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Innovative one-step immobilization of TiO_2 on polymer material by the sol–gel method under IL/MW conditions

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Abstract An innovative one-step immobilization of titanium dioxide (TiO_2) nano-particles on organic polymer (PMMA) substrate at ambient condition is reported in this article. This immobilization can be achieved by the sol–gel method under ionic liquid/microwave heating conditions. In this method, a sol–gel reaction is conducted at specific sites of the polymer surface. These sites are the tiny cavities of the rough surface resulting from the softening and swelling effect of an alcohol, such as isopropyl alcohol, on the polymer surface under microwave irradiation. The roughness of the polymer surface is an important factor for the effective immobilization. In addition, ionic liquid can induce low temperature surface anatase crystallization of immobilized titanium dioxide in a short time. From the field emission scanning electron microscopy and energy dispersive spectroscopy observation, the TiO_2 particles could be effectively immobilized on the PMMA substrate. Raman spectra analysis data showed that the immobilized TiO_2 was anatase phase. The experimental data also shows that the immobilized TiO_2 prepared by this novel method has good immobilization stability and photocatalytic water treatment performance.

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Introduction

Over the past two decades, ionic liquid (IL) has received significant attention in both academic research and industrial application due to its low-melting point (below 100 °C) and negligible vapor pressure at elevated temperature [1]. In material chemistry, it can be used as a green reaction medium for inorganic material synthesis [1–3]. Zhou et al. first synthesized TiO_2 nanocrystals by adding of a $TiCl_4$/IL mixture to water [4]. The group of Dr. D. Dionysiou systematically studied the preparation and characterization of mesoporous TiO_2 by sol–gel method with reaction of titanium tetraisopropoxide and water in the presence of IL [5, 6]. In our previous study, we found out that anatase TiO_2 nano-particles can be obtained at a relatively lower anatase crystallization temperature (around 80–150 °C), especially when the IL has a higher water-adsorbing ability. In such a system, the IL plays an important role in driving the surface crystallization of amorphous TiO_2 to the anatase phase by retaining a suitable amount of water through a dissolution–crystallization mechanism in the thermal annealing process [7, 8].

Ionic liquid has good microwave absorption ability. The ionic liquid coupled with microwave heating (IL/MW) method is widely used for organic synthesis by organic chemists [9]. The main advantages of the IL/MW method

are high reaction rate and reaction product homogeneity. In recent years, IL/MW method had come to be a new and fast route for producing inorganic crystalline nanomaterials [10]. Ding et al. first reported the synthesis of anatase TiO_2 by the sol–gel method under IL/MW conditions. They showed that this method can be developed into a general way to synthesize metal oxide nanocrystals [11].

In photocatalytic water treatment applications, anatase TiO_2 particles can be directly suspended in aqueous phase or immobilized on a substrate support [12]. In suspension-type applications, an additional step is necessary to separate TiO_2 particles from the suspension, which increases operation costs. Hence, the development of immobilized TiO_2 on a substrate support has come to be an active topic in recent years. Due to the high calcination temperature (generally above 400 °C) required to form anatase TiO_2 [13], high temperature-resistant inorganic materials, such as glass, steel, and the like, are required in the one-step (synthesis and immobilization at same process) immobilization of anatase TiO_2 particle by the sol–gel process. This is an expensive and energy-intensive process, and its commercial application is currently at a bottleneck. Accordingly, low cost organic polymer material has been considered as an immobilizing support material. Owing to the thermal sensitivity property of organic polymer materials, the immobilization of anatase TiO_2 on the organic polymer material is generally carried out by a two-step process [14]. In this two-step process, anatase TiO_2 nanoparticle product is first synthesized, and its dispersion is then spread or deposited on the polymer materials by an appropriate method [15–19]. However, anatase TiO_2 nanoparticles are easily aggregated and difficult to disperse homogeneously in these methods [20], allowing TiO_2 nano-particles to be easily scratched from the polymer material. Therefore, this immobilization technology of TiO_2 nano-particles on organic polymer materials become to be not commercially feasible.

