

Supporting Information for “**Fabrication of the binary hybrid-filled layer-by-layer coatings on flexible polyurethane foams and study on their flame-retardant and thermal properties**”

Haifeng Pan<sup>\*,a</sup>, Yushi Lu<sup>a</sup>, Lei Song<sup>b</sup>, Xiaotao Zhang<sup>a</sup>, Yuan Hu<sup>\*,b,c</sup>

<sup>a</sup>Faculty of Engineering, China University of Geosciences, Wuhan430074, People's Republic of China.

<sup>b</sup>State Key Laboratory of Fire Science, University of Science and Technology of China, 96 JinzhaiRoad, Hefei, Anhui 230026, People's Republic of China.

<sup>c</sup>Suzhou Key Laboratory of Urban Public Safety, Suzhou Institute of University of Science and Technology of China, 166 Ren'ai Road, Suzhou, Jiangsu 215123, People's Republic of China.

\* Corresponding author. Fax/Tel: +86-551-63601664.

E-mail address: hfpan19@163.com (Haifeng Pan); yuanhu@ustc.edu.cn (Yuan Hu).

## **Materials**

Expandible graphite was supplied by Qingdao Tian he Graphite Co., Ltd. (China). Potassium permanganate ( $\text{KMnO}_4$ ), sodium nitrate ( $\text{NaNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%), and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) were bought from Guangfu Fine Chemical Research Institute (Tianjin, China). Tetraethoxysilane (TEOS), 3-Aminopropyltrimethoxysilane (KH-550), toluene and absolute ethanol were all provided by Sinopharm Chemical Reagent Co. Deionized water with a resistance of 18.2 M $\Omega$  was used for all experiments.

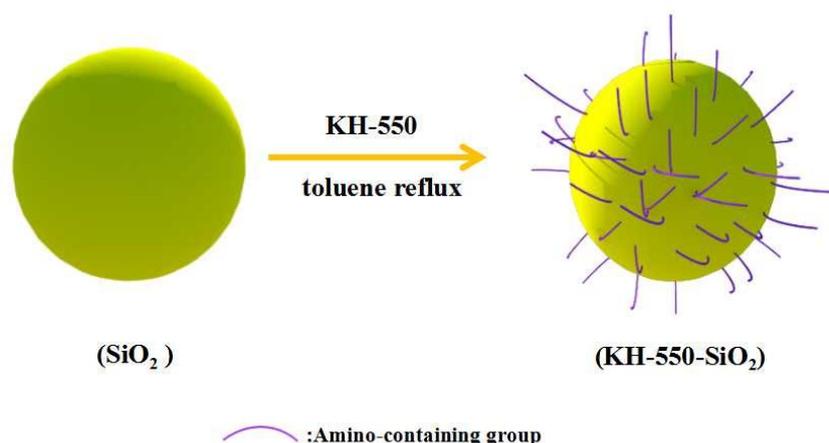
## **Preparation of GO, SiO<sub>2</sub> nanospheres and amino-terminated silica nanospheres (KH-550-SiO<sub>2</sub>)**

In a typical process, expandible graphite (10 g) and sodium nitrate (5 g) were mixed with sulfuric acid (230 ml, 98 wt%) in an ice bath. Then, potassium permanganate (30.0 g) was slowly added to the mixture under stirring conditions. Afterwards, the ice bath was removed, and the mixture was heated at 35 °C for 0.5 h. Afterwards, 460 ml of deionized water was carefully dropwised to the suspension. The reaction was allowed to proceed for 30 min at 100 °C; then the resultant bright-yellow suspension was diluted to 1400 ml and further treated with 25 ml of 30% hydrogen peroxide. GO product was purified by centrifugation and thorough washing with a 10% HCl solution and deionized water to reach a pH near 7.

SiO<sub>2</sub> nanospheres were prepared as follows. Briefly, 3 mL of TEOS was added dropwise to a solution containing 100 mL of ethanol, 2.0 mL of deionized water, and 4.5 mL of ammonium hydroxide (25%) under magnetic stirring. After the mixture

was stirred at 40 °C for 4 h, the additional 2.0 mL of TEOS was added, and the reaction was allowed to continue for another 12 h with stirring.

