

Creation of Morphology Controlled TiO₂ Nanoparticle Assemblies with Unique Surface Structures and their Applications

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論文内容の要旨

Introduction

TiO₂ is known as a promising material used in a wide area of applications. There are many methods to prepare TiO₂ nanoparticle (NP) assemblies including a previously reported one-pot single-step solvothermal reaction.^[1] This technique performs under appropriate conditions and can easily control the product morphology by adjusting reaction parameters such as precursor solution, heating rate, and reaction temperature. Besides previously synthesized solid and hollow spherical NP assemblies, namely, MARIMOs (**m**icro/**m**eso-porously **a**rchitected **r**oundly **i**ntegrated **m**etal **o**xides), higher order morphologies are expected to realize further potential applications. The creation of dimensionally controlled inorganic nanomaterials is one of the intriguing challenges in the field of material science, since it can further design applications of each prepared nanomaterial.

1. A Novel Three-dimensionally Branched TiO₂ with Cheek-brush Morphology and its Application in an Improvement of Hydrogel Polymer Strength

The current study revealed a successful synthesis of a novel TiO₂ nanoassemblies with three-dimensionally-branched nanostructure by the use of ester additives to control the morphology of product in the mentioned tunable solvothermal method. Considering the MARIMO NP synthesis with

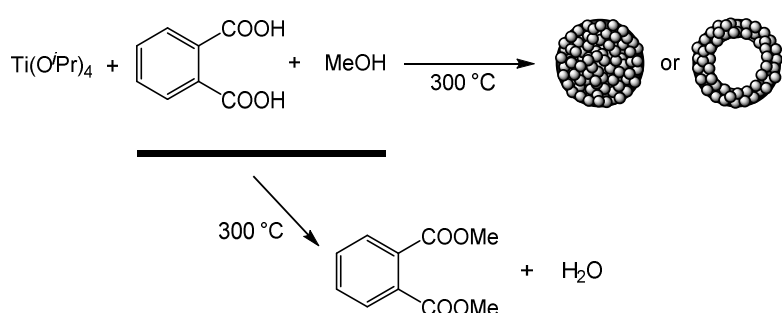


Figure 1. Schematic of solvothermal synthesis of TiO₂ MARIMO assemblies.

phthalic acid and methanol at high temperature, it is supposed that *dimethyl phthalate* could be generated in the reaction (Figure 1) and that the generated ester could be a key material in the formation of the porous spherical morphologies. Therefore, the additive in the precursor solution was changed from phthalic acid to dimethyl phthalate to clarify the effect of the ester. Then,

nanofiber bundles of TiO₂ with a unique cheek-brush morphology were serendipitously obtained in the solvothermal treatment of a titanium tetraisopropoxide and dimethyl phthalate in methanol. The precursor mixture was kept stand for 20 min after titanium source was added in order to obtain TiO₂ assemblies with a perfect cheek-brush morphology. Otherwise, urchin-shaped assemblies with short needles were obtained, suggesting that there might be weak interactions between the precursor components; and the formation of higher-ordered assemblies through weak interactions in the precursor mixture could be a key factor in obtaining a cheek-brush morphology. The precursor mixture was studied using ESI-MS to clarify what happens during standing period. The heating rate (5–6 °C/min), final reaction temperature (300 °C), and holding time at the final temperature (10 min) of the solvothermal reaction were also crucial for formation of the cheek-brush morphology.

In particular, nanoscale branching of the structure can improve physical properties, such as surface adsorption and adhesion, which facilitate strong interaction with molecules, polymers, biomaterials, and so on. Accordingly, with the uniqueness of the branch structures, such inorganic materials have gained significant attention as crosslinkers to create mechanically highly stable polymer hydrogels, where the mechanical strength of polymer hydrogels is quite sensitive to the morphologies of the

crosslinkers. Currently, various kinds of nanomaterials with different morphologies, for example, nanoparticles, nanofibers, and nanotubes, have been used as crosslinkers. Although considering the effective formation of crosslinking network between polymer and filler materials, a three-dimensional structure is still highly desirable.

