Effect of acidic aqueous alcohol solution on template sol-gel synthesis of phosphorescent hexagonal mesoporous silica film nanocomposite

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ABSTRACT

Here novel mesoporous silica film nanocomposite with a hexagonal structure is successfully synthesized by using phosphorescent columnar assembly of a trinuclear gold(I) pyrazolate complex bearing amphiphilic side chains $[Au_3Pz_3]$, formed via a weak Au^I-Au^I metallophilic interaction, as a functional template in the sol-gel synthesis. By controlling the molar ratios of alcohol to acid in an acidic aqueous alcohol solution, the sol-gel synthesis of columnar assembled $[Au_3Pz_3]$ with a silica source can provide highly ordered hexagonal mesoporous silica film composite $[Au_3Pz_3]/silica_{hex}$ consisting one-dimensional molecular assembly in the nanoscopic channels. The as-fabricated silica film nanocomposite $[Au_3Pz_3]/silica_{hex}$ with red emission have phosphorescent properties with luminescence emission centered at 693 nm ($\lambda_{ext} = 276$ nm; Stokes shift, $\Delta\lambda = 417$ nm) and lifetime at 7.8 μs ($\lambda_{ext} = 266$ nm, $\lambda_{em} = 690$ nm).

| Hexagonal | Mesoporous | Nanocomposites | Sol-gel | Template |

1. INTRODUCTION

Nanocomposite-based on organosiloxane, clay and mesoporous silica materials have been widely used in many fields such as optics, electronics, energy, membranes, catalysts, sensors, and medicine [1]. In particular, immobilization of one-dimensional (1D) nanostructured organic functional groups in the nanoscopic channels of inorganic mesoporous silica with a hexagonal structure have attracted much attention for developing anisotropic optoelectronic materials [2]. Generally, mesoporous silica materials can be functionalized with organosilica precursors by post-synthetic grafting and one-pot sol-gel synthesis methods [3]. However, all of these approaches cannot ensure dense filling of the functional groups inside the silicate nanochannels. In 2001, Aida *et al.* [4] and Brinker *et al.* [5] have independently reported a universal strategy for dense filling of the functional groups by using functional amphiphiles of diacetylenic surfactant monomers as a template in the one-pot sol-gel synthesis. The functional templates were not only ordinary polymerizable monomer amphiphiles [4-8], but also 1D columnar assembly of disk-shaped amphiphilic molecules such as triphenylene [9], metallophtalocyanine [10], hexaperi-benzocoronene [11], and Pt(II)bipyridine complexes [12].

We have recently demonstrated that mesoporous silica film nanocomposite with a hexagonal structure $[Au_3Pz_3]/silica_{hex}$ can be successfully fabricated in the colorless transparent thin film by the template sol-gel synthesis using columnar assembly of $[Au_3Pz_3]$ [13]. The silicate nanochannels contains only one columnar assembly with a chair-like coordination geometry of polymeric $[Au_3Pz_3]$ formed by a weak Au^I-Au^I metallophilic interaction. When the spin-coated film was allowed to stand at 20 ℃ for 5 h after stepwise heating to 140 ℃, the fabricated 1D columnar assemblies in the nanochannels with an interpore distance of 4.1 nm can perfectly self-repair from heat-induced structural damage due to a nanoscopic template effect [13]. More recently, we have found that the spin-coated film of $[Au_3Pz_3]/silica_{hex}$ showed heating effect on self-repairing capability, where the autonomous recovery was perfectly achieved depending on the way of heating; when the hexagonal silica film nanocomposite were heated stepwise from 20 to 140 ℃ in 45 min or directly to 160 ℃ in 11 min [14]. Here we report the systematic studies on the sol-gel synthesis for the fabrication of highly ordered mesoporous silica film nanocomposites with a hexagonal geometry by controlling molar ratios of an acidic aqueous alcohol solution in the self-assembly of $[Au_3Pz_3]$ with a silica source (Fig. 1).