SiO<sub>2</sub> nanospheres (2.5 g) were dispersed in anhydrous toluene (300 mL). KH-550 (20 g) was added into the suspension. The mixture was refluxed under stirring for 24 h. The product was filtered and then washed with anhydrous toluene (400 mL, 3 times) and absolute ethanol (400 mL, 3 times). The functionalized nanosilica (KH-550-SiO<sub>2</sub>) was dried in a vacuum oven overnight at 105 °C. The preparation of KH-550-SiO<sub>2</sub> is illustrated in **Scheme S1**.



**Scheme S1** The preparation of KH-550-SiO<sub>2</sub>.

### Characterization

X-ray diffraction (XRD) measurements were employed to characterize GO with a Japan Rigaku D=Max-Ra rotating anode X-ray diffractometer equipped with a Cu-Ka tube and Ni filter ( $\lambda=0.1542$  nm). Transmission electron microscopy (TEM) images of GO and silica nanospheres were obtained on a Jeol JEM-100SX transmission electron microscope with an acceleration voltage of 100 kV. The FTIR spectra were recorded on a Nicolet MAGNA-IR 750 FTIR spectrometer. KBr ground in a mortar with a

pestle and enough solid sample was ground with KBr to make a 1 wt. % mixture for making KBr pellets. The mixture was pressed into a tablet, which was then placed in a ventilated oven. The transition mode was used and the wavelength range was set from 4000 to 500  $\text{cm}^{-1}$ . The X-ray photoelectron spectroscopy measurement was carried out using an ESCALAB MK II (VG Co., Ltd., England) spectrometer with Al K  $\alpha$  excitation radiation ( $h\nu = 1253.6 \text{ eV}$ ) in ultrahigh vacuum conditions.

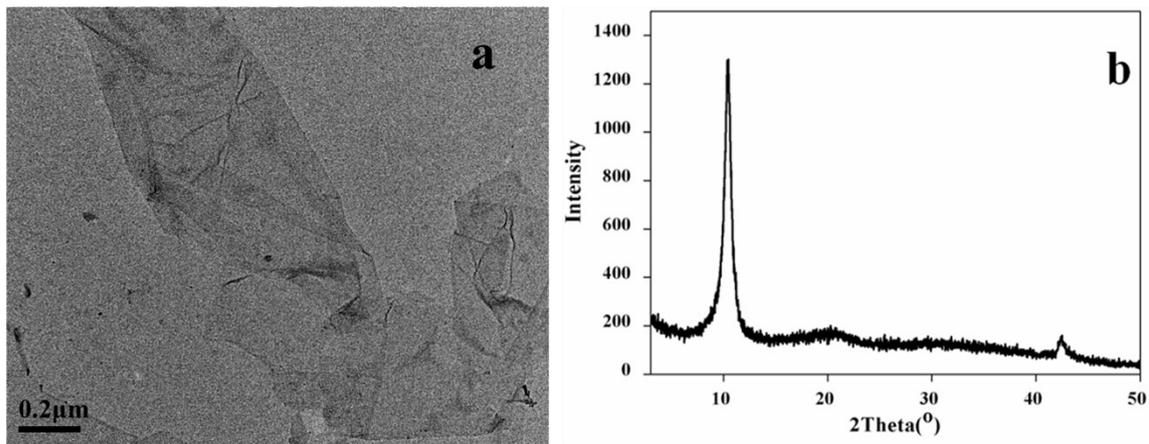
**Graphene oxide (GO), silica nanospheres ( $\text{SiO}_2$ ) and amino-terminated silica nanospheres (KH-550- $\text{SiO}_2$ ).**

Fig. S1a shows the exfoliated GO consists of large thin sheet with the diameters of several micrometers. The GO sheets are nearly transparent and crumpled resembling waves of a silk veil. The XRD patterns of GO is presented in Fig. S1b. Only one obvious diffraction peak at  $2\theta = 10^\circ$  can be observed, which is attributed to 001 peak of GO, and the interlayer spacing is about 0.86 nm.

