Electronic Supplementary information-ESI

One-potLayerCasting-guidedSynthesisofNanosphericalAluminosilica@Organosilica@AluminaCoreShellsWrappingColorantDendritesforEnvironmental Application

Experimental

Synthesis of dichloro 1,5-diphenyl-3-thiocarbazone colorant (L)

The colorant molecule of dichloro 1,5-diphenyl-3-thiocarbazone (L) was synthesized by dissolving 2 M 4-chlorophenylhydrazine hydrochloride 97% (3 g, Aldrich) in 30 mL 0.15% NaOH. Approximately 20 mL ethanol and 0.77 g (0.1 M) carbon disulfide were then added. The mixture was refluxed for 6 hours, and ethanol (100 mL) was added upon cooling. The resulting product was obtained in acidic solution with the addition of 0.1 M hydrochloric acid and had a pH of 5 (Scheme 3A, B). The product was thoroughly washed with deionized water, centrifuged, filtered, and then dried (Scheme 3).

The pureness of the (L) dye product was determined by CHNS elemental analyses as described below: C, 51.73%; H, 3.76%; N, 16.29%; S, 9.22%, each of which is consistent with the molecular formula $C_{15}H_{12}N_4Cl_2S$ (C, 52.32%; H, 3.48%; N, 16.28%; S, 9.3%). The product was characterized by ¹H NMR and ¹³C NMR spectroscopy. The ¹H NMR spectra exhibited the following resonances: δ 11.0 (2H, s, carboxylic acid), 7.81 (2H, m, CH Ph), 6.9 (H, s, Ph), 6.84 (2H, m, CH Ph), 5.9 (H, m, CH Ph), 2.1 (2H, m, CH Ph), where Ph represents a phenyl group. The ¹³C NMR spectra exhibited the following resonances: δ 154 (C–SH), 153.1 (Ph–N=N, C), 148.2 (Ph–NH–N, C), 131.1 (2Ph,CH), 130.3 (2Ph, CH), 128.7 (2Ph, CH), 130.2 (Ph, C), 120.2 (Ph, C), 115.2 (2Ph, CH), 132.4 (2Ph, CH), 132.1 (2Ph,CH), 121.4 (2Ph, CH), 161.1 (2Ph, C–OH). Furthermore, the UV–vis spectrum of the dye product indicated an absorbance band at $\lambda_{max} = 410$ nm.

Material characterizations

Field-emission scanning electron microscopy (SEM) images were acquired (Hitachi S-4300). Before inserting to the chamber, the samples were placed securely onto the SEM stage using carbon tape, and the Pt films were deposited on sample substrates at room temperature by using an ion-sputter (Hitachi E-1030); the distance between the target and the substrate was 5.0 cm.

High resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and dispersive X-ray analysis for elemental mapping (STEM-EDS) were performed at 200 kV electron microscope (JEOL 2000 EX II) that have a point-to-point resolution of 0.21 nm and a spherical aberration of 0.7 nm. The TEM images were recorded by a CCD camera.

In the performance of small angle X-ray scattering (SAXS) experiments at room temperature, a two-dimensional (2D) confocal mirror (Rigaku/SAXS NANO-Viewer) and a pinhole collimator were used to get a focused high-flux/high transmission as well as monochromatic X-ray beam of Mo-K α radiation ($\lambda = 0.07$ nm).

The surface texture properties of the aluminosilica@organosilica@alumina and VTA core shells, containing the specific surface area and the pore structure, were detected by N_2 adsorption-desorption isotherms using a BELSORP-mini II (MicrotracBEL Corp. Japan) at 77 K. With the Barrett-Joyner-Halenda method, the pore size distribution was determined from the adsorption isotherms, whereas specific surface area (S_{BET}) was calculated based on multi-point adsorption data from a linear segment of the N_2 adsorption isotherms using the Brunauer-Emmett-Teller (BET) theory. Before analyzing the N_2 isothermal, all samples were pre-treated at 300 °C for 8 hours under vacuum condition until the pressure had equilibrated to 10⁻³ Torr.

The electronic structure models of the [M-L]ⁿ⁺ complex formations were carried out with quantum chemical calculation at the DFT level. The geometrical configuration was optimized by using the B3LYP functional and the LANL2DZ, implemented in the Gaussian 03 software package, which was developed by Gaussian Inc. (Scheme 2).

