様式第２号（第５条，第１１条関係）

「課程博士用」

学 位 論 文 の 要 旨

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学位論文題目	Preparation, thermal stability and photocatalytic activity of fluorinated organic/silica/anatase titanium oxide nanocomposites （含フッ素有機/シリカ/アナターゼ酸化チタンナノコンポジット類の調製、熱安定性および光触媒活性）		

［緒言］

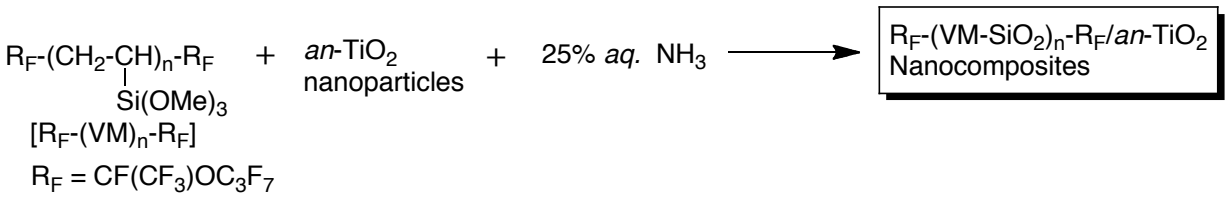
Fluoroalkyl end-capped oligomers can exhibit the unique properties such as good solubility in water and organic solvents, high surface modification ability, and the ability to form nanometer size controlled self-assembled molecular aggregates, which can not be achieved by the corresponding non-fluorinated polymers. [1)] For example, fluoroalkyl end-capped oligomers can form the nanometer size-controlled molecular aggregates and react with tetraethoxysilane (TEOS) as a cross-linker in the presence of silica nanoparticles as a guest molecule to produce the corresponding fluorinated oligomers/silica nanocomposites. [2)] Fluorinated organic/inorganic hybrid materials have been reported to afford unique characteristics arisen from the combination of organic and inorganic materials, which cannot be achieved by a single-phase material. [3)] One of the most commonly used inorganic materials is titanium dioxide, due to its high chemical stability, nontoxicity and excellent photocatalytic activity for the degradation of pollutants in natural environment. Some of fluorinated oligomers/titanium dioxide nanocomposites have been already prepared, and it was found that these nanocomposites can exhibit interesting characteristics, such as good oleophobicity imparted by fluoroalkyl segments, and UV-driven reversible switching behaviors between superhydrophobicity and superhydrophilicity. [4)] Therefore, it is of particular interest to develop novel fluorinated organic/titanium dioxide nanocomposites from the developmental viewpoint of new fluorinated functional materials. In this work, the preparation of a variety of fluorinated organic/silica/anatase titanium oxide nanocomposites are described including their thermal stabilities and photocatalytic activities.

［実験・結果・考察］

[I] Fluoroalkyl End-capped Vinyltrimethoxysilane Oligomer/Anatase Titanium Oxide Nanocomposites Possessing Photocatalytic Activity even after Calcination at 1000 ^{o}C [5, 6)]

Fluroalkyl end-capped vinytrimethoxysilane oligomer/anatase-type titanium oxide nanocomposites [R_F-(VM-SiO_2)$_n$-R_F/TiO_2] were prepared by the sol-gel reaction of the corresponding oligomer [R_F-(VM)$_n$-R_F] in

the presence of anatase-type titanium oxide nanoparticles under alkaline conditions (see Scheme 1).



Scheme 1 Preparation of R_F-(VM-SiO_2)$_n$-R_F/*an*-TiO_2 Nanocomposites

Titanium oxide in these fluorinated nanocomposites was found to keep its anatase crystalline structures even after calcination at 1000°C, although the original anatase titanium oxide nanoparticles exhibited a perfect phase transformation from anatase to rutile after calcination at 1000 °C. Fig. 1 shows that original anatase titanium oxide nanoparticles exhibit almost no photocatalytic activity after calcination at 1000 °C. However, R_F-(VM-SiO_2)$_n$-R_F/TiO_2 nanocomposites before and even after calcination at 1000 °C can exhibit the similar photocatalytic activity toward the decolorization of methylene blue (MB), due to the no phase transformation from anatase to rutile even after calcination at 1000 °C.

