Titania-based functional nanocomposite materials fabricated by liquid processes

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In this review, research on the preparation and characterization of TiO₂-containing nanocomposites is considered. The preparations of nanocomposites by sol–gel and anodization methods are mainly explored. Nanocomposites are highly desired for some applications, and the means of controlling their functions to optimize performance is reviewed. The typical applications of TiO₂-containing nanocomposites in photocatalysis and micropatterning are discussed.

Key-words : Liquid-phase synthesis, Sol–gel, Anodization, Photocatalysis

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1. Introduction

Nanocomposites are hybrid materials with two or more components mixed at the nanometer scale.¹ The first discovery of nanocomposites was not in a chemical laboratory but in nature. Bone, clay, and nacre are good examples of natural nanocomposites. These natural nanocomposites often contain an organic component that acts as soft tissue and bonds together inorganic building blocks that deliver high mechanical strength. Although traditional macroscopic composites exhibit combined characteristics of their original components, nanocomposites are often recognized as novel products because of their unique properties. Many novel nanocomposites have been fabricated for practical applications, with unique optical,²) mechanical,⁶) electrical,⁷),⁸) and even ecological characteristics.⁹) Among various choices for components, TiO₂ has often been used in nanocomposites because of its photocatalytic properties, including the Honda-Fujishima effect.¹⁰),¹¹) Good dispersion of TiO₂ nanocrystals in a nanocomposite without aggregation is needed to enhance photocatalytic activity. A large surface area, high transmittance of light, and durability against photocatalytic activity are required for the other component(s) or host matrix in which the TiO₂ nanocrystals are dispersed. Silica-based glass and gels such as siloxanes and silsesquioxanes are candidate matrices that often meet these requirements.¹²) As a result, various silica-titania, siloxane-titania, and silsesquioxane-titania nanocomposites have been studied for photocatalytic, photolithographic, transparent protective, and self-cleaning applications.¹³),¹⁴) TiO₂-based nanocomposites have also been widely studied to optimize their intrinsic photocatalytic performance.¹⁵)–¹⁷)

Control of the nanostructures in nanocomposites offers an exciting opportunity to enhance their physical and chemical properties. TiO₂-containing nanocomposites with mesoporous,¹⁵) nanorod,¹⁹) nanowire,²⁰) and nanotube²¹) structures have been fabricated to date (Fig. 1). A mesoporous structure is normally favorable for photocatalytic materials because of its large specific surface area.²²) Nanowire, nanorod, and nanotube structures, which are recognized as one-dimensional (1-D) structures, can improve the electron transport properties and reduce light scattering of nanocomposites. These characteristics of 1-D nanocomposites make them suitable for use as the electrodes of dye-sensitized solar cells (DSSCs).¹⁹),²³)

2. Synthesis of TiO₂-containing nanocomposites

2.1 The sol–gel method

The sol–gel method is often used to prepare nanocomposites from metal alkoxide precursors.²⁴) The sol–gel technique offers advantages such as low heating temperature and good controllability, producing nanocomposites with high purity, good homogeneity, wide variation of composition, and controllable pore structures. Additionally, the shape of products can be selected, including bulk, powder, monolith, fiber and film. The sol–gel method is also a promising technique for fabricating TiO₂-containing nanocomposites. Because the size and phase of TiO₂ nanocrystals influence the performance of the resulting nanocomposite, numerous attempts to crystallize TiO₂ have been carried out, such as heating in a dry atmosphere, warming in vapor,²⁵) boiling in water,²⁶),²⁷) laser irradiation,²⁸) and microwave heating.²⁹) Generally, heating gels in wet conditions results in crystallization of TiO₂ at lower temperature than that required to crystallize TiO₂ in a dry atmosphere.¹⁹),²⁶),³⁰),³¹) Some near-room-temperature crystallization methods for titania-based gels have been reported, including a chemical equilibrium reaction of aqueous ammonium hexafluorotitanate solution,³²) and direct syntheses using peroxo-modified anatase sols³³) and aqueous titanium sulfate solution.³⁴) We have also reported several low-temperature crystallizations of sol–gel-derived TiO₂-based coatings with the assistance of water.³²) The formation of TiO₂ crystals is rarely observed in the pure TiO₂ coating under the same conditions as when SiO₂–TiO₂ is used to deposit TiO₂ crystals. Anatase nanocrystals are most easily formed when the TiO₂ content of SiO₂–TiO₂ coatings is around 30%. In the case of a 75SiO₂–25TiO₂ coating, treatment in boiling water for just 1 h is needed to fully crystallize TiO₂ on the surface of the coating.³⁵) To crystallize TiO₂ in pure TiO₂ coatings, higher temperature and longer time are required; for example, 80°C and 72 h.³⁶) Because TiO₂ crystal-containing nanocomposite coatings can be prepared using low-temperature sol–gel processes, they can be fabricated on plastic substrates such as polyethylene terephthalate, acrylic resin, and polycarbonate.³⁷)
2.2 Anodization

