Supporting Information:

An Unconventional Route to Fabricate High Pure α-Al$_2$O$_3$ Nanocrystals with Tunable Surface Chemistry Based on Semi-aromatic Polyamide with Pyridine Rings as Functional Matrix

Zhaopeng Li,[§] Junle Zhang,[§] Peng Fu,* Zhe Cui,* Xinchang Pang,* Minying Liu* and Qingxiang Zhao*

School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

* To whom correspondence should be addressed. [§]These authors contributed equally to this work.

Email: zhaoqingxiang1@126.com, pangxinchang1980@163.com, cuizhezzu@126.com, fupeng@zzu.edu.cn and lmy@zzu.edu.cn.

Experimental Section

1. Materials.

2,5-pyridinedicarboxylic acid and terephthalic acid were purchased from Alfa Chem (China). 1,6-hexanediamine was provided commercially by Shenma Group (China), and purified by vacuum distillation before use. Aluminum nitrate nonahydrate (Al(NO$_3$)$_3$.9H$_2$O, ≥99.99%) was purchased from Sigma-Aldrich and used as starting materials without further purification. Carboxyl-terminated polystyrene (PS-COOH,

Mn=5200 g/mol; PDI=1.08) and carboxyl-terminated poly(ethylene oxide) (PEO-COOH, Mn=5800 g/mol; PDI=1.06) were purchased from Polymer Source Inc. All other reagents were purified by common purification procedures.

2. Characterizations.

^{1}H-NMR spectra were recorded with a Bruker DPX-400 (400 MHz), using deuterated trifluoroacetic acid and $CDCl_3$ as solvents, and tetramethyl-silane (TMS) as an internal reference. The FT-IR measurements were carried out on a NICOLET 460 spectrometer (KBr pellet) in the range of 4000-400 cm^{-1} with the resolution of 4cm^{-1}. The concentration of polyamides in KBr pellet(200mg) was about 1%. Morphology of γ-Al_2O_3/PA6Py nanocomposites, carbon-coated α-Al_2O_3 nanocrystals and core@shell α-Al_2O_3@polymer colloidal nanocrystals were characterized by transmission electron microscope (JEOL 1200EX TEM; operated at 80 kV). The preparation of TEM samples: (1) γ-Al_2O_3/PA6Py nanocomposites was firstly hot-pressed into the bulk, and then samples were prepared for TEM by using microtome (ULTRACUT E, Reichert-Jung) resulting in samples with below 100 nm thickness; (2) TEM samples of carbon-coated α-Al_2O_3 nanocrystals were prepared by applying a drop of carbon-coated α-Al_2O_3 nanocrystals ethanol solution (ultrasonically dispersed into ethanol firstly) onto a carbon coated copper TEM grid (300 mesh) and allowing ethanol to evaporate at room temperature; (3) TEM samples of core@shell α-Al_2O_3@polymer colloidal nanocrystals were prepared by applying a drop of α-Al_2O_3@polymer colloidal nanocrystals toluene (PS) or dichloromethane (PEO) solution (~5 μL at c=1 mg/mL) onto a carbon coated copper TEM grid (300 mesh) and allowing solvent to

evaporate at room temperature. In addition, for the TEM characterization of polymers as ligands coating on the surface of α-Al$_2$O$_3$ nanocrystals, the polymeric ligands (PS or PEO) were stained with ruthenium tetraoxide (RuO4) by exposing to the TEM grids to ruthenium tetraoxide (RuO$_4$) which the PS or PEO phase as shell was preferentially stained. The crystalline structures of samples were measured by X-ray diffraction (XRD; SCINTAG XDS-2000, Cu Kα radiation). The energy dispersive spectroscopy (EDS) microanalysis of samples was conducted by field emission scanning electron microscopy (FE-SEM; FEI Quanta 250). The weight fraction of the polymer phase in core@shell α-Al$_2$O$_3$@polymer colloidal nanocrystals was determined by thermogravimetric analysis (TGA; TA Instrument TGA Q 50).

3. Synthesis of γ-Al$_2$O$_3$/PA6Py nanocomposites

γ-Al$_2$O$_3$/PA6Py nanocomposites were synthesized through a three-step procedure (**Scheme S1**): salt formation, prepolymerization and solid-state polymerization.