Thermogravimetric analysis and differential thermal analysis (TGA and DTA, respectively) were measured by simultaneous DTA-TG Apparatus TG-60 (SHIMADZU Co., Japan).

The metal ion concentration was determined by a Perkin Elmer, Elan-6000, Inductively Coupled Plasma Mass spectrometry (ICP-MS). The reflectance spectra of the solid VTA core shells were recorded by UV-Visible spectrometer 3150 (SHIMADZU Co., Japan).

²⁹Si, ²⁷Al and ¹³C MAS NMR (magic-angle spinning nuclea rmagnetic resonance) spectroscopy were measured by a Bruker D8 Advance (XRD) or AMX-500 spectrometer. The samples were placed in a zirconia sample tube of 7mm diameter, and ²⁹Si, ²⁷Al and ¹³C MAS NMR spectra were taken at 125.78 MHz with a 90° pulse length of 4.7 μs. For all samples, the repetition delay was 180, 64 and 12 s with a rotor spinning at 4, 4 and 9 kHz for ²⁹Si, ²⁷Al and ¹³C MAS NMR. The chemical shift scale was given in relation to the ²⁹Si, ²⁷Al and ¹³C signals of neat tetramethylsilane (TMS), Al(NO₃)₃ and CDCl₃, respectively.

Using Meiji Techno TC TC 5300/5400 Inverted Phase Contrast Laboratory Microscope, phasecontrast microscopic images (100× magnification) were taken. The microscopic optics include plan phase objectives (PH10x and PH20x) mounted in a quintuple nosepiece and combine with two SWH10x eyepieces for magnification powers of 100x and 200x. The plain stage measures 180mm (X) x 245mm (Y), and includes a replaceable glass insert with 45mm opening. Images were recorded by using a digital camera (SHIMADZU Co., Japan) and processed by Motic Images Plus 2.0 software. The TG-DTA analyses (Fig. S1) showed evidence of the the incorporation of organic moieties into the nanospherical alminosilica@organosilica@Al₂O₃@dendritic L core-multi shells with VAT design. A 3.8 wt.% weight loss was accompanied by DTA endothermic peak around 50-150 °C, attributing to the H₂O/ethanol solvent contents into VTA. The two exothermic DTA peaks around 200–550 °C indicates the weight loss of 18.6 % of casting organic layers by APTMS and dendritic L moieties. This finding in consistent with the STEM-EDS- mapping analyses (Figure 2).



Figure S1 TG and DTA analyses of mesoporous nanospherical alminosilica@organosilica@Al₂O₃@dendritic L core-multi shells with VAT design synthesized by layer casting–guided synthesis route.

pH-controlled sensing process and metal ion species

The composition species of Hg(II) chloride in dilute solution are mainly Hg²⁺, HgCl₃- , HgCl₂ , HgOH⁺, and Hg(OH)₃⁻ that can be formed according to the pH values. The high dose accumulation of Cl⁻ and OH⁻ may affect the species of Hg(II) in Hg(II)-Cl⁻-OH⁻-H2O system. In the basic condition of pH 8.0-9.5, Hg(II) precipitates as Hg(OH)₂ which can be re-dissolved as Hg(OH)₃⁻ at pH >10, particularly at low concentration of Hg(II) on << 1ppm.^{38,39} The main species of Bi(III) chloride that exist in dilute solution are Bi³⁺, BiCl₂⁺ , BiCl₃, BiCl₄⁻, Bi(OH)₄⁻ at different pH values of 2-12.³⁸ Thus, the BiCl₂⁺ species are mainly existed at pH << 8. Furthermore, the ZnCl₂ is very soluble in water, forming tetrahedral chloro-aqua complexes of ZnCl_xH₂O_(4-x) species. Depending on the pH solution, the main species of Zn²⁺ ion in the presence of Cl⁻ ions and OH⁻ were mainly ZnCl⁺, ZnCl₂, ZnCl₃⁻, Zn(OH)₂Cl₂⁻, Zn(OH)⁻, ZnOHCl, ZnOHCl₃⁻², Zn(OH)₂Cl₂⁻², Zn(OH)