TiO₂-based porous materials can also be synthesized by anodization. TiO₂ with an ordered porous structure prepared by anodizing a Ti substrate was first reported in 1997.38),39) Unlike other methods to prepare porous TiO₂, nanotube array structures with controlled length, diameter, and smoothness can be formed by anodization with optimized applied voltage, composition of electrolyte, temperature, and duration of reaction.40) Before, after or even during anodization, secondary elements can be doped into the TiO₂ nanotube arrays to produce TiO₂-based tubular nanocomposite arrays.41)–43) Metal ions such as Fe³⁺,44) Sr²⁺,45) Nb³⁺,46) and Ce³⁺47) have been incorporated into TiO₂ nanotube arrays as well as nonmetallic elements like C,48)–51) K,52),53) and N.54),55) Semiconductor and metal nanoparticles such as CdS,56) CdSe,57) Au,58),59) and Ag60) have been deposited on TiO₂ nanotube arrays after anodizing Ti substrates to form TiO₂-based nanocomposites (Fig. 2).

2.3 Other methods to fabricate TiO₂-based nanocomposites

TiO₂-containing nanocomposites have also been prepared using methods other than sol–gel synthesis and anodization, including with a sonochemical route to fabricate graphene-TiO₂,61) liquid-phase selective deposition to form Ni-Zn-TiO₂,62) liquid-phase deposition using shrimp and crab shells to produce chitosan-TiO₂,63) a flame aerosol process to synthesize noble metal–TiO₂,64) and a templating approach to form MnCO₃-TiO₂.65)

3. Functions of TiO₂-containing nanocomposites

3.1 Advanced photocatalysis

The photocatalytic activity of TiO₂ can be improved when it is associated with a co-catalyst. These co-catalysts are typically fine particles of metals like Ag,66) or Au67) or metal oxides such as RuO₂.68) Co-catalysts do not exhibit a photoresponse upon irradiation with the wavelength chosen for the experiment. Rather, the purpose of the co-catalyst is to provide more catalytically active surface sites to improve the kinetics of the reaction at the semiconductor surface. The semiconductor absorbs light and produces charge carriers, which are then transferred to the co-catalyst particles, decreasing the probability of charge-carrier recombination.69) The recombination probability is further decreased by formation of a Schottky junction. For an n-type semiconductor, a Schottky junction allows electrons to be transferred...
from the semiconductor to the metal particles, but prevents their transfer back across the Schottky barrier (Fig. 3).\textsuperscript{68)}

Plasmonic nanostructures can be combined with TiO\textsubscript{2} to create nanocomposites with enhanced photocatalytic activity. Several mechanisms for the role of plasmonic nanostructures have been proposed, any or all of which could prove to be important under certain conditions. Typical examples of the proposed mechanisms for the enhanced photocatalysis of metal nanoparticle-TiO\textsubscript{2} nanocomposites are as follows.

1. Formation of a Schottky barrier, discussed above in the context of co-catalysts, is independent of the surface plasmon resonance (SPR) of the metal, but still plays an important role in photocatalytic performance.

2. Improved transfer of electrons from the photoexcited metal to the semiconductor,\textsuperscript{69)-71}) which increases the concentration of excited electrons in the semiconductor (Fig. 4).

3. Increased encounters with photons of incident light because of the scattering effect of SPR.\textsuperscript{72)}

4. Near-field radiative transfer of energy accumulated by SPR.\textsuperscript{73),74)}

5. SPR increasing the temperature of the system.\textsuperscript{75)}

The incorporation of nitrogen or carbon has also been found a promising approach to enable visible-light responsiveness of TiO\textsubscript{2} by reducing its band-gap energy.\textsuperscript{76)-78)} For instance, we have formed carbon-doped TiO\textsubscript{2} nanotube arrays via rapid anodic oxidation (Fig. 5).\textsuperscript{79)} The resulting photoelectrode with an aspect ratio of ³142.5, which was fabricated by anodization at 60 V for 1 h, had a remarkable ability to generate H\textsubscript{2} at an evolution rate of up to ³508.3 \(\mu\text{L min}^{-1}\text{cm}^{-2}\) and a conversion efficiency of ³2.3%.