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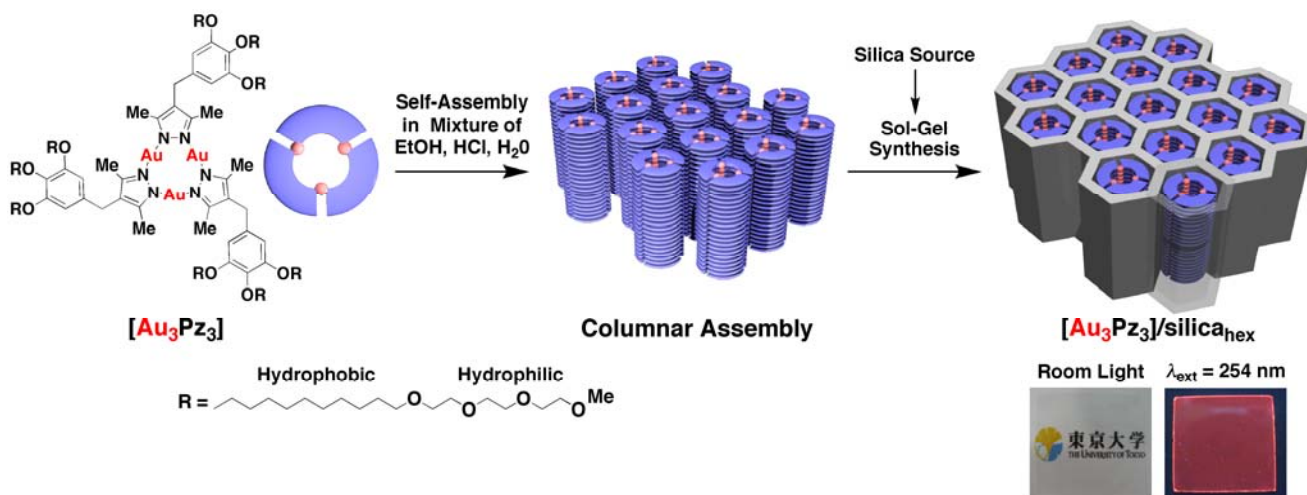*E-mail addresses: hendrik@ibnusina.utm.my (Hendrik O. Lintang)*

Figure 1: Schematic representation of fabrication of mesoporous silica film nanocomposite [Au$_3$Pz$_3$]/silica$_{hex}$ with a hexagonal geometry, templated by columnar assembly of [Au$_3$Pz$_3$] via sol-gel synthesis. Photographs were taken at room temperature under room light and on exposure to ultraviolet light at 254 nm.

2. EXPERIMENTAL

2.1 Instruments

^{1}H and ^{13}C NMR spectra (500 and 125 MHz) were recorded in CDCl$_3$ on a JEOL model GSX-500 spectrometer, where the chemical shifts were determined with respect to non-deuterated residue CDCl$_3$ at δ = 7.24 and 77.0 ppm for ^{1}H and ^{13}C NMR spectroscopy, respectively. Matrix-assisted laser desorption/ionization time-of-flight mass-spectrometry (MALDI-TOF-MS) was performed with dithranol as a matrix on a PerSeptive Biosystems model Voyager-DE spectrometer. Preparative size-exclusion chromatography (SEC) was performed at room temperature on a Japan Analytical Industry model LC-908 recycling preparative HPLC, equipped with a variable-wavelength UV-vis detector, using CHCl$_3$ as an eluent at a flow rate of 3.5 mL min^{-1}. Elemental analysis was performed on a Yanaco model CHN CORDER MT-6. Infrared spectra were recorded on a JASCO FTIR-610 spectrophotometer.

The resulting transparent films were characterized by X-ray diffraction (XRD) at room temperature at Rigaku model RINT 2400 diffractometer with CuKα radiation and a step size 0.02º at scan speed of 2º min^{-1}. X-ray photoelectron spectroscopy (XPS) were conducted on a JEOL JPS-9000MC spectrometer with MgKα radiation (1253.6 eV) and the XPS peaks are internally referenced to the binding energy of C 1s peak at 284.5 ± 0.1 eV. Emission spectra were recorded on JASCO model FP-6500 spectrometer equipped with a thin film sample folder. Transient emission spectra were measured by pumping the samples with the fourth harmonics of a light from a Nd:YAG laser (HOYA Continuum Satellite I, pulse duration of 10 ns and repetition of 10 Hz), and monitored with a HAMAMATSU Photonics model R3788 photomultiplier lifetime.