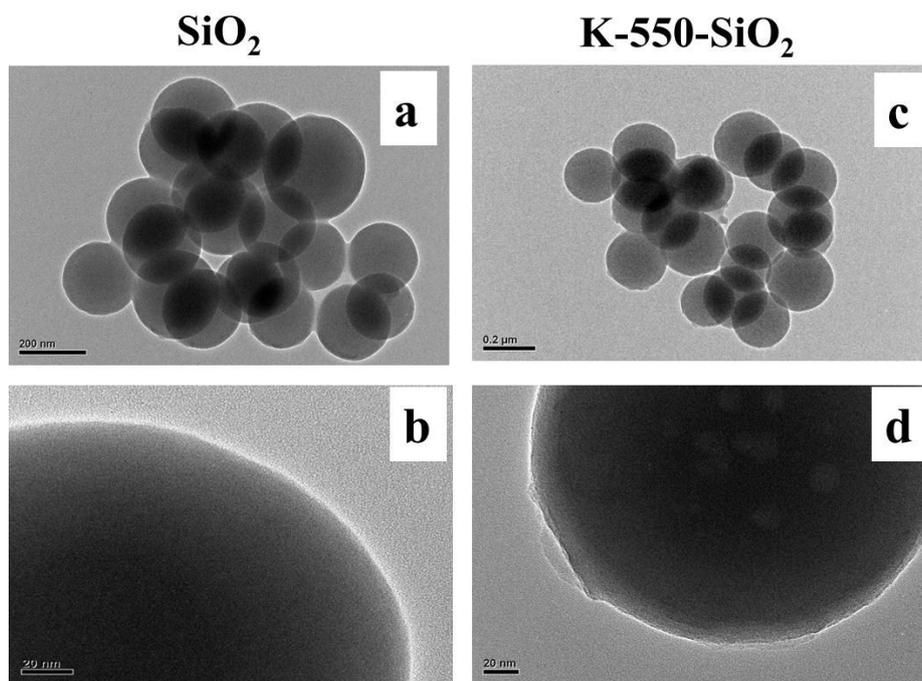
Bare silica nanospheres were synthesized by the base-catalyzed hydrolysis and condensation of TEOS. Then, amino groups were first introduced to the surface of  $\text{SiO}_2$  nanospheres by treatment with KH-550. As a result, silica- $\text{NH}_2$  particles were obtained, which is named as KH-550- $\text{SiO}_2$ . The presence of amino groups on  $\text{SiO}_2$  nanospheres surface rendered the nanoparticle positively charged under acidic solution.<sup>1</sup> Therefore, KH-550- $\text{SiO}_2$  can be used as the positively charged ingredient in LbL assembly. Fig. S2 shows a typical TEM image and the size distribution of the  $\text{SiO}_2$  and KH-550- $\text{SiO}_2$  nanospheres. Noticeably, the average size of silica particles calculated based on TEM images was  $200 \pm 5 \text{ nm}$ . Bare  $\text{SiO}_2$  nanospheres have smooth

surface, but the surface of KH-550-SiO<sub>2</sub> nanospheres becomes rough and coated with a layer of materials which come from the condensation reaction between silica particles surface and KH-550. The FTIR spectra of SiO<sub>2</sub> and KH-550-SiO<sub>2</sub> nanospheres is shown in Fig. S3. The peak at 1100 cm<sup>-1</sup> was caused by Si-O-Si vibrations, whereas the peak at 3400 cm<sup>-1</sup> was caused by the O-H vibration of Si-OH group. The vibration peak at 1630 cm<sup>-1</sup> indicated the presence of physically adsorbed water molecules. Compared with the spectrum of pure SiO<sub>2</sub> nanospheres, KH-550-SiO<sub>2</sub> nanospheres displayed some new peaks (1400, 2935 and 2870 cm<sup>-1</sup>).<sup>2</sup> The bands around 2935 and 2870 cm<sup>-1</sup> are attributed to CH<sub>2</sub> asymmetric and symmetric stretches, respectively, and the absorption at 1400 cm<sup>-1</sup> is the absorption characteristics of amino groups.

Nanoparticles were further analyzed by XPS. XPS spectra of SiO<sub>2</sub> and KH-550-SiO<sub>2</sub> nanospheres are presented in Fig. S4 a. The survey spectrum of the bare SiO<sub>2</sub> nanospheres show the Si2s, Si2p, C1s, and O1s peaks. For silica-NH<sub>2</sub> nanospheres, a new peak at approximately 400 eV appeared, which can be attributed to the binding energy of N1s, and other peaks are similar with that of bare SiO<sub>2</sub> nanospheres. Compared with the survey spectrum of bare SiO<sub>2</sub> nanospheres, a substantial increase was observed in the carbon peak after modification with KH550. The high-resolution C1s spectrum is presented in Fig. S4 b. The major peak at 284.8 eV corresponded to C-C bond, and the peak around 286 eV corresponded to C-N bond.<sup>3</sup>