The cheek-brush TiO_2 assemblies were used to crosslink a poly(*N*-isopropylacrylamide) hydrogel; the brushes enhanced the physical adhesion properties of the hydrogel (Figure 2). The hydrogel prepared from 20wt% of poly(*N*-isopropylacrylamide) with only 0.02wt% of cheek-brush TiO_2 shows ultimate tensile strength and elongation ability improvement of 11% and 9%, respectively, compared with a prototype hydrogel without a crosslinker. On the contrary, a hydrogel prepared using TiO_2 spheres of a similar size resulted an 11% and 18% lower ultimate tensile strength and elongation ability, respectively, compared with the prototype hydrogels.

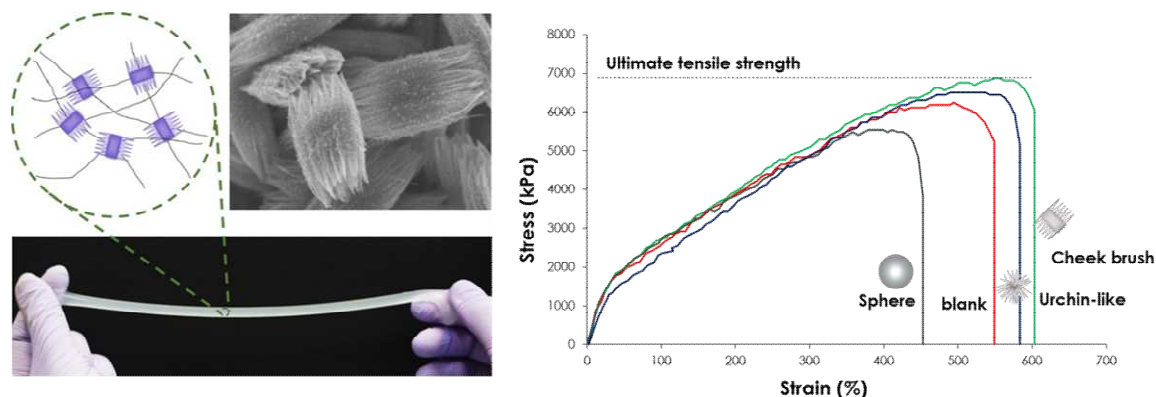


Figure 2. Cheek-brush TiO_2 as a cross-linker for polymer hydrogel and stress–strain curves for 20wt% poly(*N*-isopropylacrylamide) hydrogels without crosslinker and with 0.02wt% differently shaped TiO_2 crosslinkers, i.e., cheek-brush, urchin-like, and spherical (MARIMO).

2. Surface Activation of TiO_2 Spherical Nanoparticle Assemblies by Atmospheric Pressure Plasma Jet and their Photocatalytic Activity Enhancement

Apart from the controllable morphology, one of the most important parameters to decide the nanomaterial applications is their surface properties. Therefore, post treatments of as-prepared materials should be well considered to emerge their intrinsic performance. Then, a selection and adjustment of surface treatment technique and conditions could be also explored through a greater amount of applications of the TiO_2 nanoassemblies.

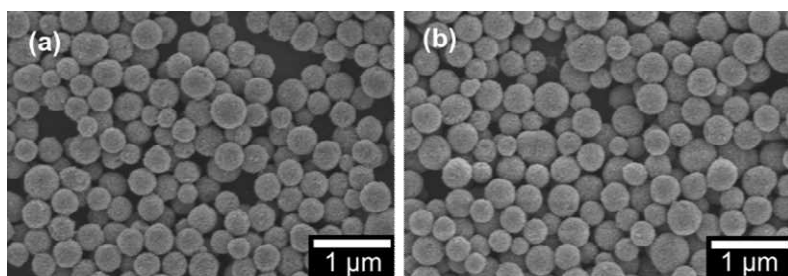


Figure 3. SEM images of MARIMO assemblies before (a) and after (b) plasma treatment.