2.2 Synthesis of [Au$_3$Pz$_3$]

Complex [Au$_3$Pz$_3$] was synthesized according to the synthetic protocol reported previously [13]. Typically, to a dry THF (20 mL) solution of amphiphilic pyrazole ligand (400 mg, 0.35 mmol) was added [Au(SMe$_2$)]Cl (103.2 mg, 0.35 mmol), and the resulting mixture was stirred at room temperature for 5 min under Ar (Scheme 1). To this solution was dropwise added a dry MeOH solution of KOH
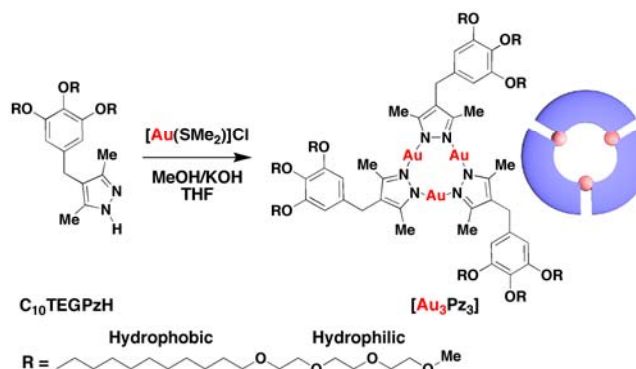
Scheme 1: Synthesis and molecular structure of [Au$_3$Pz$_3$].

(0.26 M, 1.4 mL) using a Schlenk technique, and the resulting mixture was stirred for 12 h under Ar at room temperature in the dark condition. The reaction mixture was filtered off from insoluble substances, and the filtrate was evaporated to dryness under reduce pressure at room temperature. The residue was chromatographed on silica gel with AcOEt/MeOH (10:1) as an eluent, where the first fraction was then collected and evaporated to dryness. The residue was subjected to preparative size exclusion chromatography (SEC) with CHCl$_3$ as an eluent, where the

first fraction was collected, evaporated and freeze-dried from benzene, to give [Au$_3$Pz$_3$] as pale-yellow sticky solid in 70% yield (325.9 mg) [13]; ^{1}H NMR (500 MHz, CDCl$_3$, 20 °C): δ 6.25 (s, 6H, ArH), 3.86 (t, 18H, ArOCH$_2$), 3.64 (s, 6H, ArCH$_2$C), 3.63–3.52 (m, 108H, OCH$_2$CH$_2$), 3.42 (t, 18H, CH$_2$O), 3.36 (s, 27H, OCH$_3$), 2.14 (s, 18H, py-CH$_3$), 1.72–1.67 (m, 18H, ArOCH$_2$CH$_2$), 1.55–1.53 (m, 18H, CH$_2$CH$_2$O), 1.43–1.37 (m, 18H, ArOCH$_2$CH$_2$CH$_2$), 1.26 ppm (overlapped, 90H, (CH$_2$)$_5$); ^{13}C NMR (125 MHz, CDCl$_3$, 20 °C): δ 152.9, 146.3, 136.3, 135.9, 113.7, 106.6, 73.3, 71.8, 71.4, 70.5–70.4, 69.9, 69.0, 58.9, 30.2, 29.6–29.5, 29.5–29.4, 29.4, 26.0–26.0, 12.2 ppm; IR (KBr): v = 3435 m (O–H), 2924 s (C–H), 2855 s (C–H), 1587 s (C=C), 1503 s (N=C), 1466 s, 1436 s, 1374 m, 1351 m, 1332 m, 1301 m, 1225 m, 1200 m, 1116 s, 1033 m cm^{-1}; MALDI-TOF-MS (dithranol as a matrix, *m/z*): [M + H$^+$] calcd for C$_{189}$H$_{345}$N$_6$Au$_3$O$_{45}$: 4011.40; found: 4011.47; Anal. calcd. for C$_{189}$H$_{345}$N$_6$Au$_3$O$_{45}$: C 56.57; H 8.67; N 2.09; found: C 56.30; H 8.85; N 2.11.

