Photocatalytic Activity of Vinylidene fluoride-Containing Copolymers/anatase Titanium Oxide/Silica Nanocomposites

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Abstract

A series of three fluorinated copolymers (FP) based on vinylidene fluoride (VDF) were involved in the preparation of original FP / anatase titanium oxide (*an*-TiO₂), and FP / silica / *an*-TiO₂ nanocomposites. These FP copolymers were prepared by conventional free radical copolymerization of VDF with various functional fluorinated comonomers such as F₂C=CFCO₂Me, FCH=CFCO₂H, and F₂C=CFC₃H₆OCOCH₃ in good yields (> 60%) and had number average molecular weights of ca. 50,000 g.mol⁻¹. Anatase titanium oxide in the FP / *an*-TiO₂ nanocomposites underwent an effective modification into rutile polymorphism after calcination at 1000 °C. Although the parent *an*-TiO₂ nanoparticles changed completely into rutile nanoparticles after calcination at 1000 °C, *an*-TiO₂ embedded in the FPs / silica / *an*-TiO₂ nanocomposites retained their structures without any phase transformation into rutile, **due to locking the Ti-O species at the interface of TiO₂ domains by the Ti-O-Si units, whose lattice can be formed by the interaction of silica with *an*-TiO₂ nanoparticles.** Even after such a thermal treatment, these nanocomposites displayed a higher photocatalytic activity for the discoloration of methylene blue as well as those of the corresponding nanocomposites before calcination, although the original *an*-TiO₂ nanoparticles could not exhibit a photocatalytic ability after calcination. Among these nanocomposites based on VDF-containing copolymers, poly(VDF-*co*-CF₂CFCO₂CH₃)/SiO₂/*an*-TiO₂ before and after calcination displayed better photocatalytic properties than those of the other FP nanocomposites. More interestingly, this FP /silica / *an*-TiO₂ nanocomposite even after calcination at 1000 °C was able to preserve the same photocatalytic activity as that before calcination. In addition, these FP/TiO₂ and FP/SiO₂/TiO₂ composites exhibited high thermal stability up to 800 °C with a loss weight of 2 % (or ca. 14 % for the acidic FP) only.

Introduction

Titanium oxide (TiO₂) is the most important white pigment involved in coating and plastic industry because of the high refractive index of TiO₂ nanoparticles ($n_D \sim 2.6$), which enables it to produce high gloss composites.¹ It is widely used because it efficiently scatters visible light, thereby imparting whiteness, brightness, and opacity when incorporated in coatings, as well as in cosmetics and toothpastes. It has been utilized in many applications ranging from photocatalysis,² catalyst supports,³ dye-sensitized solar cells,⁴ semiconductors and capacitors,⁵ photovoltaics,⁶ ductile ceramics,⁷ lithium ion batteries (LIB)⁸ (especially anatase, rutile TiO₂ and TiO₂(B) polymorphs are promising structures for anode materials in LIB), and to gas sensors.⁹ In addition, organic polymer matrices containing dispersed TiO₂ oxide nanoparticles have found a practical use for mediating photochemical process in membranes, catalytic sensors, and photosensitive materials and for stimulating numerous biochemical and biophysical process.^{10,11} However, the dispersion of the nanoparticles uniformly throughout organic polymeric matrices is an issue, because the nanoparticles can easily agglomerate or coalesce forming large particles which result in a reversed effect on the catalyst efficiency.^{12,13} In their comprehensive review, Fröschl *et al.*⁵ reported selective synthetic methods towards TiO₂ *nano*-materials and these authors mentioned that TiO₂ displays various phases: amorphous, rutile, anatase and brookite. The last one has been involved in various applications, especially for electrochemical Lithium insertion.¹⁴ A few polymer / TiO₂ composites have been reported in the literature, for example by Thomas *et al.*¹⁵⁻¹⁸ who used isotactic polystyrene,¹⁵ natural rubber-EPDM,¹⁶ nitrile rubber,¹⁷ and also synthesized natural rubber/nanoSiO₂/TiO₂ composites.¹⁸ In addition, Chu *et al.*¹⁹ described original PEO-*b*-PPO-*b*-PEO triblock copolymer/TiO₂ composites. As a matter of fact, fluorinated polysoaps are well-known to exhibit a superior surface active property than that of the corresponding non-fluorinated homologues.²⁰⁻²¹ Thus, it was of particular interest to develop fluorinated polymers/TiO₂ nanocomposites that possess satisfactory dispersibility and stability.