Figure S2 Study the pH-dependent response (A-C) as a function of target ion-concentrations of [0.5 and 2 ppm] Bi^{3+} , Zn^{2+} , and Hg^{2+} ion . (A-C, insets) Reflectance signaling responses (%) as function of pH value that obtained at $\lambda_{max} = 502$, 555, and 4520 and at [0.5 and 2 ppm] Bi^{3+} , Zn^{2+} , and Hg^{2+} ion concentration, a response time of 2.0 min at 25 °C with the VTA-1, VTA-2, and VTA-3 sensing/capture assays, respectively. The pH-dependent profiles indicated the excellent Bi^{3+} , Zn^{2+} , and Hg^{2+} ion sensing/removal/recovery of VTA-1, VTA-2, and VTA-3 workability at specific pH values of 4.5, 9and 10.5, respectively. Note: R and Ro represent the signaling reflectance spectra of the VTA-1, VTA-2, and VTA-3 at λ max 502, 555, and 520 nm, with (R) and without (R_o) the addition of target Bi³⁺, Zn²⁺, and Hg²⁺ ion sto VTA-1, VTA-2, and VTA-3, respectively.



Figure S3 (A, B) Calibration plots of the reflectance spectra of VTA-1, VTA-2, and VTA-3 for Bi³⁺, Zn²⁺, and Hg²⁺ ion concentrations at λ max 502, 555, and 520 nm, contact time of 2 min, and temperature = 25 °C based on the relationship between R–Ro as a function of target ion concentrations. The insets in the graphs show a linear fit line in the linear concentration range before saturating step in the calibration curve. The solid and dotted lines represent the calibration plots of the target ions in the absence and presence of active interfering species (such as Pb²⁺, Co²⁺, Cu²⁺, Ni²⁺, Fe³⁺, Sb³⁺, Pd²⁺, Mn²⁺, Al³⁺, Mo³⁺, Cr⁶⁺, Sn²⁺, Cd²⁺, and Se⁴⁺) and under the same sensing/removal conditions. Note: R and Ro represent the signaling reflectance spectra of the VTA-2, and VTA-3, at λ max 555, and 520 nm, with (R) and without (Ro) the addition of target Bi³⁺, Zn²⁺, and Hg²⁺ ions to VTA-1, VTA-2, and VTA-3, respectively. (B) Adsorption isotherm for the uptake of Bi³⁺, Zn²⁺, and Hg²⁺ ion concentrations by VTA-1, VTA-2, and VTA-3 for at pH 4.5, 9, and 10.5, volume 20 ml, contact time ≈ 2 min, and at a temperature of 25 °C (A-C). Insets, the linear form of the Langmuir isotherms for the adsorption of Bi³⁺, Zn²⁺, and Hg²⁺ ions into VTA-1, VTA-2, and VTA-1, VTA-2, and VTA-3 at optimized removal/capture conditions. Note: the q_e and C_e were determined by ICP-MS analysis.



Figure S4 Selectivity studies of the VTA-2, and VTA-3 for target ions (T) of Zn²⁺, and Hg²⁺ ion concentrations at λ max 555, and 520 nm, contact time of 2 min, and temperature = 25 °C by addition of a group of interfered ion- sensing, and -removal systems (i.e. VTA +T + G), respectively. (A,B) Effect of addition of multi-interfered species system of feed solution containing a group of interfered cations (i.e., G1 to G5) with tolerance concentrations of 1-50 times greater than those of the additive [2ppm] Zn²⁺, and Hg²⁺ target ions on the color response and signaling reflectance spectra of VTA-2 and VTA-3 at λ_{max} 555 and 520 nm and at pH 9, 10.5. Notably, the interfered G1: Na⁺, Li⁺, K⁺, and Ca²⁺; G2: Sr²⁺, Cr⁶⁺, Al³⁺, and Mg²⁺, and Ni²⁺; G3: Mo³⁺. Sn²⁺, Sb³⁺, and Mn²⁺; G4: V⁵⁺, Se⁴⁺, Cd²⁺, Ti⁴⁺; G5: Fe³⁺, Pb²⁺, Co²⁺, and Cu²⁺. (B) Study the effect of the addition of each interfered ions (binary system) on the reflectance response of VTA-2 and VTA-3 at λ_{max} 555 and 520 nm and at pH 9, and 10.5, respectively.



Figure S5 Reusability profiles of VTA-1, VTA-2, and VTA-3, in terms of spectral changes (R) signifying the recognition and removal of 2 ppm of Bi^{3+} , Zn^{2+} , and Hg^{2+} ions after six regeneration/reuse cycles at pH values of 4.5, 9, and 10.5 (A–C), respectively.