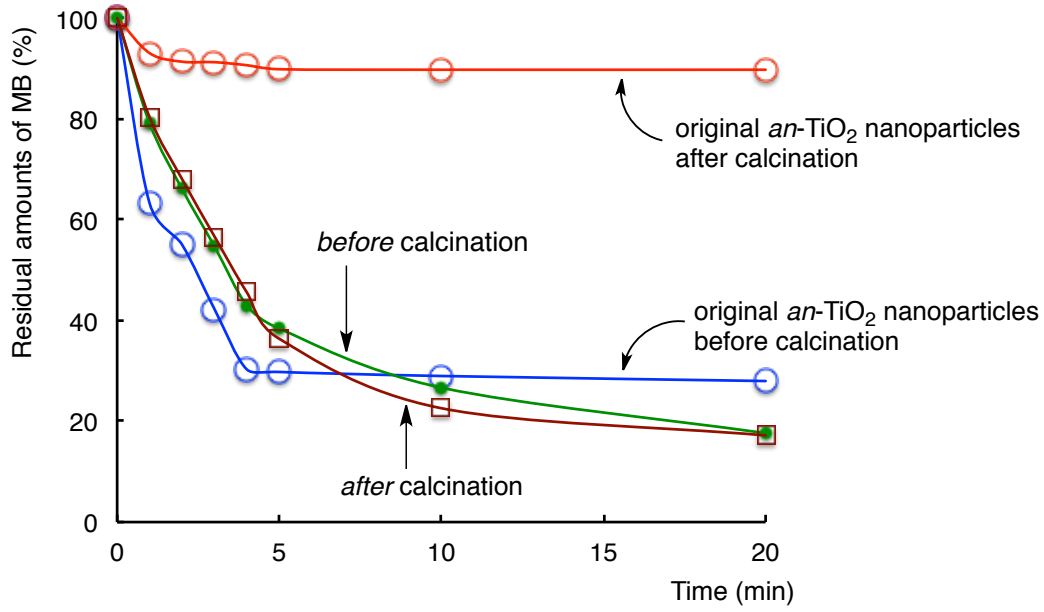
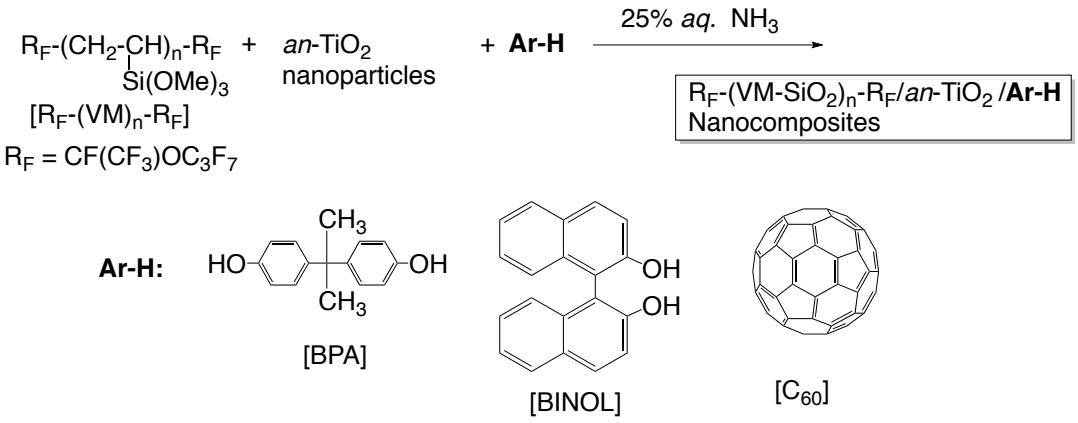


Fig. 1 Relationship between the residual amounts of MB and photoirradiation (λ_{max}: 365 nm) time in the presence of original *an*-TiO_2 nanoparticles and R_F-(VM-SiO_2)$_n$-R_F/*an*-TiO_2 nanocomposites before and after calcination at 1000 °C
Concentration of MB: 2.5 mg/dm^3;
Concentration of nanocomposites: 25 mg/dm^3

[II] Preparation and Photocatalytic Activity of Fluoroalkyl End-capped Vinyltrimethoxysilane Oligomer/Anatase Titanium Oxide Nanocomposites – Encapsulated Low Molecular Aromatic Compounds [6, 7]

R_F-(VM-SiO_2)$_n$-R_F/*an*-TiO_2 nanocomposites - encapsulated low molecular weight aromatic compounds such as bisphenol A [BPA], 1,1'-bi(2-naphthol) [BINOL] and fullerene have been prepared by the sol-gel reactions under alkaline conditions (see Scheme 2). The encapsulated aromatic compounds such as BPA and BINOL into these nanocomposite cores can exhibit no weight loss corresponding to the contents of the aromatic compounds even after calcination at 800 °C.