Actually, only a few publications focus on the fluoropolymers/TiO₂ composites based on poly(tetrafluoroethylene), PTFE,²² poly(vinylidene fluoride), PVDF,²³ poly(fluoroacrylate)s,²⁴ fluoroalkyl end capped polymers (that displayed good dispersibility and stability in various solvents),²⁵ fluoroalkyl end-capped vinyltrimethoxysilane oligomer,²⁶ poly(TFE-*co*-HFP) copolymer,²⁷ and poly(VDF-*co*-TrFE) copolymer²⁸ (where HFP and TrFE stand for hexafluoropropylene and trifluoroethylene, respectively). In addition, anatase titanium oxide (*an*-TiO₂) seems to behave as a more efficient photocatalyst than the rutile one. However, *an*-TiO₂ can be irreversibly modified into rutile *an*-TiO₂ at elevated temperatures.²⁹⁻³¹ Concerning the thermally stable TiO₂ nanocomposites for various applications, it was worth exploring new fluorinated (co)polymers / *an*-TiO₂ nanocomposites that possess not only a good dispersibility in solvents as well as satisfactory chemical and thermal stabilities but also a higher photocatalytic activity without any phase transformation into rutile under higher temperature conditions. It has been hitherto reported that the fluorination of TiO₂, involving either fluorine adsorption or lattice fluorine-doping, is effective for the enhancement of the photocatalytic activity of TiO₂,³²⁻³⁶ compared to that of the original TiO₂. Therefore, it is expected that reactions of *an*-TiO₂ nanoparticles with fluorinated polymers to generate original composites should enhance the photocatalytic property of *an*-TiO₂ in the resulting fluorinated copolymers/ TiO₂ composites. The present study attempts to investigate if fluorinated copolymers may enhance not only the photocatalytic ability of *an*-TiO₂ but also the thermal stability of these fluorinated copolymers through reactions of these corresponding copolymers with *an*-TiO₂ nanoparticles and SiO₂ nanoparticles. In particular, it was of interest to investigate if original resulting fluorinated copolymers / silica / *an*-TiO₂ nanocomposites could enable to preserve the *an*-TiO₂ structure after calcination at 1000 °C and display a good photocatalytic activity imparted by such a nanofiller within the composites. These are the objectives of this present study.

Experimental

Materials

Titanium oxide nanoparticles (average particle size: 20 nm) were received from Ishihara Sangyo Kaisha Ltd. (Osaka, Japan). Vinylidene fluoride (VDF) copolymers, poly(VDF-*co*-CF₂CFCO₂CH₃)³⁷, poly(VDF-*co*-CFHCFCO₂H)³⁸, and poly(VDF-*co*-CF₂CF(CH₂)₃OCOCH₃)³⁹ copolymers were prepared by reported methods of conventional free radical copolymerizations of vinylidene fluoride (VDF) with F₂C=CO₂CH₃, FCH=CFCO₂H, and F₂C=CF(CH₂)₃OCOCH₃ comonomers, respectively. Their molecular weights (assessed by size exclusion chromatography, Figures S1-S3 in the Supporting Information) were ca. 50,000 g.mol⁻¹ (with poly(methyl methacrylate), PMMA standards) while their microstructures (i.e. the mol. contents of VDF and fluorinated functional comonomers in the copolymers) were determined by ¹⁹F NMR spectroscopy, supplied in Figure 1 and in Figures S4-S5.

Analytical Techniques

Molecular weights of VDF copolymers were assessed at 40 °C by using SEC with columns 2HR5E and 1HR2E types with DMF/LiBr in 0.1 mol.l⁻¹ as the eluent with an isocratic pump and PMMA standards. Dynamic light-scattering (DLS) measurements were carried out using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Field emission scanning electron micrographs (FE-SEM) and energy dispersive X-ray (EDX) spectra were obtained using JEOL JSM-7000F (Tokyo, Japan). X-ray diffraction (XRD) measurements were performed by the use of Mac Science M18XHF-SRA (Tokyo, Japan). ¹H NMR spectra were recorded using JEOL JNM-400 (400 MHz) FT NMR SYSTEM (Tokyo, Japan). ¹⁹F NMR spectra were recorded on Bruker AC 400 instruments in DMF- *d*₇ with CFCI₃ as the reference. The experimental conditions for recording ¹H (or ¹⁹F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s

(or 0.7 s), pulse delay 2 s (or 2 s), number of scans 128 (or 512, and 1024 for ^{13}C NMR), and a pulse width of 5 μs for ^{19}F NMR.

Thermal analyses were carried out by raising the temperature up to around 800 $^{\circ}\text{C}$, at a heating rate of 10 $^{\circ}\text{C}.\text{min}^{-1}$, under air atmospheric conditions, by the use of Bruker axis TG-DTA2000SA differential thermobalance (Kanagawa, Japan).

