

Communications

Luminescence for Grafting Organic Molecules on γ -Alumina via the Reaction of Alumina and Organic Compounds

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The grafting of organic moieties onto the surface of inorganic compounds is an important in numerous applications such as organic synthesis on solid phases and the modification of the surface properties of solids.¹

Alumina is one of the most interesting inorganic materials for grafting organic moieties.² Alumina has pore structure for ease diffusion of organic compounds and excellent properties as high melting point, low electrical conductivity, thermal and chemical stability and oxidation and corrosion resistance.³ However there are not many reports on preparing methods and optical properties of organic-alumina hybrid materials. Here we report the preparation of hybrid material grafting organic moieties on alumina and investigation of their photoluminescence (PL) properties. Although several reactions of phosphoric or phosphonic derivatives with alumina have been reported,⁴ the other organic functional groups do not have been used for grafting organic moieties on alumina. We have prepared the hybrid materials which used to graft organic moieties on alumina through the microwave irradiation or reflux, and investigated their PL properties.

To prepare the hybrid materials with organic moieties on alumina, the readily available commercial γ -alumina **2** (surface area is 132 m²/g) is used, and benzoyl chloride (**1a**), hexanoyl chloride (**1b**), heptyl bromide (**1c**), naphthoic acid (**1d**) were used as organic compounds. Benzoylalumina hybrid material **3aM** was prepared from the reaction of benzoyl chloride (**1a**) and γ -alumina **2** without solvent in microwave irradiation for 15 minutes. On the other hand, benzoylalumina hybrid material

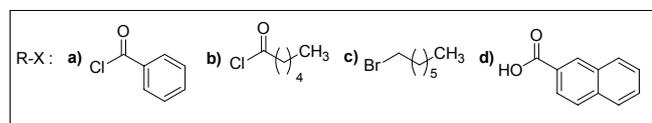
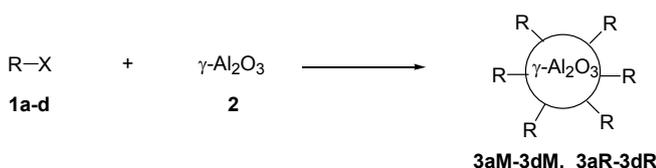
3aR was prepared in the reflux condition for 12 hours. After cooling to room temperature, the crude products were washed with dichloromethane (3 × 50 mL), ethylacetate (3 × 50 mL), hexane (3 × 50 mL), and methanol (3 × 50 mL). Hexanoyl-alumina **3bM**, **3bR** and heptylalumina **3cM**, **3cR** were prepared using hexanoyl chloride (**1b**) and heptyl bromide (**1c**) with γ -alumina **2** on microwave irradiation or reflux conditions. The toluene solution of naphthoic acid (**1d**) and γ -alumina **2** was irradiated by microwave at 150 W for 15 minutes and same solution was refluxed for 12 hours to get naphthoicalumina **3dM** and **3dR**. Each washed material, **3aM**, **3aR**, **3bM**, **3bR**, **3cM**, **3cR**, **3dM**, **3dR** was dried in vacuum as well as in oven, each for 24 hours to remove the organic solvent in porous site (Scheme 1) and (Table 1).

Each organic grafting alumina was characterized by elemental analysis and IR. Graft densities (δ) of the covalently attached organic molecules (**1a-d**) in γ -alumina **2** were determined by carbon elemental analysis (eq 1), where g_E is the C content, M_E is the molecular weight of C, Z is the number of C atoms per organic group.⁵

$$\delta = g_E/M_E Z \quad (1)$$

The organic groups/nm² (χ) was calculated from Avogadro's number (A_N) and the specific surface area(S) (eq 2).

$$\chi = \delta A_N/S \quad (2)$$



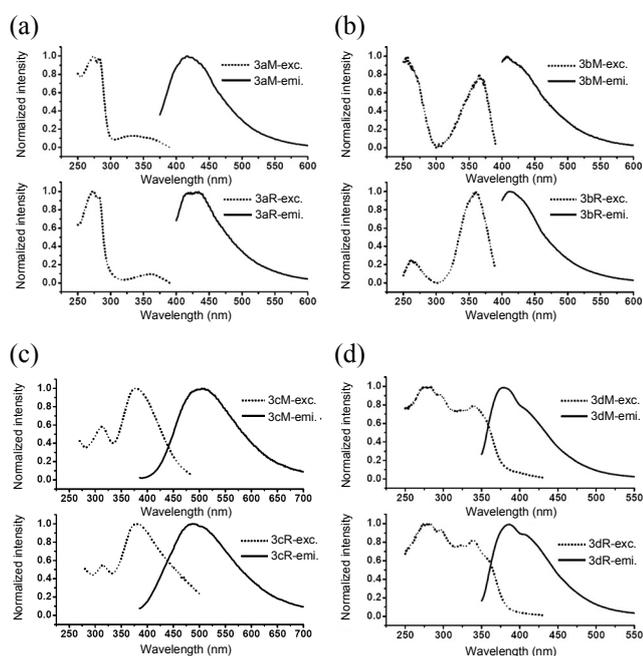
Scheme 1. Reaction of organic molecules with γ -alumina under microwave irradiation or reflux.