2.3 Synthesis of [Au$_3$Pz$_3$]/silica$_{hex}$

Nanocomposites [Au$_3$Pz$_3$]/silica$_{hex}$ were fabricated by spin-coating method according to our procedure [12,13]. In this case, an acidic aqueous EtOH solution (EtOH, 29.1-–87.5 mg, 0.6–1.8 mmol; HCl, 12 M, 0.15–0.46 mg, 1.5 x 10^{-3} – 4.5 x 10^{-3} mmol; H$_2$O, 6 mg, 0.3 mmol) of a mixture of [Au$_3$Pz$_3$] (5 mg, 1.25 x 10^{-3} mmol) and tetrabutoxysilane (TBOS, 24 mg, 74.9 x 10^{-3} mmol) was held for 12 h at room temperature ([Au$_3$Pz$_3$]/[TBOS]/[EtOH]/[HCl]/[H$_2$O] = 1:60:504–1520:1.2–3.7:266), upon which partial oligomerization of silica source to the columnar assembled [Au$_3$Pz$_3$] took place. The resulting viscous solution (20 μL) was spin-coated onto a quartz plate at 3000 rpm for 15 s, affording a colorless transparent film (Fig. 1, inset photograph), which was then dried in air for 24 h at room temperature and additional 12 h at 40 °C.

3. RESULTS & DISCUSSION

In the sol-gel synthesis of mesoporous silica, self-assembly of [Au$_3$Pz$_3$] containing two N atoms in the azole ring in an acidic aqueous alcohol solution is one of the importance steps for the formation of the nanocomposites. In fact, we confirmed that acidolysis of [Au$_3$Pz$_3$] in the mixture of EtOH, HCl, and H$_2$O did not take place due to the presence of the emission band centered at 706 nm (λ_{ext} = 276 nm), which is characteristic of the metallophilic interaction [13]. For the formation of highly ordered mesoporous silica nanocomposites with a hexagonal structure, we varied the molar ratios of EtOH to HCl in the acidic aqueous alcohol solution from 1520:3.7 to 504:1.23 ([Au$_3$Pz$_3$]/[TBOS] = 1:60).

When the molar ratio of EtOH to HCl was 1520 to 3.7, the spin-coated film showed diffraction peaks at 2θ = 2.18º and 4.32º, which can be indexed as d_{100} and d_{200}, (Fig. 2A, a). This diffraction pattern was almost similar to other samples, when the molar ratios of EtOH to HCl were 1520:1.23, 760:1.23, and 504:1.23 (Fig. 2A, b-d). However, the calcination of this silica film sample ([EtOH]/[HCl] = 1520:3.7) at 450 ºC for 3 h showed no diffraction peaks (Fig. 2B, a). This result indicates that as-synthesized spin-coated film forms a lamellar structure with an interlayer distance of 4.1 nm (Fig. 2A, a). Even we reduced the concentration of HCl to three times lowest than previous sample ([EtOH]/[HCl] = 1520:1.23), the ordered mesoporous silica with a hexagonal geometry cannot be fabricated (Figs. 2A,B, b). Interestingly, at the same concentration of HCl, the diffraction patterns of the calcined sample prepared with half of the concentration of EtOH compared to the previous sample ([EtOH]/[HCl] =
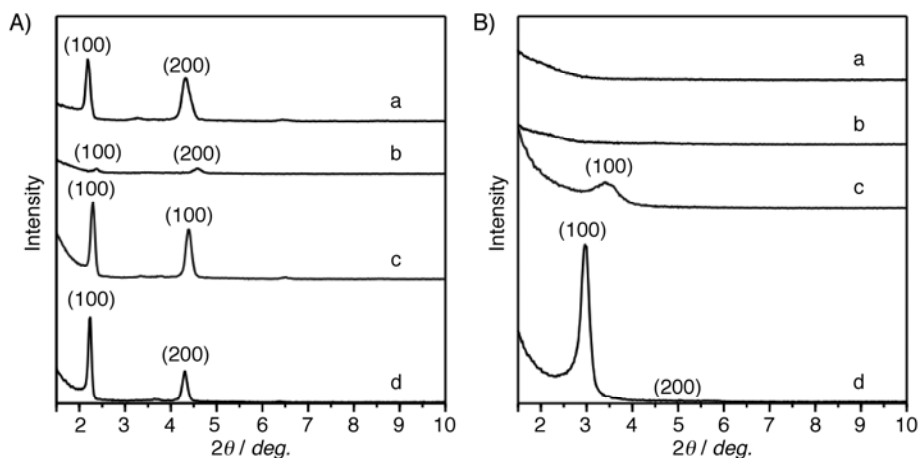