Preparation of poly(VDF-*co*-M₂) copolymer / silica / anatase titanium oxide nanocomposites

A typical procedure for the preparation of fluorinated copolymers / silica / anatase TiO_2 nanocomposites is as follows: to a methanol solution (20 ml) of a fluorinated copolymer (number average molecular weight, $M_n = 50.000 \text{ g.mol}^{-1}$, 250 mg) were added 250 mg of *an*- TiO_2 nanoparticles, 0.25 ml of tetraethoxysilane (TEOS), silica nanoparticles average particle size of 11 nm (wt.) 30 %, THF [1.60 g; (Methanol Silica-sol (TR))], and 0.25 ml of 25 % aqueous ammonia solution. The mixture was stirred with a magnetic stirring bar at room temperature for 5 h, and then was centrifuged for 30 min. The fluorinated copolymer/ TiO_2 nanocomposites were easily separated from the methanol solution. Methanol (20 mL) was added to the obtained total product mixture and the methanol solution was stirred at room temperature for 1 day. After centrifugal separation of the mixture, the obtained product was dried under vacuum at 50 $^{\circ}\text{C}$ for 2 days to produce purified white fluorinated composite powders (560 mg). The different weights of reactants, yields, and particles sizes of other FP/ TiO_2 and FP/ $\text{SiO}_2/\text{TiO}_2$ composites are listed in Table 1.

Discoloration of methylene blue under UV light irradiation in the presence of fluorinated copolymers/silica/anatase titanium oxide nanocomposites

Methanol or DMF solution (0.8 mL) of methylene blue (10 mg.dm^{-3}) and well-dispersed fluorocopolymer/silica/*an*- TiO_2 nanocomposites (200 mg.dm^{-3}) methanol (or DMF) solution (0.4 mL) were added in 2 mL THF solution. UV-vis spectra of the suspension methanol solution thus

obtained exhibited absorption bands around 652 nm assigned to methylene blue dye. The discoloration of methylene blue dye was examined by irradiating this suspension solution with UV lamp (λ_{max} : 365 nm) for 20 min at room temperature.

Results and discussion

Preparation of poly(VDF-*co*-M) Copolymer/*an*-TiO₂ Nanocomposites and poly(VDF-*co*-M) Copolymer / SiO₂ / *an*-TiO₂ Nanocomposites

The radical copolymerizations of vinylidene fluoride (VDF) with various functional comonomers, F₂C=CFCO₂CH₃, FCH=CFCO₂H, and F₂C=CF(CH₂)₃OCOCH₃ were initiated by *t*-butyl peroxyphthalate at 70 °C, and led to statistical poly(VDF-*co*-CF₂CFCO₂CH₃)³⁷, poly(VDF-*co*-FCHCFCO₂H)³⁸, and poly(VDF-*co*-CF₂CF(CH₂)₃OCOCH₃) copolymers³⁹ in satisfactory yields (> 60 %) (Scheme 1).

Scheme 1: Free Radical Copolymerization of Vinylidene fluoride (VDF) with Functional Fluorinated XYC=CX-spacer-G comonomer

After reaction and precipitation in cold pentane (or water), the molecular weights of the resulting poly(VDF-*co*-M) copolymers were ca. 50,000 g.mol⁻¹ (assessed by size exclusion chromatography with PMMA standards, Figures S1-S3 in the Supporting Information). The microstructures (i.e. the molar contents of VDF and functional comonomers) of these fluorinated copolymers were determined by ¹H and ¹⁹F nuclear magnetic resonance (NMR) spectroscopy (Figure 1 and Figures

S4-S5 in the Supporting Information) from the characteristic signals assigned to the fluorinated groups in VDF and functional comonomers. As an example, Figure 1 displays ^{19}F NMR spectrum of poly(VDF-*co*-CF₂CFC₃H₆OCOCH₃) copolymer that exhibits the expected signals centered at -92, -113 and -116, and -110 ppm attributed to difluoromethylene groups in head-to-tail and head-to-head VDF-VDF dyads,³⁷⁻³⁹ and to alternated VDF-trifluoropentenyl acetate (FAC) dyad,³⁹ respectively, and to those assigned to CF₂ or CF on FAC functional comonomers (Figure 1). The ratios of the integrals of the signals corresponding to both comonomers enabled to determine the molar percentages of these fluorinated comonomers in each VDF-containing copolymer.

Figure 1: ^{19}F NMR Spectrum of Poly(VDF-*co*-CF₂CFC₃H₆OCOCH₃) Copolymer (recorded at room temperature in d₇-DMF). The integrals of the characteristic signals of each comonomer led to a VDF: F₂C=CF(CH₂)₃OCOCH₃ mol/mol ratio of 97:3.

Then, VDF copolymers/ *an*-TiO₂ nanocomposites and VDF copolymers/ SiO₂/ *an*-TiO₂ nanocomposites were prepared under slightly basic conditions that enable crosslinking⁴⁰ in mild conditions enough to avoid any dehydrofluorination of VDF units (Scheme 2). The results are presented in Table 1.

Scheme 2: Preparation of poly(VDF-co-M) copolymers/an-TiO₂ nanocomposites and poly(VDF-co-M) copolymers /SiO₂/an-TiO₂ nanocomposites

Nanocomposite formations involving poly(VDF-co-M) copolymers were found to proceed under slightly alkaline conditions to give the expected poly(VDF-co-M)/an-TiO₂ and poly(VDF-co-M)/SiO₂/an-TiO₂ nanocomposites in 31-68 % isolated yields (Scheme 2 and Table 1).