In the second part of this work, surface activation using atmospheric pressure plasma jet (APPJ) on the one-pot solvothermally synthesized MARIMO assemblies of TiO_2 was studied. The assemblies (Figure 3) have anatase crystals with large surface area derived from their porous structure, which is considered as their advantage capable of being used in various applications including

catalysts.^[2,3] However, some of organic compounds used as additives in the preparation step remained in the final products. In order to remove the contaminants, the treatment by APPJ containing radical and ion species in medium gas flow was employed. The temperature of the species in the plasma jet should be really high judging from their high kinetic energy, however the overall gas temperature is as low as room temperature not to damage the NP fine structures.

A cylindrical dielectric barrier discharge (DBD) system consisted of a 15 cm glass tube with inner diameter of 2.5 mm was used to treat the samples as shown in Figure 4.^[4] Helium gas was fed at a flow rate of 1.6 L/min into the tube and electrical potential was applied using a metallic external electrode to ignite helium plasma. The sample powder was set at 2 cm under the helium outlet. After treatment for optimum time, surface morphology of the NP assemblies were observed by SEM and the crystalline patterns were investigated by XRD. SEM images show that the treated samples completely retained their original morphologies (Figure 3). Also, XRD patterns in Figure 5a resulted in similar shapes comparing the samples with and without the plasma treatments. Quantitative analysis of contaminants was executed using surface assisted laser desorption ionization (SALDI) mass spectroscopy technique. The mass spectra of the NP assemblies (Figure 5b) showed that almost all peaks observed in as-prepared sample were disappeared after the plasma treatment. Hence, I have successfully developed a new method for surface activation of mesoporous NP assemblies.

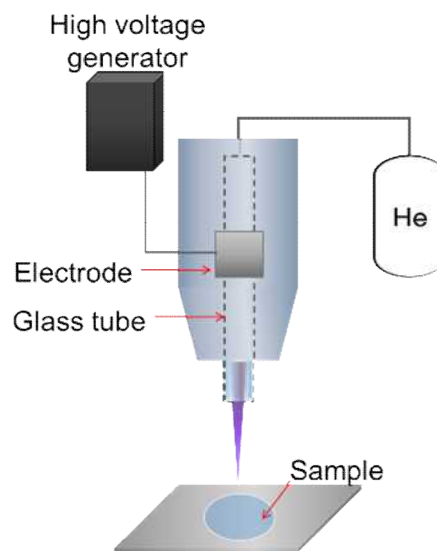


Figure 4. A schematic illustration of APPJ generator.

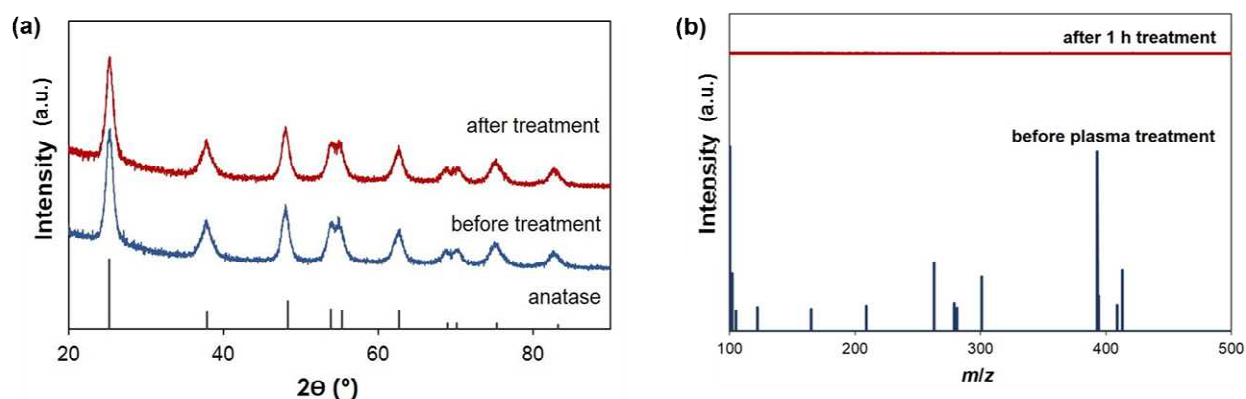


Figure 5. XRD spectra (a), and mass spectra (b) of TiO₂ MARIMO assemblies before and after plasma

Photocatalytic performance of MARIMO assemblies with and without plasma treatments was evaluated by methylene blue (MB) degradation as a model reaction under UV irradiation. An aqueous solution of methylene blue (10 mg/L) containing the MARIMO assemblies was irradiated under UV light at room temperature. The absorbances of the solutions were measured by UV-Vis spectroscopy to follow the methylene blue degradation by the MARIMO assemblies. The plasma treated MARIMO assemblies exhibited the highest activity and degraded 78% of methylene blue in 1 h reaction, while as-prepared assemblies degraded it only 34% (Figure 6). The rate constants increased significantly from 0.0083 to 0.0315 min^{-1} .