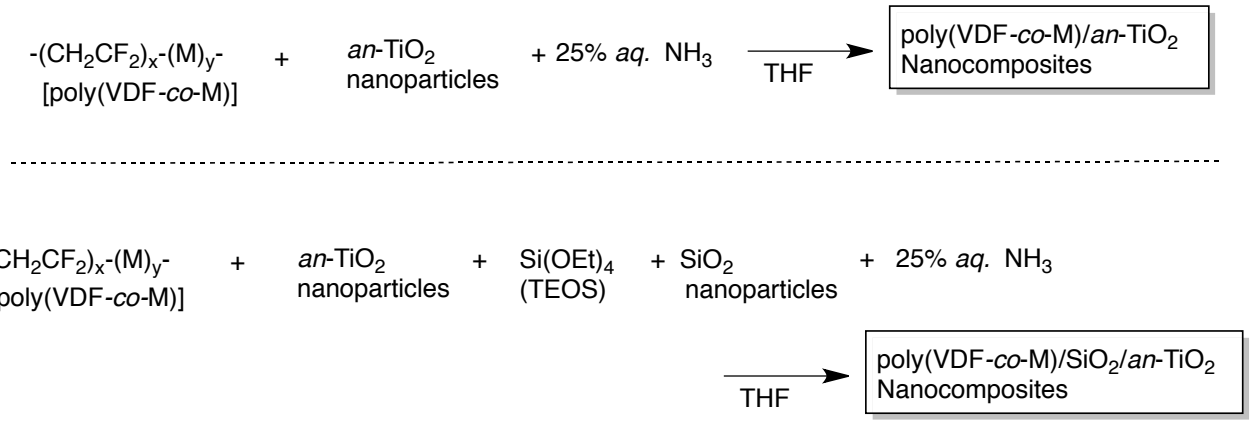


Scheme 2 Preparation of R_F-(VM-SiO_2)$_n$-R_F/*an*-TiO_2 /**Ar-H** nanocomposites

Especially, the fluorinated titanium oxide nanocomposites - encapsulated these aromatic compounds before and after calcination at 1000 °C can exhibit anatase crystal structures and higher phototcatalytic activities for the decolorization of methylene blue under UV light irradiation than that of the corresponding R_F-(VM-SiO_2)$_n$-R_F/*an*-TiO_2 nanocomposites or the original *an*-TiO_2 nanoparticles.

[III] Vinylidene Fluoride - containing Copolymers/Anatase Titanium Oxide/Silica Nanocomposites Exhibiting Photocatalytic Activity even after Calcination at 1000 °C [8]

Vinylidene fluoride copolymers [poly(VDF-*co*-fluorofunctional M)]/anatase titanium oxide nanocomposites and poly(VDF-*co*-fluorofunctional M)/silica/anatase titanium oxide nanocomposites have been prepared as shown in Scheme 3. These obtained nanocomposites were found to exhibit a high thermal stability. In fact, the weight loss of fluorinated poly(VDF-*co*-CF_2CFCO_2Me)/SiO_2/*an*-TiO_2 nanocomposites was only 2% even after calcination at 800 °C.

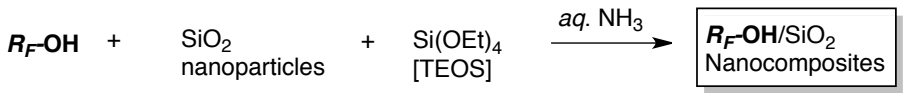


Scheme 3 Preparation of poly(VDF-*co*-M)/*an*-TiO_2 nanocomposites and poly(VDF-*co*-M)/SiO_2/*an*-TiO_2 nanocomposites