Table 1. The reaction conditions in preparation of organic alumina hybrid materials.

Entry	Product	Method		
		Heating	Rxn. time	Solvent
1	3aM	MW	15 min	neat
2	3aR	Reflux	12 hr	neat
3	3bM	MW	15 min	neat
4	3bR	Reflux	12 hr	neat
5	3cM	MW	15 min	neat
6	3cR	Reflux	12 hr	neat
7	3dM	MW	15 min	toluene
8	3dR	Reflux	12 hr	toluene

Table 2. Elemental analysis of organic alumina hybrid materials.

Product	Carbon Elemental Analysis	Graft Density (mmol/g)	No. of Groups ($10^{18}/\text{m}^2$)	No. of Groups (/particle)
Alumina	0.05			
3aM	2.35	28	84	1.1×10^{15}
3aR	4.98	59	178	2.4×10^{15}
3bM	1.71	24	71	1.0×10^{15}
3bR	3.14	44	131	1.8×10^{15}
3cM	0.86	10	31	4.1×10^{14}
3cR	1.31	16	47	6.3×10^{14}
3dM	4.31	33	98	1.3×10^{15}
3dR	9.91	75	226	3.1×10^{15}

**Figure 1.** (a) PL spectra of samples **3aM** and **3aR**, (b) PL spectra of samples **3bM** and **3bR**, (c) PL spectra of samples **3cM** and **3cR**, (d) PL spectra of samples **3dM** and **3dR**.

The organic groups/particle (ψ) was calculated from average particle radius (eq 3).

$$\psi = \chi(4\pi r^2) \quad (3)$$

Compound **3aM** which is prepared from benzoyl chloride (**1a**) and γ -alumina **2** is calculated graft density ($\delta = 28$), number of organic groups/ nm^2 ($\chi = 84 \times 10^{18}$) and number of organic groups/particle ($\psi = 1.1 \times 10^{15}$) from carbon elemental analysis (2.35%) using equations 1-3.

The other compounds (**3aR**, **3bM**, **3bR**, **3cM**, **3cR**, **3dM**, and **1dR**) were calculated graft density (δ), number of organic groups/ nm^2 (χ) and number of organic groups/particle (ψ) from carbon elemental analysis using same methods. The data of each compound were summarized in Table 2. By these data, samples prepared from refluxing are the larger value than the

samples prepared from microwave assisted method.

IR peak tell us the differences between functionalized alumina (**3aM**, **3aR**, **3bM**, **3bR**, **3cM**, **3cR**, **3dM**, **3dR**) and γ -alumina **2**. IR peaks come out at 3600 (strong) and 1635 (weak) cm^{-1} in γ -alumina **2**. IR peaks of benzoyl and naphthoyl grafted alumina (**3aM**, **3aR**, **3dM**, **3dR**) which has carbonyl and aryl group are 3600(s), 1635(w), 1610(w) and 1450(w) cm^{-1} . In the case of hexanoyl grafted alumina (**3bM**, **3bR**), IR peaks show up at 3600(s), 1635(w), 1610(w), and 1450(w) cm^{-1} . On the other hand, IR peaks of heptyl grafted alumina (**3cM**, **3cR**) which has no carbonyl group are similar to γ -alumina **2** in 3600 and 1635 cm^{-1} region. The difference in IR spectra supports that the γ -alumina **2** is functionalized with organic moieties.

The PL spectrum measurement was performed on a Fluorolog FL-3-221 from Jobin-Yvon Horiba. Figure 1(a) shows PL spectra of sample **3aM** and **3aR**, respectively, taken under excitation with the 340 and 360 nm of a Xe lamp. The emission band of samples **3aM** and **3aR** are 414 nm each. The PL spectra of sample **3bM** and **3bR** taken under excitation 360 and 370 nm shows the emission band of both samples at 414 nm (Fig. 1(b)). Fig 1(c) presents PL spectra of sample **3cM** and **3cR** taken under excitation with 375 nm. The emission band of samples **3cM** and **3cR** are 510 and 525 nm respectively. Also, Fig 1(d) presents PL spectra of sample **3dM** and **3dR** taken under excitation with 343 nm. The emission band of samples **3dM** and **3dR** are 450 nm.

In summary, we prepared benzoyl, hexanoyl, heptyl, and naphthoyl grafted alumina under the reflux and microwave irradiation conditions. These hybrid materials were characterized by elemental analysis and IR to confirm that organic components were attached to alumina. Interestingly we investigated that these hybrid materials are luminous and were checked by PL spectrometer. The preparation of porous alumina hybrid materials and the investigation of luminescent are continued.

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