Table 1: Preparation of poly(VDF-co-M) copolymers/an-TiO₂ nanocomposites and poly(VDF-co-M) copolymers /SiO₂/an-TiO₂ nanocomposites

Run	poly(VDF-co-M) (mg)	an-TiO ₂ (mg)	TEOS (ml)	SiO ₂ (mg)	aq. NH ₃ (ml)	Product yield ^{a)} (%)	Size of composites ^{b)} (after calcination) (nm) ± STD
M: CF ₂ =CFCO ₂ Me							
1	400	500	-	-	0.25	57	27.9 ± 5.8 (30.2 ± 7.3)
2	250	250	0.25	480	0.25	31	23.4 ± 5.5 (46.3 ± 10.3)
M: CHF=CFCO ₂ H							
3	400	500	-	-	0.25	59	39.1 ± 8.7 (24.9 ± 6.3)
4	250	250	0.25	480	0.25	36	143.2 ± 30.6 (143.8 ± 32.7)
M: CF ₂ =CFC ₃ H ₆ OCOMe							
5	400	500	-	-	0.25	68	26.1 ± 5.6 (32.8 ± 5.4)
6	250	250	0.25	480	0.25	40	21.8 ± 5.3 (18.1 ± 4.4)

a) Yield based on poly(VDF-co-M) and TiO₂ (or TEOS or SiO₂ nanoparticles).

b) Determined by DLS (dynamic light scattering) measurements in methanol solutions.

Figure 2: FE-SEM (Field Emission-Scanning Electron Microscopy) images of methanol solutions of poly(VDF-*co*-CF₂CFCO₂Me) copolymer/SiO₂/*an*-TiO₂ nanocomposites before and after calcination at 1000 °C (used sample: Run 2 in Table 1). The scale is 1 μm

Interestingly, under these mild conditions, poly(VDF-*co*-functional comonomer) copolymers did not undergo any dehydrofluorination as reported in a previous work⁴¹ and these obtained nanocomposites exhibited good dispersibility and stability in methanol, ethanol and tetrahydrofuran. The sizes of the obtained composites before and after calcination at 1000 °C assessed by DLS were nanometer size-controlled (18-144 nm). FE-SEM images of poly(VDF-*co*-CF₂CFCO₂Me) copolymer /SiO₂/ *an*-TiO₂ composites (Run 2 in Table 1) also show the formation of fine nanoparticles with the almost same sizes before (90 nm) and after (54 nm) calcination (Figure 2). Interestingly, the white color of the nanocomposite powders did not change before and after calcination at 1000 °C.

The XRD spectra of poly(VDF-*co*-M) copolymers/*an*-TiO₂ nanocomposites and poly(VDF-*co*-M) copolymer /SiO₂/*an*-TiO₂ nanocomposites in Table 1 before and after calcination at 1000 °C (Table 1) were compared to those of pristine *an*-TiO₂ nanoparticles (see Figures 3-5).

Figure 3: X-ray diffraction patterns of original *an*-TiO₂ nanoparticles (bottom spectrum), poly(VDF-*co*-CF₂CFCO₂Me)/*an*-TiO₂ nanocomposites (Run 1 in Table 1), poly(VDF-*co*-CF₂CFCO₂Me)/*an*-TiO₂ /SiO₂ nanocomposites (Run 2 in Table 1) before (middle) and after (top) calcinations at 1000 °C

Figure 4: X-ray diffraction patterns of original *an*-TiO₂ nanoparticles (bottom spectrum), poly(VDF-*co*-CHF₂CFCO₂H)/*an*-TiO₂ nanocomposites (Run 3 in Table 1), poly(VDF-*co*-CHF₂CFCO₂H)/SiO₂/*an*-TiO₂ nanocomposites (Run 4 in Table 1) before (middle) and after (top) calcinations at 1000 °C

Poly(VDF-*co*-M)/*an*-TiO₂ nanocomposites before calcination (Runs 1, 3 and 5 in Table 1) displayed almost the same XRD characteristic peaks (Figures 3-5) as those of original *an*-TiO₂ nanoparticles (Figure 6). However, TiO₂ in the nanocomposites underwent a complete phase transformation into rutile after calcination at 1000 °C (Figures 3, 4 and S8) as well as that of pristine *an*-TiO₂ nanoparticles (Figure 5).

Figure 5: X-ray diffraction patterns of original *an*-TiO₂ nanoparticles (bottom spectrum), poly(VDF-*co*-CF₂CFC₃H₆OCOME)/*an*-TiO₂ nanocomposites (Run 5 in Table 1) and poly(VDF-*co*-CF₂CFC₃H₆OCOME)/SiO₂/*an*-TiO₂ nanocomposites (Run 6 in Table 1) before (middle) and after (top) calcinations at 1000 °C

On the other hand, poly(VDF-*co*-M) copolymers /SiO₂/*an*-TiO₂ nanocomposites (Runs 2, 4 and 6 in Table 1), which were prepared by the composite formations of the corresponding copolymers with *an*-TiO₂ nanoparticles, SiO₂ nanoparticles and TEOS, were found to preserve their crystalline anatase structure even after calcination at 1000 °C (Figures 3-5).