In the absence of silica, these fluorinated copolymers/*an*-TiO_2 composites underwent a complete phase transformation from anatase into rutile TiO_2 after calcination at 1000 °C. However, poly(VDF-*co*-fluorofunctional M)/SiO_2/*an*-TiO_2 nanocomposites completely preserved the anatase structure without any phase transformation into rutile even after calcination at 1000 °C. Before the calcinations, these fluorinated copolymers/SiO_2/*an*-TiO_2 nanocomposites exhibited a good photocatalytic activity for the discoloration of methylene blue dye, as well as that of original *an*-TiO_2 nanoparticles. After the calcination, fluorinated poly(VDF-*co*-CF_2CFCO_2Me)/SiO_2/*an*-TiO_2 nanocomposites led to the similar photocatalytic activity as that of original *an*-TiO_2 nanoparticles before calcination.

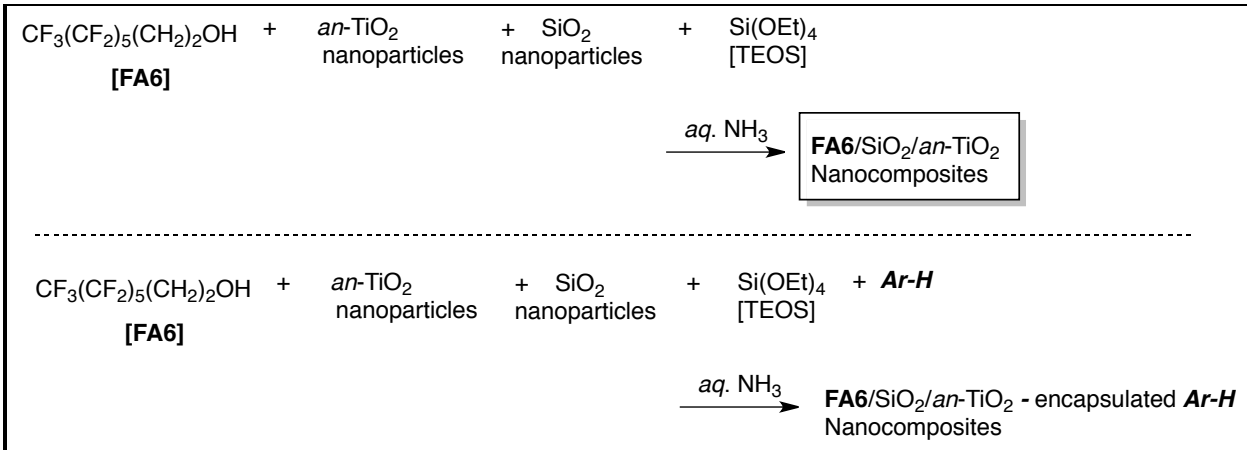
[IV] Preparation and Properties of Fluorinated Aliphatic Alcohol/Silica Nanocomposites - Application to the Encapsulation of Anatase Titanium Oxide Nanoparticles into These Composite Cores [9)]

A variety of fluorinated aliphatic alcohols/SiO_2 nanocomposites have been prepared by the sol-gel reactions as shown in Scheme 4. These obtained nanocomposites were found to give no weight loss corresponding to the contents of the alcohols even after calcination at 800 °C. The modified glass surface treated with these fluorinated silica nanocomposites can exhibit the superoleophobic and superhydrophilic characteristics on the surface.



***R_F*-OH:** $CF_3(CF_2)_3(CH_2)_2OH$ **[FA4]**, $CF_3(CF_2)_5(CH_2)_2OH$ **[FA6]**, $CF_3(CF_2)_7(CH_2)_2OH$ **[FA8]**, $CF_3(CF_2)_3CH_2(CF_2)_5(CH_2)_2OH$ **[DTFA]**

Scheme 4 Preparation of ***R_F*-OH**/SiO_2 nanocomposites



Scheme 5 Preparation of **FA6**/SiO_2/*an*-TiO_2 nanocomposites and **FA6**/SiO_2/*an*-TiO_2 **-** encapsulated ***Ar-H*** nanocomposites.

Moreover, anatase titanium oxide nanoparticles were effectively encapsulated into these fluorinated alcohol/silica nanocomposite cores to give the corresponding fluorinated alcohol/silica/anatase TiO_2 nanocomposites (see Scheme 5), and these fluorinated nanocomposites before and even after calcination can afford a higher photocatalytic activity than that of original anatase TiO_2 nanoparticles under similar conditions.

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