In this article, an innovative one-step TiO_2 nano-particle immobilization on polymer materials under IL/MW conditions was reported. Based on the multiple IL characteristics, including structure-ordering, lower temperature anatase crystallization, and high microwave absorption ability, TiO_2 nano-particles can be synthesized and immobilized simultaneously on polymer material at ambient condition in a short time. The photocatalytic water treatment performance of the immobilized TiO_2 is also demonstrated in this article.

Experimental

The materials used in this experiment included titanium tetraisopropoxide (TIP) (Aldrich), isopropyl alcohol (IPA) (J. T. Barker), and IL. The IL used was hydrophilic 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]^+[BF_4]^-$) (Merck). Polymethyl methacrylate (PMMA) (CM-207) was supplied from Chi Mei Corporation, Taiwan. In the immobilization experiments, the molar ratio of the reaction mixture was $TIP:IPA:IL:H_2O = 1:3:1:100$. Deionized water was added to the reaction mixture of TIP, IPA, and IL and the mixture containing several virgin PMMA chips. The mixture was stirred and then microwave irradiated for 30 min at a microwave power of 800 W and a frequency of 2.45 GHz.

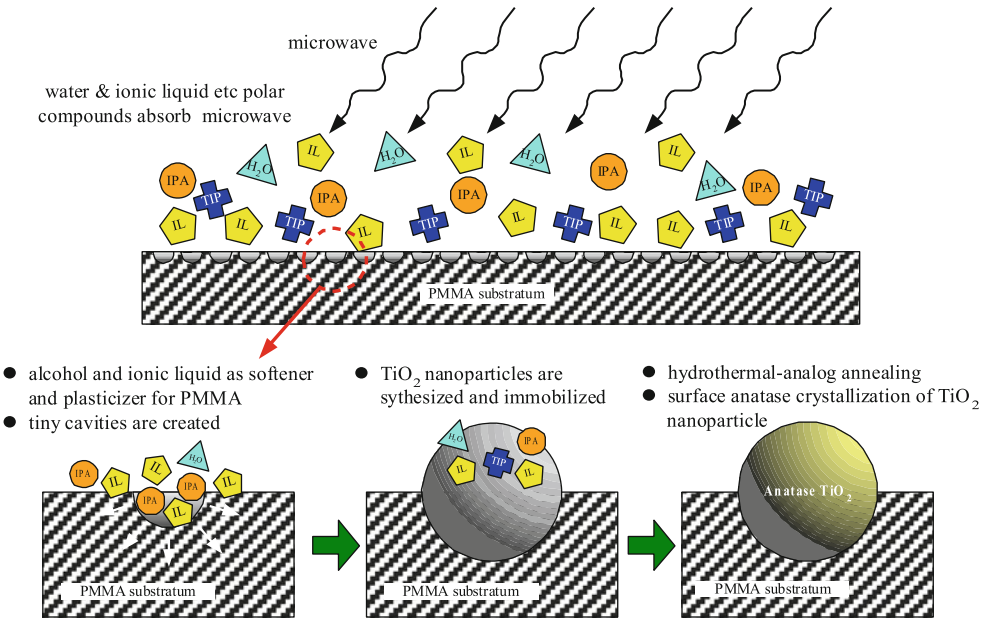
The microwave device used for sample preparation was equipped with an Milestone START D MR system (power 800 W) from Milestone Srl, Italy. It was fitted to a water reflux condenser (cooling water temperature was 10 °C) for operation at atmospheric pressure. The microwave reactor vessel had a volume of 500 mL. The temperature of the reaction system during irradiation was monitored online using infrared sensors connected to a computer.

The sample's surface topography was investigated by contact mode atomic force microscope (AFM) using a Nanoscope IIIa (Digital Instruments). Samples were imaged using a cantilever with a spring constant of 0.06 N/m and a silicon carbide pyramidal-tip of 20 nm radius. All measurements were taken in air with a resolution of 512 × 512 data points. The surface morphology and energy dispersive spectroscopy (EDS) of the TiO_2/PMMA samples were examined by the field emission scanning electron microscopy (FESEM) using a JSE-6500F instrument. The crystal phase of immobilized TiO_2 on PMMA chip was characterized by Raman spectroscopy using a Horiba Jobin–Yvon LabRam HR800 spectrometer. The laser source was used 632.8 mm HeNe laser at a power of 17 mW.