The traditional approach to improve the photocatalytic performance of TiO\textsubscript{2} is the addition of a co-catalyst, which does not directly interact with light, but increases semiconductor activity through the above-mentioned effects. However, recently it has been demonstrated that the addition of metal nanoparticles or nonmetallic elements can enhance semiconductor activity through a range of possible interaction mechanisms, each of which can enhance photoactivity under certain conditions.\textsuperscript{73),69)-71,(73),24) 3.2 Micropatterning

Micropatterns are generally fabricated by photolithography, and the patterns produced are used for fundamental research on cellular biology, biomaterials engineering,\textsuperscript{79),80)} and optical applications such as photonic devices\textsuperscript{81)} and microlens arrays (Fig. 6).\textsuperscript{82)-84)} TiO\textsubscript{2}-containing inorganic–organic nanocomposites have been extensively studied for application as optical coatings and in micro-optic devices because of their high refractive indices as well as good thermal and chemical durability.\textsuperscript{85)} Chemical structure has a strong influence on the physical and mechanical properties of nanocomposite films. Ultraviolet (UV) radiation can readily destroy films by inducing formation of radicals in them, followed by breakage of chemical bonds. Through the photocatalytic activity of TiO\textsubscript{2} component, Si–C bonds in nanocomposite films are cleaved photocatalytically. Clear micropatterns can be formed on homogeneous, amorphous RSiO\textsubscript{3}–TiO\textsubscript{2} films (R: vinyl, methyl, ethyl, phenyl, and benzyl organic functional groups) by UV irradiation through a photomask (Fig. 7).\textsuperscript{86)} The photocatalytic changes of TiO\textsubscript{2}-containing inorganic–organic nanocomposite films have been investigated to reveal the structure and mechanical properties of the films before and after UV irradiation. The main reactions occurring upon the exposure of such films to UV light are main chain scission, oxidation, side-group abstraction, and destruction.\textsuperscript{77)} Understanding
these changes in physical and chemical properties upon exposure to UV radiation is essential for developing embossing and photolithographic micropatterning processes using TiO2-containing inorganic–organic nanocomposite films. Detailed studies on the effects of the content of TiO2 component on the structural changes in the films have also been carried out to determine the most effective conditions to use such films in micropatterning applications.88) Increasing the content of TiO2 was found to increase the cleavage of Si–C bonds in RSiO3·2TiO2 films, which resulted in an increased refractive index and decreased film thickness. A marked increase in the Meyer hardness of the films was also observed upon UV irradiation, which became larger as the content of TiO2 component was increased. Interestingly, rewritable wettability patterns can be fabricated on R2SiO3·2TiO2 nanocomposite films by UV irradiation through a photomask.89) Application of micropatterning technique to hologram formation has also been reported.90)–95) The basic concept is to fabricate sub-micropatterns in recording media, which contain TiO2. Reversible hologram formation was demonstrated in AgCl nanoparticle-doped RSiO3·2TiO2 films (R: glycidoxypropyl organic functional group) by visible light irradiation and heat treatment (Fig. 8).93) Angle- or polarization-dependent holographic properties were investigated, which realizes multiple recording of information at one place.92),95)

3.3 Other functions of TiO2-containing nanocomposites
TiO2-containing nanocomposites are also expected to find use in some other applications. Pt–carbon–TiO2 nanocomposites have been prepared and investigated as electrocatalysts for fuel cells.96) The high stability of the nanocomposites against corrosion under anodic polarization conditions relative to commercially available electrocatalysts was confirmed. Silanizing TiO2 nanoparticles with 3-mercaptopropyltrimethoxysilane and subsequent photopolymerization produced TiO2 nanocomposites with a high loading capacity and high capture efficiency for use as a chromatographic packing material.97) The agglomerated TiO2 nanocomposite particles could be retained within the chromatographic cartridge, and had twice the phosphate binding capacity of pure TiO2 particles. Fe3O4/TiO2 with a core/shell structure was prepared, where the iron core imparted magnetic properties on the spheres, allowing a material–target conjugate to be isolated from solution simply by using a magnet.98) However, these magnetic-core microspheres had an ill-defined structure, and poor selective affinity for phosphopeptides. For tissue engineering applications, TiO2 has been integrated into bioactive glass composites for use as scaffolds for bone tissue generation.99) Notably, TiO2 is biologically inert, allowing hydroxyapatite to form on its surface and act as a bonding layer for further bone development.

Au, Ag, and Al nanoparticle-coated TiO2 nanoparticles and nanotube arrays are promising materials as the photoanode of DSSCs.100) For this application, the SPR of the metal nanoparticles harvests solar energy quite efficiently, and the generated ‘hot electrons’ are used to excite electrons of the dye. Because the absorption coefficient of a photoanode can be quite large, the
cells are able to become very thin, reducing the amount of precious natural resources needed, as well as the weight of cells.

4. Conclusions

The methods used to synthesize TiO$_2$-containing nanocomposites with different functions were summarized. The procedures used to prepare such nanocomposites are complex, and several factors can affect the properties of the final products; nevertheless, various unique functions have been obtained by carefully selecting composition, controlling morphology, and using appropriate external conditions. The desirable characteristics of TiO$_2$-containing nanocomposites mean they will continue to be used and further developed for different industrial purposes, from photocatalysis to biological applications, as well as fundamental scientific research.

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