Additionally, transient photocurrent response tests were performed to evaluate the effect of the plasma on the photocatalyst activity as an alternative way. The time response of photocurrent generation was measured in a standard three-compartment cell. The working electrodes were made by drop-casting of the MARIMO assemblies on ITO glasses. The electrodes were soaked in aqueous solution of 0.1 mol/L KCl as an electrolyte and 0.1 mol/L triethylamine as a sacrificial electron donor. The responses of as-prepared and plasma treated MARIMO assemblies were recorded for several on-off cycles of UV irradiation. Considering Figure 7, the measured photocurrent of plasma treated MARIMO assemblies were significantly higher than those of the assemblies without the treatment. Especially for the first cycle, the APPJ treatment led to an almost 100% improvement in the activity.

From these results, it can be concluded that the facile treatment of non-thermal helium APPJ activated the surface of the MARIMO assemblies without damage of their morphology and surface properties.

3. High Surface Roughness of Mesoporous Spherical Nanoparticle Assembly of TiO_2 for Supporting Well-dispersed Au Nanoparticle

The last part of this work focuses on another interesting application of the metal oxides, which is a surface modification by depositing nano-sized noble metal catalysts on their surface, particularly the use of metal oxides as catalyst supports. TiO_2 has been widely used as a catalyst support due to its high physical and chemical stabilities. Specially, the MARIMO assemblies consist of fine primary particles of which the average size is less than 5 nm, and high surface area with mesopores in their structure. Their unique surface roughness from their fine primary particles resulted in plausibly high surface defects, which are expected to disperse metal nanoparticle well.

Meanwhile, catalyst sintering is one of the most serious problems of catalyst deactivation. A major cause of the sintering is a nanoparticle migration, which usually occur at high temperature due to an increase of the catalyst mobility, leading to the particle growth into large size and the decrease of active sites on the catalysts. To prevent the sintering, confinement of catalyst NPs by support material

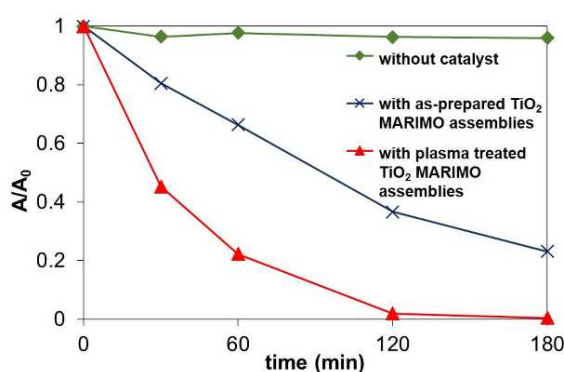


Figure 6. Photocatalytic degradation of methylene blue over as-prepared and plasma treated MARIMO assemblies of TiO_2 .

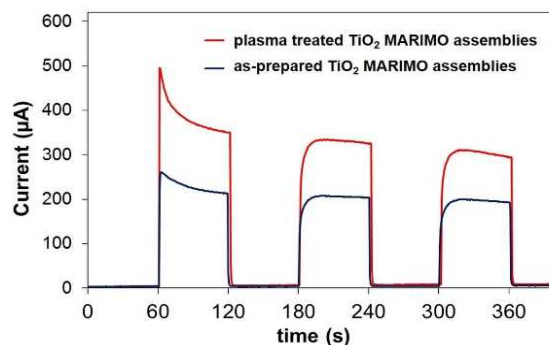


Figure 7. Transient photocurrent response over as-prepared and plasma treated MARIMO assemblies of TiO_2 .

structure is considered as one of the strategies. On the other hand, good-dispersion and strong interaction of metal NPs on the support are crucial factors to prevent the sintering. Then, I propose a hypothesis of the synthesized MARIMO assemblies of TiO₂ as an effective and stable catalyst support to prevent catalyst sintering, whose metal particles will be isolated and will not easily migrate to aggregate together (Figure 8).