Results and discussion

The conceptual diagram of our one-step immobilization of TiO_2 on the polymer material is depicted in Scheme 1. The polymer can be thermoplastic polymer such as PMMA and the like. Thermoplastic polymers are commonly considered as microwave transparent materials [21]. Using these polymers, only the polymer surface containing polar compounds such as water, IL, and alcohol, etc., are microwave superheated in our system. Accordingly, the temperature of the polymer material can be kept below the polymer's glass transition temperature (T_g) (the T_g of PMMA is 116 °C). Hence, the dimensional stability and mechanical properties of the whole polymer material are not affected.

In our one-step immobilization method, IL and IPA may act as plasticizer or softener of PMMA when microwave is



Scheme 1 Conceptional diagram of one-step immobilization of TiO_2 nano-particles on a thermoplastic polymer by the sol–gel method under IL/MW conditions

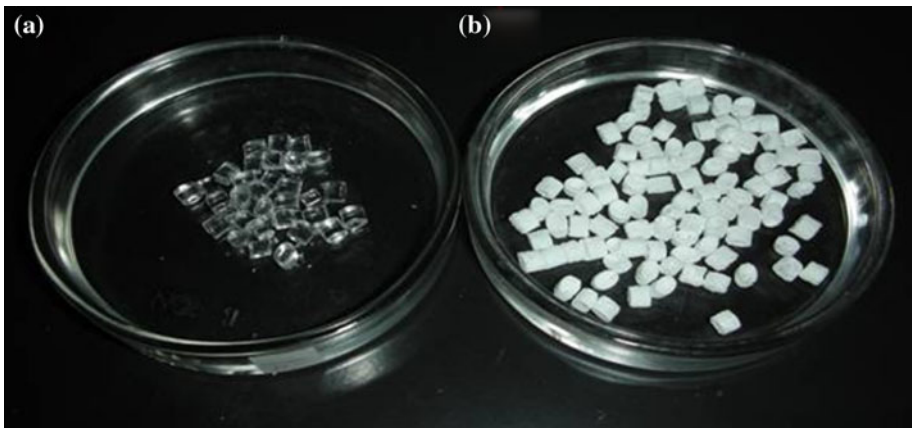


Fig. 1 Pictures of virgin (*left*, **a**) and immobilized (*right*, **b**) PMMA chips, with a TIP:IPA:IL:H_2O = 1:3:1:100 M ratio

applied [22]. As shown in Scheme 1, the polymer surface becomes rough and creates many tiny cavities under local microwave superheating. The sol–gel reaction occurs to form the TiO_2 nano-particles, which are then immobilized directly in the tiny cavities on the polymer surface. When TiO_2 nano-particles are immobilized, the surface anatase crystallization of the TiO_2 nano-particle can occur. This crystallization is resulted from the hydrothermal-analogy anatase crystallization effect of the IL. The remaining water and IL around the amorphous TiO_2 nano-particles are the critical components for this surface anatase crystallization [7].

In one typical immobilization experiment, the reaction mixture containing TIP, IPA, IL, H_2O, and virgin PMMA chips, as shown in Fig. 1a, was stirred and then microwave irradiated for 30 min. The PMMA chips after immobilization are shown in Fig. 1b. We found that the

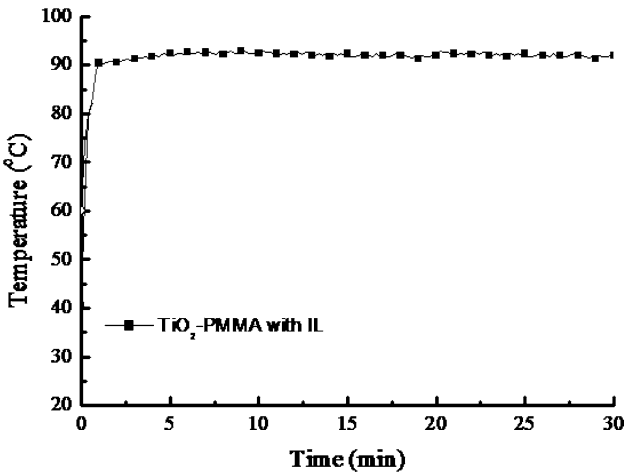


Fig. 2 Temperature profile of the TiO_2/PMMA immobilization process with a TIP:IPA:IL:H_2O = 1:3:1:100 M ratio. The reaction temperature under 100 °C is shown