Figure 2: XRD patterns of mesoporous silica film nanocomposites of A) before and B) after calcination prepared with variation of molar ratios of EtOH to HCl in the sol-gel synthesis. a) 1520 : 3.70, b) 1520 : 1.23, c) 760 : 1.23, and d) 540 : 1.23.
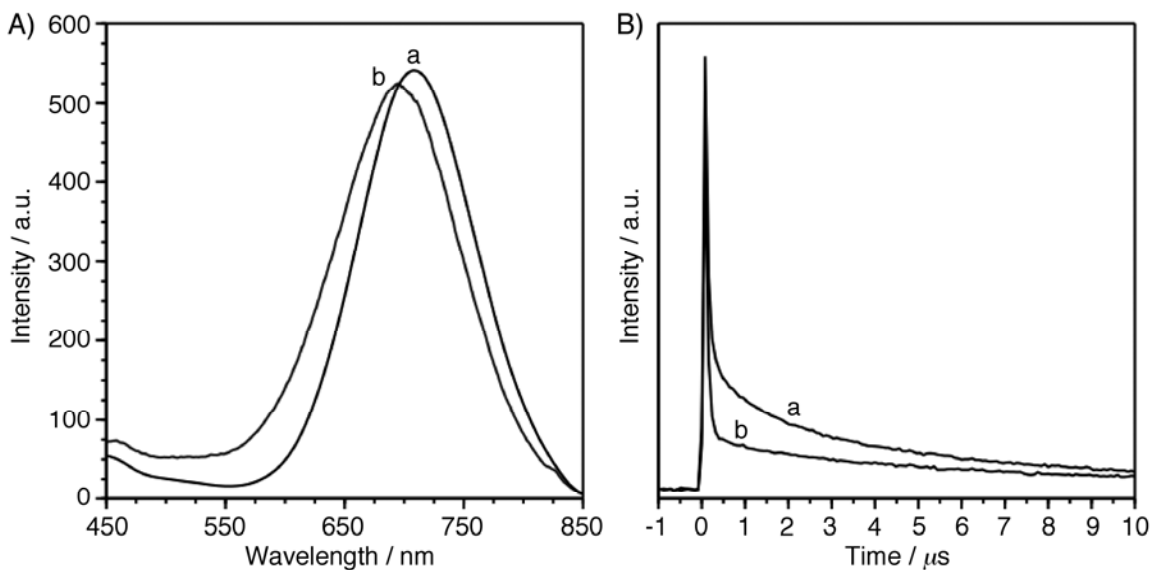
Figure 3: A) Emission spectra (λ_{ext} = 276 nm) and B) luminescence decay profiles (λ_{ext} = 266 nm, λ_{em} = 690 nm) of a) [Au_3Pz_3]/silica$_{hex}$ and b) bulk [Au_3Pz_3] (without normalized).