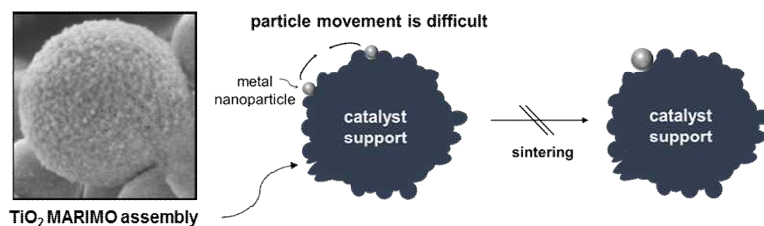


Figure 8. An illustration indicating high surface roughness of TiO₂ MARIMO assembly for sintering prevention of metal NPs.

Au catalysts (1wt% and 5wt%) on different kinds of TiO₂ supports (MARIMO, ST-01, and P25) were prepared by conventional deposition-precipitation method using chloroauric acid as Au source in aqueous dispersion of TiO₂.^[5] TEM and HAADF-STEM images of the obtained TiO₂ supported Au NP catalysts clearly indicate excellent dispersibilities of Au NPs on both synthesized MARIMO and a reference ST-01 TiO₂ (Figure 9). However, several aggregation of Au clusters were observed in Au/ST-01 (Figure 9c, d). Similar aggregation of Au clusters was also observed in the case of Au/P25. The Au amounts were estimated by HAADF-STEM/EDX or STEM/EDX analyses as listed in Table 1. For Au/P25 catalysts with smaller specific surface area comparing to both of MARIMO and ST-01, total amounts of Au loading resulted in significantly lower than those in the precursor mixtures, which can be ascribed to leaching of Au NPs from the surface of P25 during washing process in the preparation step. The result indicates that wider surface area and/or nanoscale surface concave-convex structure originated from their small primary particle size would catch and fix larger amounts of Au NPs on the surface.

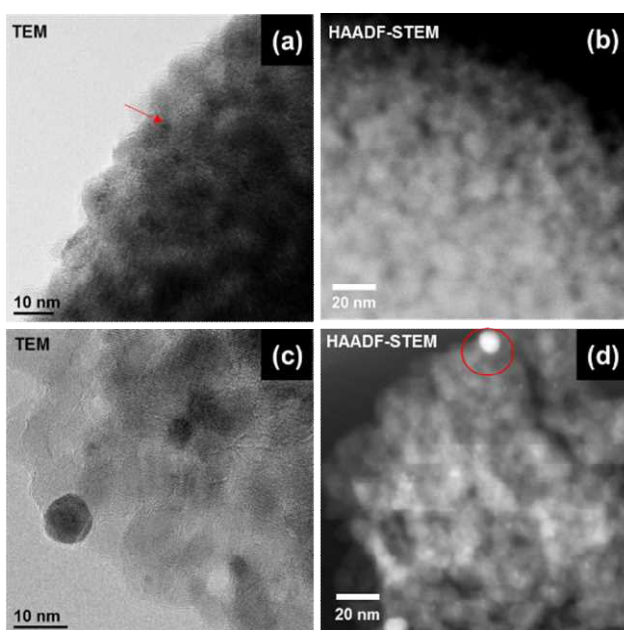


Figure 9. TEM and HAADF-STEM images of 1wt% Au/MARIMO (a, b), and Au/ST-01 (c, d).

An extremely exothermic CO oxidation reaction was performed as a probe reaction using the prepared Au/TiO₂ as catalysts. CO conversions in Figure 10a show high activity of 1wt% Au on

Table 1. Au/TiO₂ catalyst information.