These obtained poly(VDF-*co*-M)/SiO₂/*an*-TiO₂ nanocomposites exhibited a good dispersibility and stability in methanol, ethanol and tetrahydrofuran illustrated in Scheme 2 and Table 1. Dynamic light scattering (DLS) technique was a suitable tool to assess the sizes of these composites before and after calcination (Table 2) and evidenced that the sizes of these composites were nanometer size-controlled (10-51 nm). The white color of poly(VDF-*co*-M)_y/SiO₂/*an*-TiO₂ nanocomposite powders did not change before and after calcination at 1000 °C.

However, no transformation into rutile after calcination at 1000 °C was interestingly observed in poly(VDF-*co*-M)/SiO₂/*an*-TiO₂ nanocomposites (Runs 2, 4 and 6 in Table 1).

In this way, poly(VDF-*co*-M)/*an*-TiO₂ nanocomposites were able to effectively modify their crystalline structure from anatase into rutile after calcination at 1000 °C. In addition, it was

demonstrated that the incorporation of silica moieties into these above nanocomposites cores *via* the sol-gel processes involving TEOS and SiO₂ nanoparticles under alkaline conditions preserved their crystalline anatase structure completely without any phase modification into rutile, even after calcination at 1000 °C.

Figure 6: X-ray diffraction patterns of pristine (or original) *an*-TiO₂ nanoparticles before (bottom spectrum) and after (top) calcinations at 1000 °C

Photocatalytic activity of fluorinated copolymers/ *an*-TiO₂ and fluorinated copolymers/ SiO₂ / *an*-TiO₂ nanocomposites

Anatase titanium oxide is known to irreversibly undergo a phase transformation into rutile at elevated temperatures⁴² in air (ranging between 600 and 750 °C).^{5,29,30} Actually, the incorporation of silica moieties into TiO₂ enabled to prevent the phase transformation into rutile.⁴³ In fact, Hilonga *et al.*⁴⁴ reported that titania-silica composite, which was prepared by the sol-gel reaction of titanium oxychloride and sodium silicate, can preserve anatase structure at ca. 600-900 °C, although the phase transformation from anatase into rutile was partly observed in this nanocomposites after calcination at 1000 °C.

Therefore, it is presumed that the synergistic interaction between silicon and fluorine atoms in

such fluorinated polymers/SiO₂/*an*-TiO₂ nanocomposites should enhance the thermal stability of *an*-TiO₂ in the resulting nanocomposites. Actually, fluorinated polymers/SiO₂/*an*-TiO₂ nanocomposites lattice lock the Ti-O species at the interface of the TiO₂ domains through the formation of Ti-O-Si species and Ti-F species, preventing from the nucleation that is necessary for the phase transformation into rutile at 1000 °C. In fact, Gao *et al.*⁴⁵ reported that Ti-O-Si species were formed in TiO₂-SiO₂ mixed oxides, while Ti-F species can be obtained by a simple ligand exchange reaction between surface hydroxyl groups on TiO₂ (Ti-OH) and fluoride anion (F⁻).^{46,47} In addition, Ti-F species have been generated through the fluoride doping (TiO_{2-x}F_x) technique.⁴⁸ Especially, fluoride doping has been found to enhance the crystallization of the anatase phase and the photocatalyst activity.^{34,49-50} Surface-fluorinated TiO₂ can also display enhanced photocatalyst ability.⁵¹⁻⁶⁰ From these results, it is suggested that thermally stable anatase structure in these present fluorinated polymers/SiO₂/*an*-TiO₂ nanocomposites would arise from the presence of not only silica nanoparticles but also from fluorine moieties in the nanocomposites cores.

Indeed, fluorine counterparts in polymers are expected to interact efficiently with *an*-TiO₂ in the nanocomposites to enhance the photocatalytic activity of fluorinated polymer nanocomposites related to the presence of *an*-TiO₂. First, the photocatalytic activity of poly(VDF-*co*-CF₂CFCO₂Me) copolymer/SiO₂/*an*-TiO₂ nanocomposites (Run 2 in Table 1) before and after calcination at 1000 °C was evaluated in terms of discoloration of methylene blue dye (MB) under UV light irradiation. The residual amounts of MB *versus* time were estimated by the decrease of the absorption band at 652 nm related to MB by UV light irradiation, and the results are shown in Figure 7.

The photocatalytic activity is linked to the residual amounts of MB, and as shown in Figure 6, original *an*-TiO₂ nanoparticles display a photocatalytic activity toward MB, although the corresponding TiO₂ nanoparticles with a complete phase transformation from anatase to rutile

after calcination at 1000 °C did show any photocatalytic property, even after 20 min-photoirradiation.