2,5-pyridinedicarboxylic acid (5.01g, 30mmol) was dissolved in distilled water (30mL) at 50°C. Then the solution was slowly added into 30 ml of distilled water mixture of 1,6-hexanediamine (3.48g, 30mmol) with vigorous stirring and then stirred for 2h at 50°C. Finally, a slight excess of 1,6-hexanediamine (0.03g, 0.3mmol) was added into the solution with continuous stirring for 1h at 50°C. The white 1,6-hexanediamine -2,5-pyridinedicarboxylic acid salt (nylon 6Py salt) precipitated from the solution.

After filtered over a Buchner funnel and dried in a vacuum desiccator for 8h, the white nylon 6Py salt, aluminum nitrate nonahydrate (Al(NO$_3$)$_3$.9H$_2$O) and distilled

water (20 mL) were added into an autoclave (the molar ratio of $Al(NO_3)_3$ as precursors to pyridine ring= 1:1). The reaction was then conducted at 200°C with 1.5 MPa pressure under the atmosphere of carbon dioxide. After 1h, the pressure was gradually decreased to normal pressure in 2h by deflating and the reaction temperature was increased to 220°C. After another 1 h reaction, the prepolymer composite of PA6Py and Al_2O_3 was obtained.

The prepolymer composite of PA6Py and Al_2O_3 was ground into particles with the diameter of 0.1-2 mm and dried at 90°C in a vacuum oven for 4 h. Then the prepolymer composites of PA6Py and Al_2O_3 were added into a solid-state polymerization kettle, the reaction was carried out at 210°C for 8h under a vacuum of 10Pa. Finally, the kettle was cooled to room temperature and yellow γ-Al_2O_3/PA6Py nanocomposites were obtained.

4. Synthesis of carbon-coated α-Al_2O_3 nanocrystals

The γ-Al_2O_3 nanoparticles embedded into semi-aromatic polyamide (PA6Py) with pyridine rings as functional matrix can be transferred into α-Al_2O_3 nanocrystals under calcinations at 1300°C in Ar (2h), at the same time, and the outer semi-aromatic polyamide capping on the surface of γ-Al_2O_3 nanoparticles was calcinated into carbon as shell. During the calcination, carbon coating as shell on the surface of α-Al_2O_3 nanocrystals can prevent aggregation of α-Al_2O_3 nanoparticles.

5. Removal of carbon coating on the surface of α-Al_2O_3 nanocrystals

After core@shell α-Al_2O_3@carbon nanocrystals were obtained, the carbon shell of these nanoparticles can be firstly removed by calcinations at 500°C in air (5h). Owing

to the thermodynamically stable crystalline structures, α-Al$_2$O$_3$ nanocrystals can keep their shapes after calcination at 500 ^{o}C in air. After the removal of carbon coating as shell, the color of samples was changed from black to gray.

6. Preparation of core@shell α-Al$_2$O$_3$@polymer colloidal nanocrystals

After the carbon coating on the surface of α-Al$_2$O$_3$ nanocrystals was removed by calcinations in air, α-Al$_2$O$_3$ nanocrystals (50mg) were dispersed into 50 mL of toluene by ultrasonic equipments for 2h, and then target end-carboxyl polymers as ligands (e.g., PS-COOH, 200mg) were added into this toluene solution for other 2h ultrasonic dispersion. During ultrasonic dispersion, functionalized polymers as ligands can absorb onto the surface of α-Al$_2$O$_3$ nanocrystals, and then target α-Al$_2$O$_3$ nanocrystals capped with PS as ligands (e.g., α-Al$_2$O$_3$@PS nanocrystals) can be obtained. The excess polymeric ligands can be removed by centrifuging (12000 rpm, 20min). Due to the PS ligands on the surface of α-Al$_2$O$_3$ nanocrystals, they can be dispersed into target solvent (e.g., toluene) very well. When polymeric ligands were changed from PS-COOH to PEO-COOH, the dichloromethane was used as solvent, and the other conditions were kept fixed.
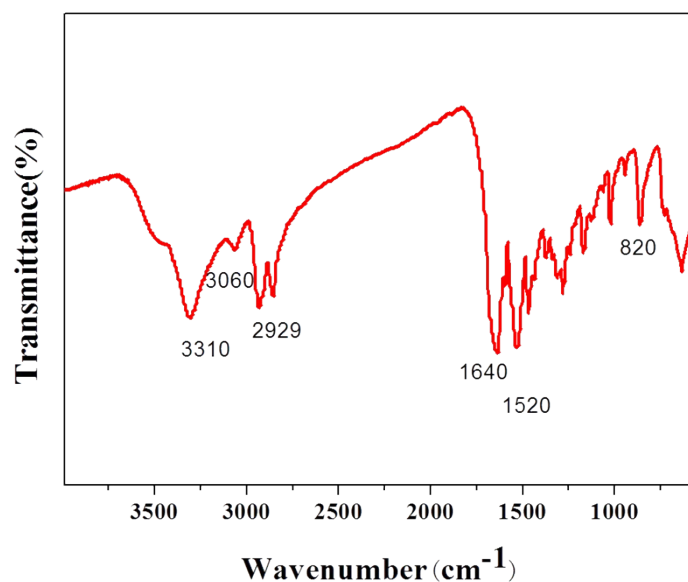