Sample name	Support	in precursor solution	Au content (wt%)		
			EDX measurements of catalysts		
			As-prepared	After cycle test	After CO oxidation at 400 °C
1-Au/MARIMO	MARIMO TiO ₂	1	2.0	1.9	2.0
5-Au/MARIMO	MARIMO TiO ₂	5	6.2	6.1	6.3
1-Au/ST01	ST-01 TiO ₂	1	1.8	1.0	1.6
5-Au/ST01	ST-01 TiO ₂	5	7.6	6.8	8.3
1-Au/P25	P25	1	0.0	-	0.3
5-Au/P25	P25	5	4.4	~5-2.3	3.3

MARIMO support even at lower temperatures of 60 °C as compared to those of other kinds of support. Especially, in the case of high surface area ST-01 support with good Au dispersion, the reaction started at the temperature around 120 °C with CO conversion of 65 %. For P25 support, however, lower

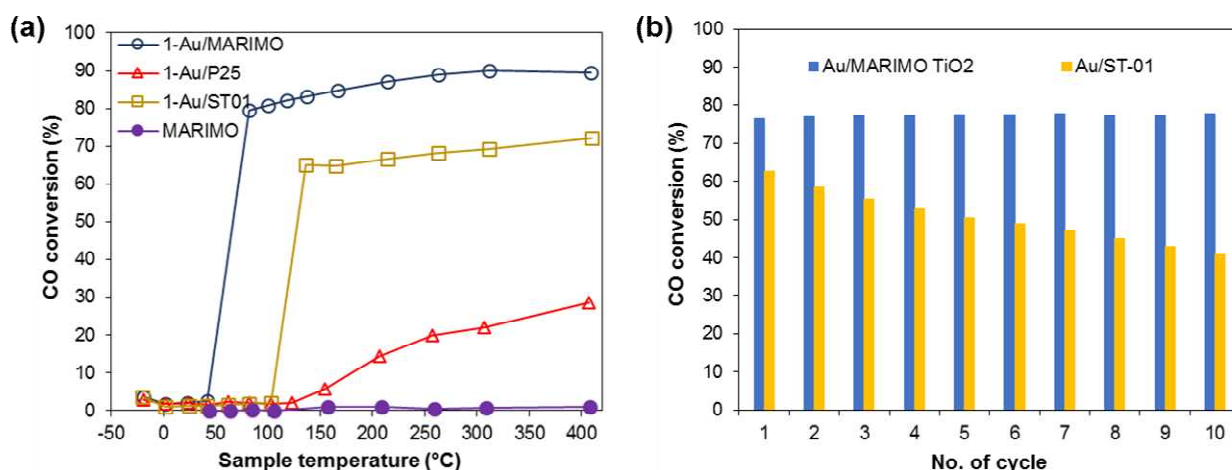


Figure 10. CO conversion obtained at different reaction temperature (a), and during cycle test (b) of CO oxidation using different type of Au/TiO₂ catalysts.

conversion was observed through all temperature.

Stability and durability of the catalysts were tested by repeating high (140 °C) and low temperature (0°C) reactions alternatively for 10 times. CO conversion shown in Figure 10b confirmed the significantly higher stability and durability of Au/MARIMO without significant change in CO conversion (0.9%) comparing to that of Au/ST-01 (35%) after 10 cycles of reaction.

The results clearly prove an effective ability for sintering prevention of metal nanoparticle by using the MARIMO assemblies as a support material, which affords and maintains high catalytic activity of the catalyst.

Summary

In summary, TiO₂ NP assemblies with controlled morphology were prepared by the solvothermal method and the applications of each assemblies depended on their morphology and surface properties. TiO₂ NP assemblies with three-dimensional branch morphology named “cheek-brush” were successfully synthesized and their growth mechanism and application as a crosslinker to improve mechanical strength of polymer hydrogel were proposed. Surface activation was confirmed by facile treatment using helium APPJ on the MARIMO assemblies of TiO₂, where photocatalytic activities were significantly improved without any damage in morphologies and surface properties. The assemblies having unique surface roughness originated from their fine primary particles showed an excellent ability as a catalytic support. The assembly surface provided high dispersibility of metal NPs and high stability of them under high temperature conditions, resulting in high catalytic activity and durability of the catalyst.

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