Figure 7: Residual amounts of methylene blue dye (MB) versus photoirradiation (λ_{max} : 365 nm) time in the presence of poly(VDF-*co*-CF₂CFCO₂Me) copolymer /SiO₂/*an*-TiO₂ nanocomposites: diamonds and full squares (or original *an*-TiO₂ nanoparticles: open circles) before and after calcination at 1000 °C (used sample: Run 2 in Table 1); concentration of methylene blue dye: 2.5 mg/dm³; concentration of nanocomposites (or pristine) *an*-TiO₂ nanoparticles before and after calcination at 1000 °C): 25 mg/dm³

Actually, this resulting rutile TiO₂ displayed 90 % residual MB after 20 min in contrast to initial *an*-TiO₂ that induced 29 %. This indicates that original *an*-TiO₂ nanoparticles can possess no photocatalytic activity after calcination at 1000 °C. Interestingly, poly(VDF-*co*-CF₂CFCO₂Me) copolymer/SiO₂/*an*-TiO₂ nanocomposites before calcination at 1000 °C exhibited a higher photocatalytic activity for the discoloration of MB than that of original *an*-TiO₂ nanoparticles. It is also worth noting that, after calcination at 1000 °C, these poly(VDF-*co*-CF₂CFCO₂Me) copolymer/SiO₂/*an*-TiO₂ nanocomposites exhibit the same photocatalytic activity as that of original *an*-TiO₂ nanoparticles after 20 min-photoirradiation.

The photocatalytic activity of other poly(VDF-*co*-M) copolymers/SiO₂/*an*-TiO₂ nanocomposites have also been studied for 20 min-UV light irradiation before and after calcination at 1000 °C (Table 2) under the same conditions as those of the case above (Figure S7), and the results are summarized in Figure 8.

Figure 8: Photo-discoloration of methylene blue dye in methanol solutions of poly(VDF-*co*-M) copolymer/SiO₂/*an*-TiO₂ nanocomposites in Table 1 before (gray scale) and after (black scale) calcination at 1000 °C; concentration of poly(VDF-*co*-M) copolymer/SiO₂/*an*-TiO₂ nanocomposites (or original *an*-TiO₂ nanoparticles): 25 mg/dm³; concentration of methylene blue dye: 2.5 mg/dm³ UV irradiation ($\lambda_{\max}$: 365 nm) time: 20 min.

Figure 8 shows that the photocatalytic activity of poly(VDF-*co*-M)/SiO₂/*an*-TiO₂ nanocomposites before calcination were found to increase more than twice, compared to that of original *an*-TiO₂ nanoparticles before calcination. After calcination, poly(VDF-*co*-M)/SiO₂/*an*-TiO₂ nanocomposites also induced a photocatalytic activity higher than that of original TiO₂ nanoparticles after calcination. In the poly(VDF-*co*-CF₂CFCO₂Me)/SiO₂/*an*-TiO₂ nanocomposite, a higher photocatalytic activity was observed before and after calcination (Run 2 in Table 1).

Unexpectedly, fluorinated nanocomposites that possess COOH units (Run 4 in Table 1), after calcination, displayed a photocatalytic activity lower than that of other nanocomposites. This observation can arise from the presence of higher acidic carboxyl groups since they are adjacent to electron-withdrawing CF-CHF groups in the composites.

To clarify the effect of carboxyl groups for the photocatalytic activity of such fluorinated nanocomposites, fluorinated derivative that bears a higher acidic carboxylic acid, $C_3F_7OCF(CF_3)COOH$ [R_F -COOH], was involved in a nanocomposite reaction (Scheme 3). This structure was chosen since it is more simple than that of carboxylic acid-containing fluorinated polymers in poly(VDF-*co*-CFHCFCO₂H)/SiO₂/*an*-TiO₂ nanocomposites.

* Yield based on R_FCOOH , TiO_2 , SiO_2 and TEOS

**Determined by DLS measurements in methanol solution

***Particle size of the composites after calcination at 1000 °C assessed by DLS measurements in methanol solution

Scheme 3: Preparation of $R_FCOOH/SiO_2/an\text{-}TiO_2$ nanocomposites from R_FCOOH (where R_F stands for $C_3F_7OCFCF_3$)

Even after calcinations, $R_F\text{-COOH}/SiO_2/an\text{-}TiO_2$ nanocomposites (Scheme 3) did not undergo any phase transformation into rutile at all, as well as those of the present fluorinated polymers/ $SiO_2/an\text{-}TiO_2$ nanocomposites (Figure S10 in the Supporting Information). As above, photocatalytic activity of $R_F\text{-COOH}/SiO_2/an\text{-}TiO_2$ nanocomposites was evaluated in terms of discoloration of MB under UV light irradiation under similar conditions as those of Figure 6, and

the results are displayed in Figure 9.