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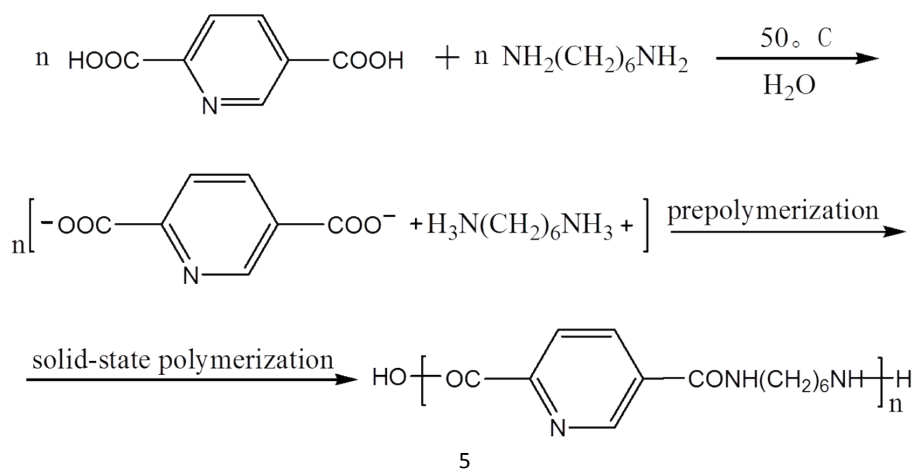
Scheme S1. The synthetic route of PA6Py.

Fig. S1. FT-IR spectrum of γ-Al$_2$O$_3$/PA6Py nanocomposites.

FT-IR spectrum of γ-Al$_2$O$_3$/PA6Py nanocomposites was shown in **Fig. S1**. All the characteristic peaks of amide groups and methylene segments of PA6Py are listed as follows: 1640 cm^{-1}(amide I, C=O stretching vibration), 1520 cm^{-1}(amide II, C-N stretching and CO-N-H bending vibration), 2929 cm^{-1}(N-H inplane bending vibration and CH$_2$ vibration), 3310 cm^{-1}(hydrogen-bonded and N-H stretching vibration), 3060 cm^{-1}(N-H inplane bending), 820 cm^{-1}(CH$_2$ wagging).
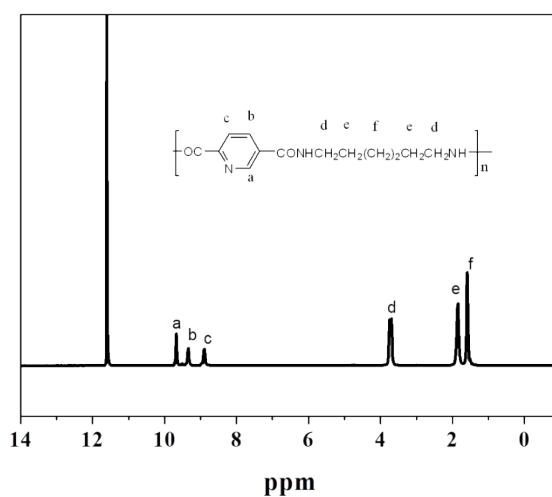
Fig. S2. ^{1}H-NMR spectrum of γ-Al$_2$O$_3$/PA6Py nanocomposites (deuterated trifluoroacetic acid as solvent).

Fig. S2 presents the ^{1}H-NMR spectrum of γ-Al$_2$O$_3$/PA6Py nanocomposites in deuterated trifluoroacetic acid (TFA). For the sequence analysis, the chemical shifts of the protons with different chemical environments were monitored. ^{1}H-NMR spectrum of PA6Py from the unsymmetrical diacid showed three proton peaks (a-c) at 9.66 (1H), 9.31 (1H) and 8.89ppm (1H), the chemical shift at 3.69ppm (4H) originates from the protons at the position (d) while that at 1.82ppm (4H) comes from the protons at the position (e). The peak at 1.57ppm (4H) belongs to the other protons of