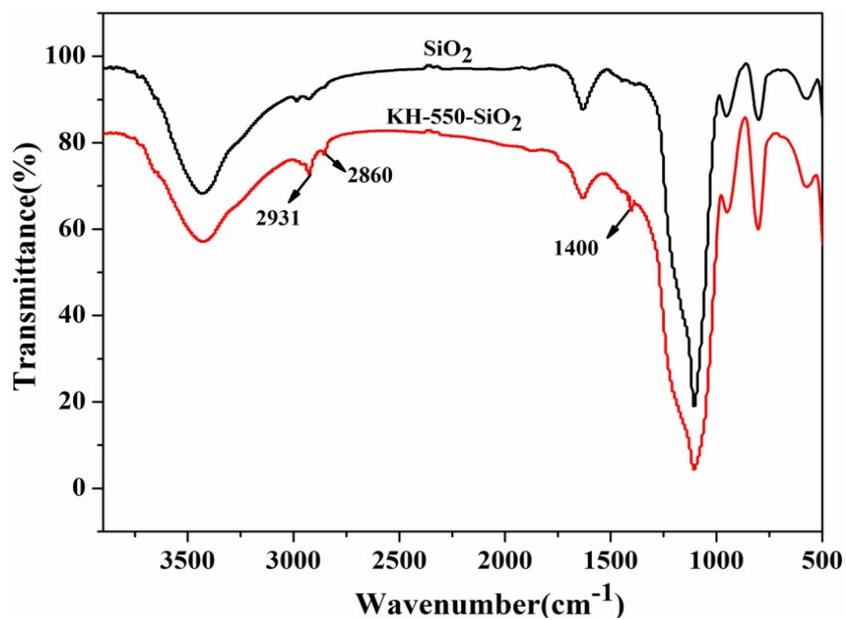


**Fig. S1** TEM images of GO (a) and XRD patterns of GO (b).

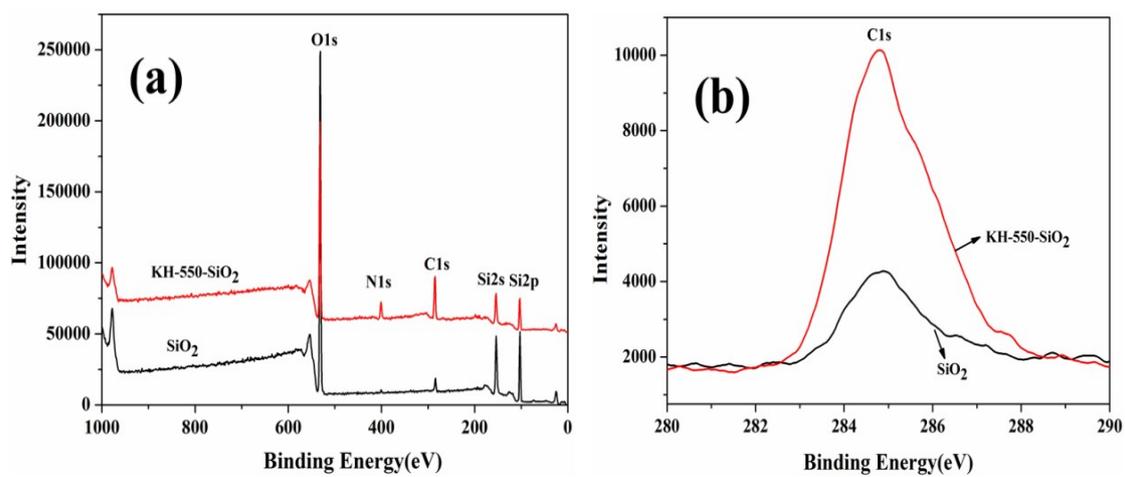


**Fig.S2** TEM image of the SiO<sub>2</sub> nanospheres (a and b) and KH-550-SiO<sub>2</sub> nanospheres

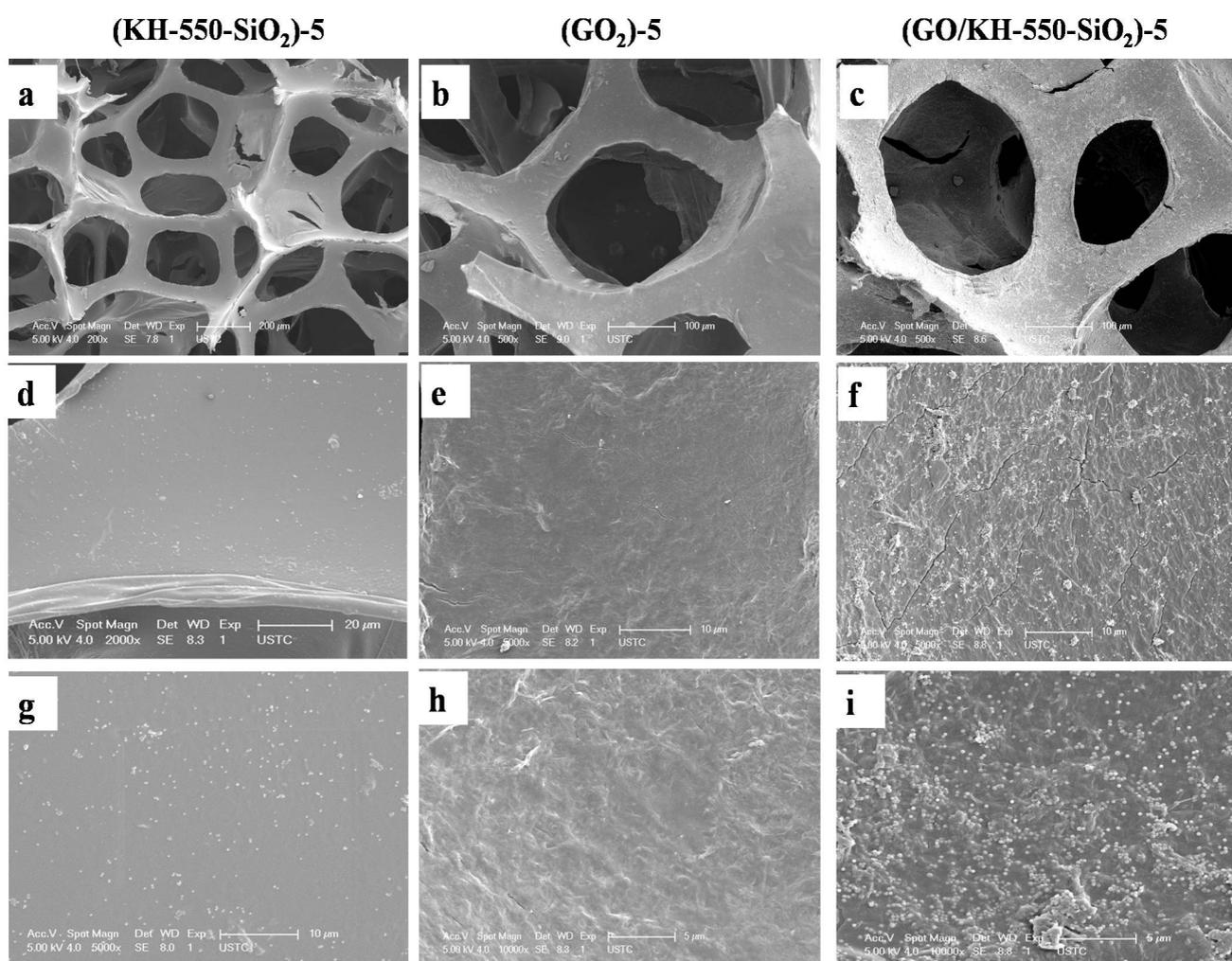
(c and d).



**Fig. S3** FTIR spectra of SiO<sub>2</sub> and KH-550-SiO<sub>2</sub> nanospheres.



**Fig.S4** The XPS spectra of SiO<sub>2</sub> and KH-550-SiO<sub>2</sub> nanospheres (a); C 1s spectrum (b).



**Fig.S5** SEM images of the center of coated foams: (KH-550-SiO<sub>2</sub>)-5 (a, d, and g),

(GO)<sub>2</sub>-5 (b, e, and h) and (GO/KH-550-SiO<sub>2</sub>)-5 (c, f, and i).

## References

- 1 Y. Zhao, Z. Xu, X. Wang and T. Lin, *Langmuir*, 2012, **28**, 6328-6335.
- 2 D. Gao, Z. Zhang, M. Wu, C. Xie, G. Guan and D. Wang, *J. Am. Chem. Soc.*, 2007, **129**, 7859-7866.
- 3 S. S. Balamurugan, E. Soto-Cantu, R. Cueto and P. S. Russo, *Macromolecules*, 2009, **43**, 62-70.