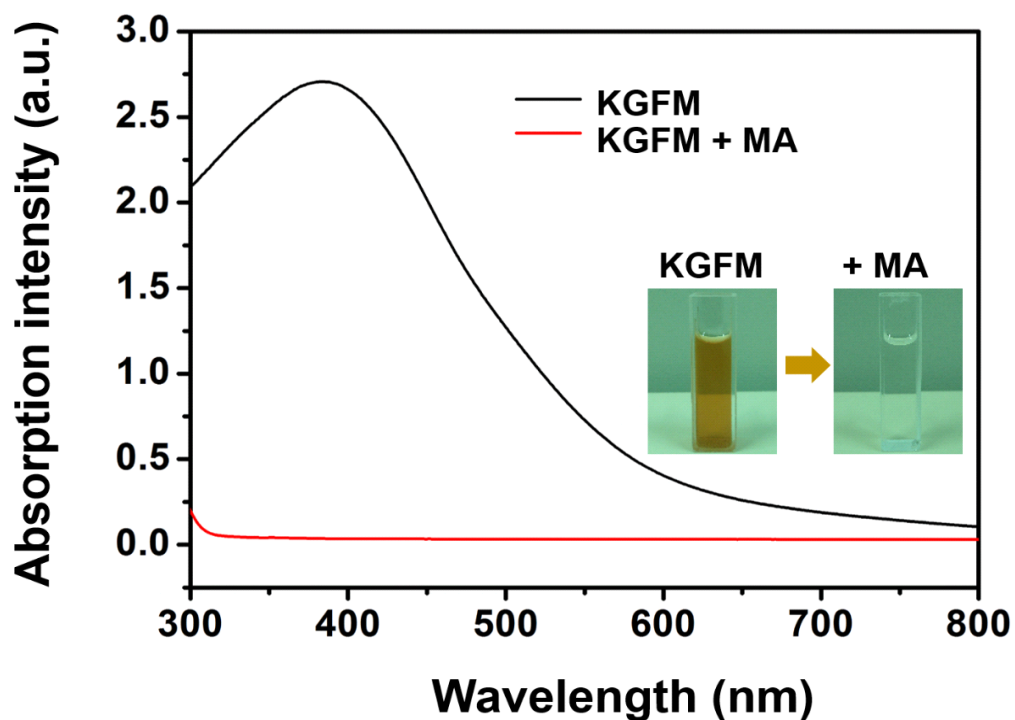

Fig. S4 Absorption spectra and photographs (inset) of KGFM aqueous solution before (black line) and after (red line) loading MA.
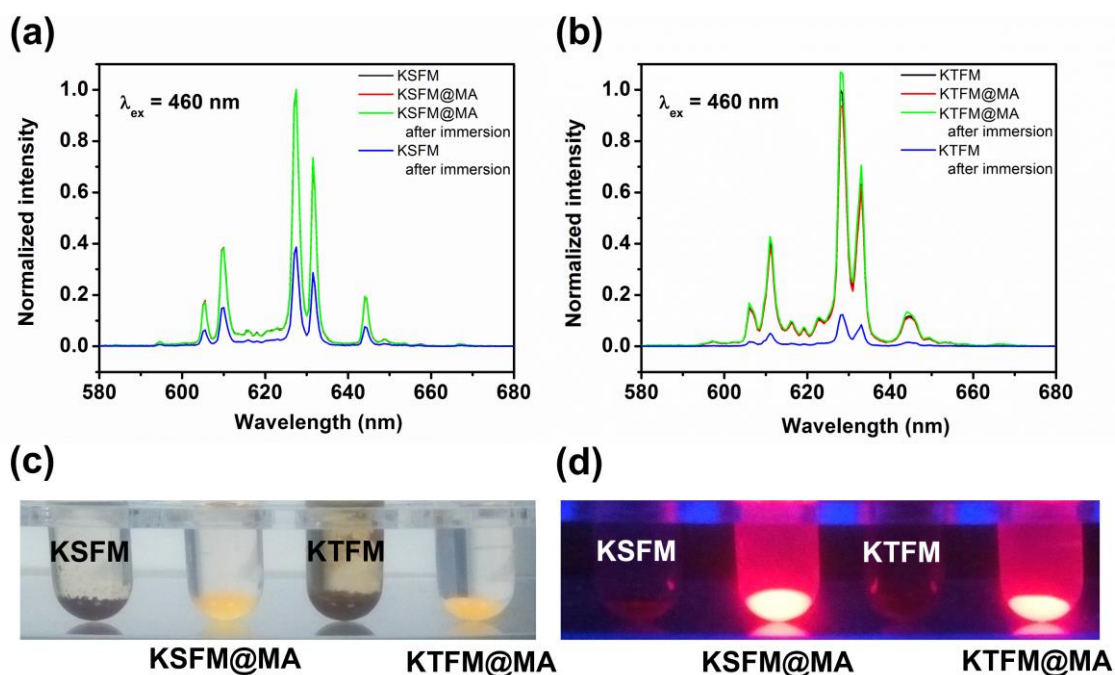
Fig. S5 Normalized PL spectra of (a) KSFM / KSFM@MA and (b) KTFM / KTFM@MA before/after water erosion for 168 hours, and their photographs after immersion in water for 168 hours, taken under (c) natural light and (d) 365-nm UV-light.

Table S3 Compared emission intensity (a. u.) of (a) KGFM / KGFM@MA, (b) KSFM / KSFM@MA and (c) KTFM / KTFM@MA before/after water erosion for 168 hours

Group	Sample	Initial intensity*	After water erosion*
a	KGFM	100%	33.2%
	KGFM@MA	99.4%	98.3%
b	KSFM	100%	38.7%
	KSFM@MA	100%	100%
c	KTFM	100%	12.8%
	KTFM@MA	95.9%	108%

* The ratio value is normalized by the integrated intensity of each group's original sample.

Notes and references

1 W. Zhou, M. H. Fang, S. Lian and R. S. Liu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 17508-17511.