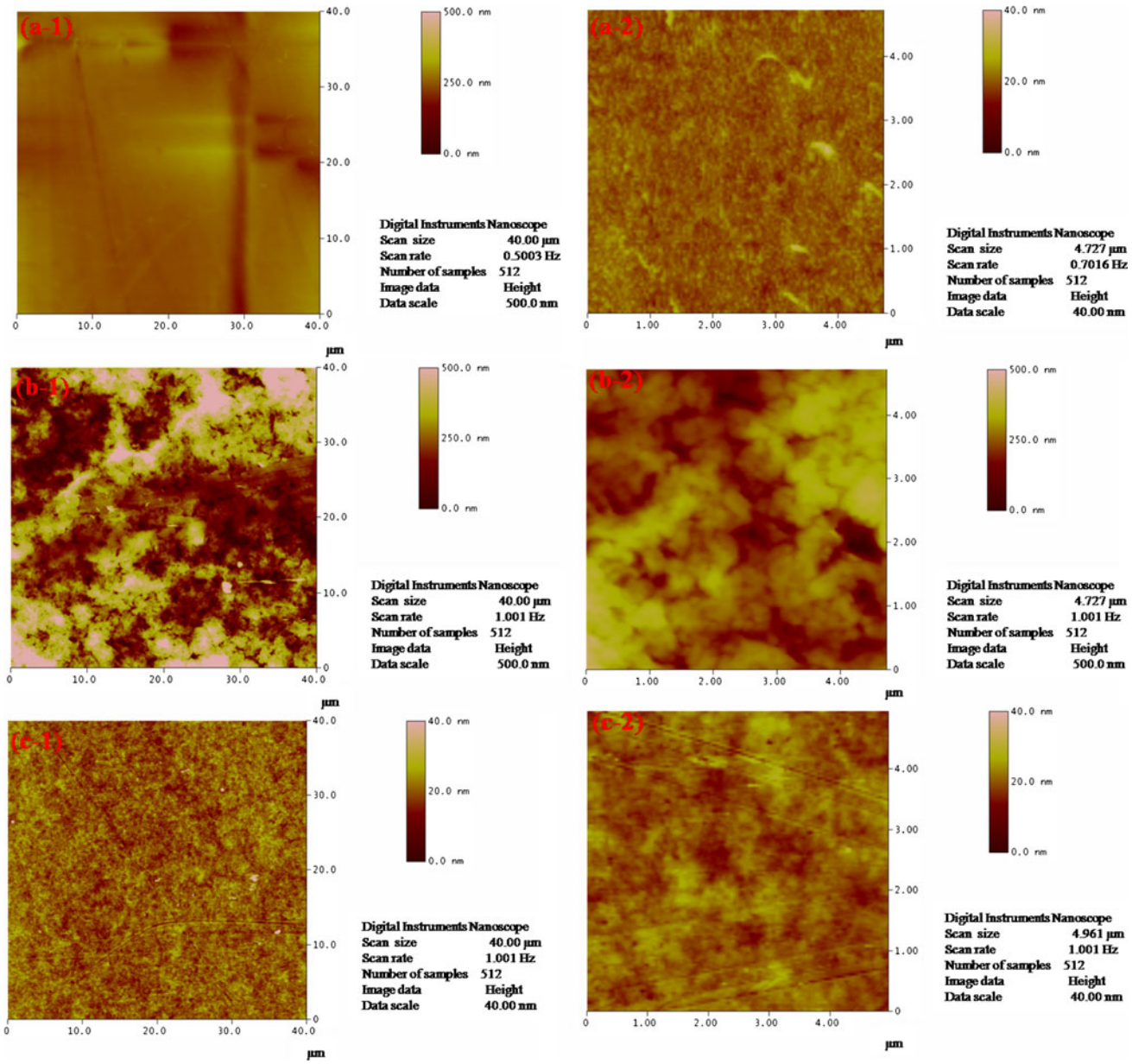


Fig. 3 AFM phase images of the PMMA chip mixing with IPA or ionic liquid under microwave heating for 30 min, **a-1**, **a-2** virgin PMMA at different magnification levels, **b-1**, **b-2** with IPA after microwave heating at different magnification levels, **c-1**, **c-2** with ionic liquid after microwave heating at different magnification levels

immobilization strength between the TiO_2 nano-particles and the polymer material was still retained after 30 min of ultrasonic treatment. The temperature profile data reveal that the temperature of the reaction site was below 100 °C, as shown in Fig. 2.