Figure 9: Relationship between the residual amounts of methylene blue dye and photoirradiation ($\lambda_{\max}$: 365 nm) time in the presence of $R_F\text{COOH}/\text{SiO}_2/\text{an-TiO}_2$ nanocomposites: open circles and full diamonds and squares (or original an-TiO_2 nanoparticles: open circles and full diamonds) before and after calcination at 1000 °C; concentration of methylene blue dye: 2.5 mg/dm³; Concentration of nanocomposites (or original an-TiO_2 nanoparticles before and after calcination at 1000 °C): 25 mg/dm³

Figure 9 reveals that $R_F\text{COOH}/\text{SiO}_2/\text{an-TiO}_2$ nanocomposites before calcination exhibit the same photocatalytic activity as that of parent an-TiO_2 nanoparticles. However, after calcination, they displayed a quite poor photocatalytic activity. This result suggests that higher acidic carboxylic groups in the nanocomposites would reduce the photocatalytic ability in the nanocomposites after calcination, as well as that of poly(VDF-*co*-CHFCFCO₂H) copolymer/ $\text{SiO}_2/\text{an-TiO}_2$ nanocomposites after calcination (Run 4 in Table 1, Figure 11).

In this way, poly(VDF-*co*-M) copolymer/ $\text{SiO}_2/\text{an-TiO}_2$ nanocomposites before calcination displayed a higher photocatalytic activity for the discoloration of methylene blue dye under UV light irradiation, compared to that of original an-TiO_2 nanoparticles under similar conditions. Poly(VDF-*co*-CF₂CFCO₂Me)/ $\text{SiO}_2/\text{an-TiO}_2$ nanocomposites exhibited a higher photocatalytic activity before and after calcination. In contrast, poly(VDF-*co*-CFHCFCO₂H)/ $\text{SiO}_2/\text{an-TiO}_2$

nanocomposites after calcination reduced their photocatalytic activity. The contents of TiO₂ and SiO₂ in poly(VDF-*co*-CF₂CFCO₂Me)/SiO₂/*an*-TiO₂ and in poly(VDF-*co*-CFHCFCO₂H)/SiO₂/*an*-TiO₂ nanocomposites before and after calcination at 1000 °C by energy dispersive X-ray (EDX) spectra measurements were estimated as follows:

	TiO ₂ (%)	SiO ₂ (%)
poly(VDF- <i>co</i> -CF ₂ CFCO ₂ Me)/SiO ₂ / <i>an</i> -TiO ₂	16 (13*)	64 (77*)
poly(VDF- <i>co</i> -CFHCFCOOH)/SiO ₂ / <i>an</i> -TiO ₂	11 (11*)	23 (51*)

*) After calcination

EDX spectra show that the contents of TiO₂ in the composites before and after calcination are estimated to be 11-16 % and 11-13 %, respectively. Thus, it should be said that our present fluorinated nanocomposites can possess a better photocatalytic activity than that of original *an*-TiO₂ nanoparticles.

In addition, the thermal stabilities of poly(VDF-*co*-M)/SiO₂/*an*-TiO₂ nanocomposites (where M stands for CF₂=CFCO₂Me, CFH=CFCOOH, and CF₂=CF(CH₂)₃OCOMe) were assessed under air and the corresponding thermograms are displayed in Figures 10, 11 and S11. These thermograms show the following weight losses (%) corresponding to the contents of fluorinated polymers in the nanocomposites at 800 °C, as follows:

	Weight Loss (%) at 800 °C (under air)
poly(VDF- <i>co</i> -CF ₂ CFCO ₂ Me) copolymer/SiO ₂ / <i>an</i> -TiO ₂	2
poly(VDF- <i>co</i> -CF ₂ CF(CH ₂) ₃ OCOMe) copolymer /SiO ₂ / <i>an</i> -TiO ₂	17
poly(VDF- <i>co</i> -CFHCFCOOH) copolymer /SiO ₂ / <i>an</i> -TiO ₂	20

Figure 10: Thermogravimetric curves (under air) of original SiO₂ nanoparticles (a), which were prepared from TEOS and silica nanoparticles, *an*-TiO₂ nanoparticles (b), poly(VDF-*co*-CF₂CFCO₂Me) copolymer /*an*-TiO₂ nanocomposites (Run 1 in Table 1) (c), poly(VDF-*co*-CF₂CFCO₂Me) copolymer /SiO₂/*an*-TiO₂ nanocomposites (Run 2 in Table 1) (d), and poly(VDF-*co*-CF₂CFCO₂Me) copolymer (e).

Previously, we reported that fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers/silica nanocomposites⁶¹ and poly(VDF-*ter*-TFMA-*ter*-HFP) terpolymers/silica nanocomposites (where TFMA and HFP stand for 2-trifluoromethacrylic acid and hexafluoropropylene, respectively)⁴¹ can exhibit almost no weight loss even after calcination at 800 °C through a dehydrofluorination process that released hexafluorosilicate anions.