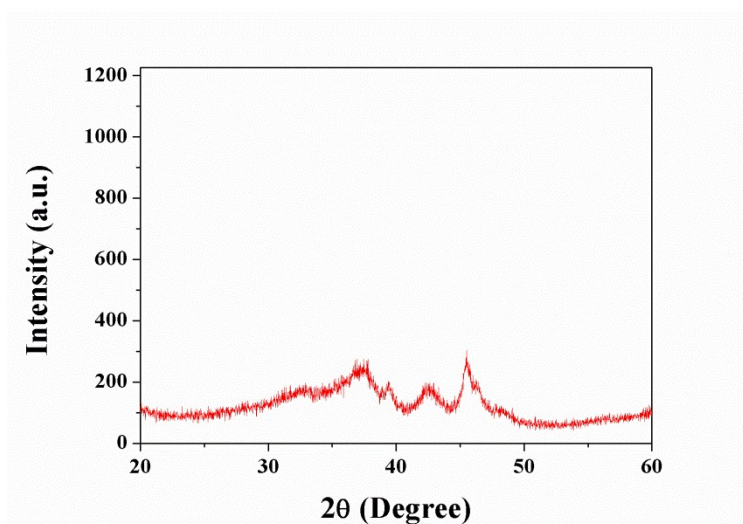the aliphatic chains (f). The peak at 12.0ppm is assigned to TFA.

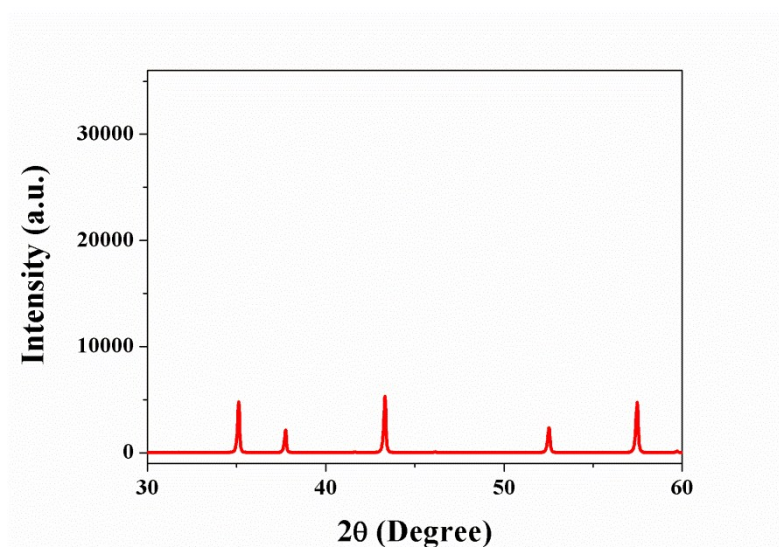**Fig. S3.** XRD pattern of γ-Al$_2$O$_3$/PA6Py nanocomposites.[1]

Fig. S4. XRD pattern of carbon-coated α-Al$_2$O$_3$ nanocrystals (JCPDS file no. 42-1468).[2]

Element	Weight%	Atomic%
C K	43.51	55.70
O K	30.97	29.76
Al K	25.52	14.54
Totals	100.00	
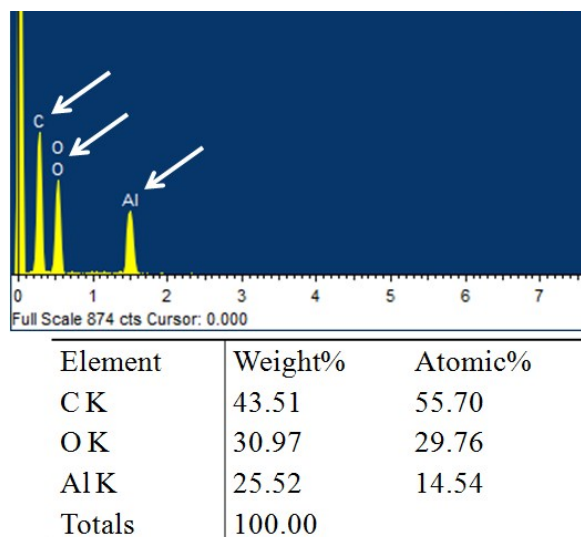
Fig. S5. EDS spectrum of carbon-coated α-Al_2O_3 nanocrystals.