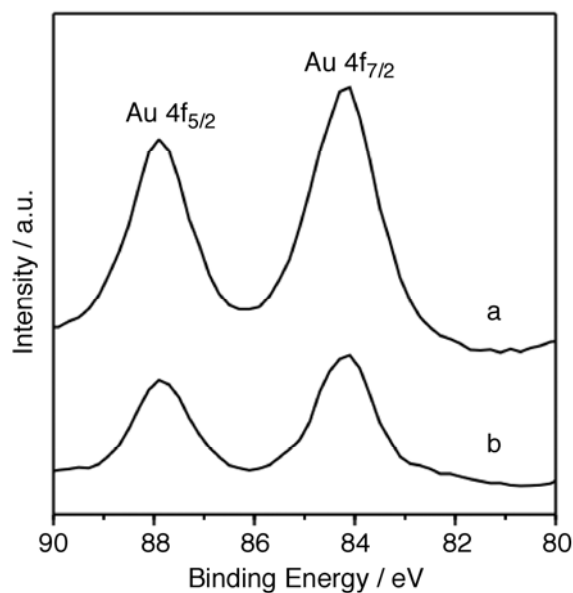**Figure 4**: XPS spectra with Au 4f$_{5/2}$ and 4f$_{7/2}$ peaks at 84.3 and 88.1 eV of a) [Au_3Pz_3]/silica$_{hex}$ and b) bulk [Au_3Pz_3] (without normalized).

760:1.23) showed a little ordered mesoporous silica nanocomposite (Fig. 2B. c). This diffraction peak at d_{100} was intensified drastically (Fig. 2B, d) by decreasing the concentration of EtOH and HCl to three times lowest than the first sample ([EtOH]/[HCl] = 504:1.23). The spin-coated film of the last sample showed diffraction peaks at 2θ = 2.95° and 5.00° due to the substantial reduction of the interpore distance from 4.1 to 2.9 nm (Fig. 2B, d). Because TEM image of the cross-section thin film prepared by an argon ion milling method with a Ion Slicer displayed the hexagonally aligned nanopores [13] and the diffraction patterns preserved the peaks after calcination (Fig. 2B, d), this result strongly indicates the formation of highly ordered mesoporous silica nanocomposite with a hexagonal structure [Au_3Pz_3]/silica$_{hex}$. Therefore, the effect of the molar ratios of EtOH to HCl in the acidic aqueous alcohol solution for the self-assembly of [Au_3Pz_3] with a silica source is one of the most important parameters in the formation of the highly ordered hexagonal silica nanocomposite [12,15].

Upon exposure to 254 nm UV light with a hand-held lamp in the dark room, the as-fabricated film sample ([EtOH]/[HCl] = 504:1.23) with highly ordered hexagonal structure emitted in red (Figure 1, inset photograph) with a luminescence center at 693 nm upon excitation at 276 nm (Figure 3A, b) with a very large Stokes shift ($\Delta\lambda$ = 417 nm) and luminescence lifetime at 7.8 μs upon excitation at 266 (Figure 3B, b; λ_{em} = 690 nm). Moreover, the luminescence properties of bulk [Au_3Pz_3] gave the center at 700 nm (Figure 3A, a) and the lifetimes at 6.3 μs (Figure 3B, c).

These luminescence intensities and lifetimes are characteristic of phosphorescing events from metal-centered triple excited state modified with the week Au^I–Au^I metallophilic interaction [13]. Moreover, the photochemical properties of [Au_3Pz_3] are essentially maintained in the hexagonal silica of the nanocomposites. Noteworthy, XPS spectrum of [Au_3Pz_3] with Au 4f peaks at 84.3 and 88.1 eV (Fig. 4) was almost similar to that of [Au_3Pz_3]/silica$_{hex}$ due to the isolation of the complex in the nanoscopic channels of mesoporous silica nanocomposite.

4. CONCLUSION

By controlling the molar ratios of EtOH to HCl in the acidic aqueous alcohol solution, we highlighted that the template sol-gel synthesis of phosphorescent columnar assembled [Au_3Pz_3] with a silica source can provide highly ordered mesoporous silica film nanocomposite with a hexagonal structures. Development of optical chemosensors using these mesoporous silica would be worthy of further investigation due to phosphorescent properties of the complex and physical properties of hexagonal silica nanocomposites.

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