Figure 11: TGA thermograms (under air) of original SiO₂ nanoparticles (a), which were prepared from TEOS and silica nanoparticles, *an*-TiO₂ nanoparticles (b), poly(VDF-*co*-CFHCFCOOH) copolymer /*an*-TiO₂ nanocomposites (Run 3 in Table 1) (c), poly(VDF-*co*-CFHCFCOOH) copolymer/SiO₂/*an*-TiO₂ nanocomposites (Run 4 in Table 1) (d), and poly(VDF-*co*-CFHCFCOOH) copolymer (e).

Thus, poly(VDF-*co*-CF₂CFCO₂Me)/SiO₂/*an*-TiO₂ nanocomposites, the weight loss of which is 2 %, are likely to give hydrogen fluoride through the calcination process to interact with *an*-TiO₂ nanoparticles. Such *an*-TiO₂ nanoparticles interacted with hydrogen fluoride and could enhance the photocatalytic activity in the composites.

Conclusions

For the first time, poly(VDF-*co*-fluorofunctional M) copolymers have been utilized with *an*-TiO₂ nanoparticles under slightly alkaline conditions to obtain fluorinated copolymers/*an*-TiO₂ nanocomposites. Similarly, successful syntheses of fluorinated copolymers/ SiO₂/ *an*-TiO₂ nanocomposites by using silica nanoparticles and TEOS were achieved under such above conditions. These fluorinated copolymers/*an*-TiO₂ composites underwent a complete phase transformation from anatase into rutile TiO₂ after calcination at 1000 °C. A similar phase

transformation into rutile was observed from original (or pristine) *an*-TiO₂ nanoparticles in these conditions that confirm the literature.³⁵ However, nanocomposite formations from these fluorinated copolymers with *an*-TiO₂ nanoparticles, SiO₂ nanoparticles and TEOS under alkaline conditions, enabled to obtain fluorinated copolymers/ SiO₂/ *an*-TiO₂ nanocomposites that completely preserved the crystalline anatase structure without any phase transformation into rutile, even after calcination at 1000 °C. Before calcinations, these fluorinated copolymers/SiO₂/*an*-TiO₂ nanocomposites exhibited a good photocatalytic activity as evidenced by the discoloration of methylene blue dye under UV light irradiation, as well as that of original *an*-TiO₂ nanoparticles. After calcinations, fluorinated poly(VDF-*co*-CF₂CFCO₂Me)/SiO₂/*an*-TiO₂ nanocomposites led to similar photocatalytic activity as that of original *an*-TiO₂ nanoparticles before calcinations, and much higher than both other F-copolymers/TiO₂/SiO₂ composites. In addition, these nanocomposites display a high thermal stability (for example at 800 °C, 2 wt.% only was lost for poly(VDF-*co*-CF₂CFCO₂Me)/SiO₂/*an*-TiO₂ composites). Therefore, these present fluorinated copolymers/SiO₂/*an*-TiO₂ nanocomposites exhibit a high potential for specific applications such as dye sensitized solar cell, or binders and electrodes for Lithium ion batteries since these original fluorinated polymer nanocomposites are thermostable and have demonstrated a good photocatalytic ability relative to anatase titanium oxide even after calcination at 1000 °C. Deeper characterizations are required to explain the structures of such composites (e.g. XPS, BET, and chemical analyses since some HF release may enhance the photocatalytic activity) and are under progress.

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Supporting Information Available: ^{19}F NMR spectra of poly(VDF-*co*-methyltrifluoroacrylate) and poly(VDF-*co*-FCH=CF CO_2H) copolymers, X-ray diffraction patterns of poly(VDF-*co*-CF $_2$ CFCO $_2$ Me)/*an*-TiO $_2$, poly(VDF-*co*-CF $_2$ CFCO $_2$ Me)/SiO $_2$ /*an*-TiO $_2$, poly(VDF-*co*-CHFCFCO $_2$ H)/*an*-TiO $_2$, poly(VDF-*co*-CHFCFCO $_2$ H)/SiO $_2$ /*an*-TiO $_2$, poly(VDF-*co*-CF $_2$ CFC $_3$ H $_6$ OCOME)/*an*-TiO $_2$, poly(VDF-*co*-CF $_2$ CFC $_3$ H $_6$ OCOME)/SiO $_2$ /*an*-TiO $_2$, and R $_f$ COOH/SiO $_2$ /*an*-TiO $_2$ nanocomposites; TGA thermograms of poly(VDF-*co*-CF $_2$ CFC $_3$ H $_6$ OCOCH $_3$) copolymer, poly(VDF-*co*-CF $_2$ CFC $_3$ H $_6$ OCOCH $_3$)/*an*-TiO $_2$, and poly(VDF-*co*-CF $_2$ CFC $_3$ H $_6$ OCOCH $_3$)/SiO $_2$ /*an*-TiO $_2$ nanocomposites.

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