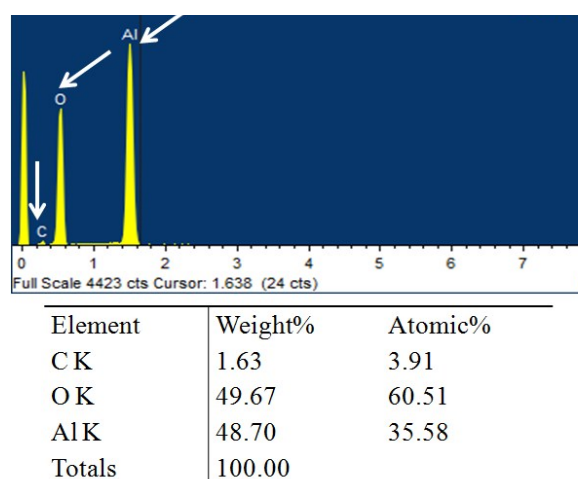| Element	Weight%	Atomic%
C K	1.63	3.91
O K	49.67	60.51
Al K	48.70	35.58
Totals	100.00	

Fig. S6. EDS spectrum of α-Al_2O_3 nanocrystals after the removal of the carbon coating by the calcination (500 ^{o}C) in air.
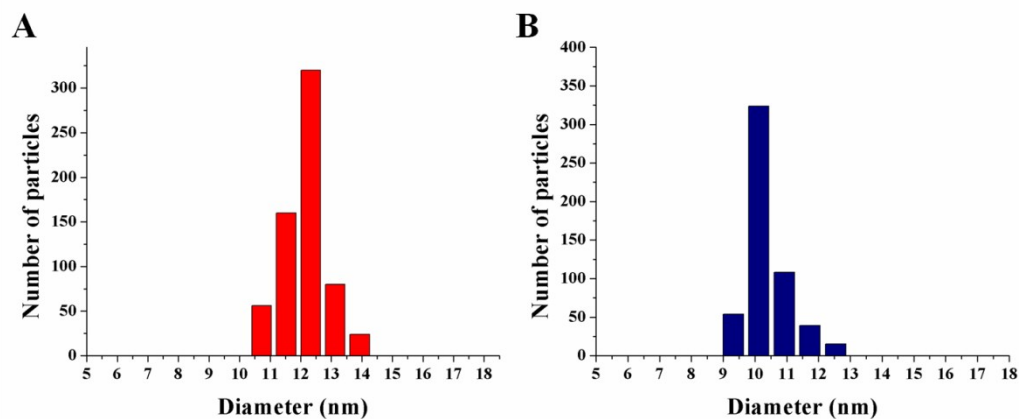
Fig. S7. The size distributions of the α-Al$_2$O$_3$ colloidal nanocrystals with and without the functional PA6Py polymeric matrix based on TEM images (Fig. 1 and Fig. 3). (A) γ-Al$_2$O$_3$ nanoparticles embedded into PA6Py polymeric matrix. (B) Core@shell α-Al$_2$O$_3$@PS colloidal nanocrystals.
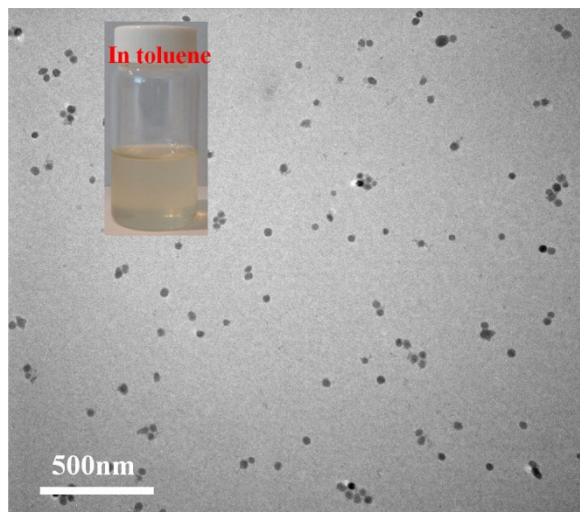
Fig. S8. Representative TEM image of α-Al$_2$O$_3$ nanocrystals capped with PS as ligands with the average diameter of 39.1±3.2nm when the molar ratio of precursors to pyridine rings was increased to 10:1; Inset: digital image of toluene solution of α-Al$_2$O$_3$ nanocrystals capped with PS as ligands with the average diameter of 39.1±3.2nm.

References and notes:

1.   C. Sadik, I.-E. El Amrani and A. Albizane, *J. Asian Ceram. Soc.*, 2014, **2**, 83-

     96.

2.   T. Zaki, K. I. Kabel and H. Hassan, *Ceram. Int.*, 2012, **38**, 2021-2026.