As described in above section, IL and IPA may act as plasticizer or softener of the PMMA under local microwave superheating. However, it is important to know that which one is the main softener that can create rough polymer surface under IL/MW conditions. This can be determined by AFM study. AFM is often used to measure the roughness of material and the surface roughness can be quantitatively analyzed using AFM images [23]. Quantitative AFM pictures and data for the roughness average (R_a) of our softened sample treated by IPA and IL are shown in Fig. 3. The AFM image of the surface of a virgin PMMA chip is shown in Fig. 3a, which shows a R_a roughness of 2 nm. An AFM image of the surface of PMMA chip treated by IPA for 30 min under microwave irradiation is shown in Fig. 3b, showing a R_a roughness of 80 nm. An AFM image of the surface of PMMA chip treated by $[Bmim]^+[BF_4]^-$ for 30 min under microwave irradiation is shown in Fig. 3c. Unlike the IPA case, the R_a roughness of the surface is only 2–5 nm. These results

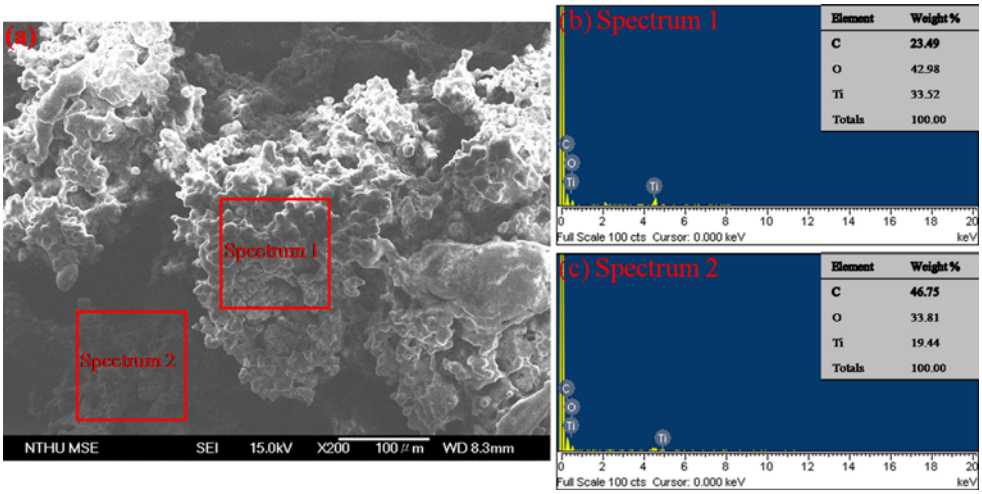


Fig. 4 SEM and EDS analysis of the TiO_2/PMMA chip after ultrasonic treatment. **a** SEM micrograph of the TiO_2/PMMA chip surface, **b** and **c** EDS analysis of the TiO_2/PMMA chip surface at different selection ranges

indicated that the IPA actually acted as a main softener for the polymer surface. This is probably caused by the adsorption and diffusion of lower molecular weight IPA producing a softened and swollen polymer surface under microwave irradiation [24]. As a result, the weak bond between the polymer chains was broken and then the tiny cavities leading to rough surface were formed. More irregular surfaces are more readily covered by TiO_2 nano-particles, providing greater interfacial contact between the TiO_2 nano-particles and the polymer surface of tiny cavities. Hence, increasing the surface roughness can enhance the immobilization strength and stability in our system [25].

Morphology and structure analysis of TiO_2/PMMA chip

The SEM pictures and element distribution by EDS analysis of one immobilized TiO_2/PMMA chip after ultrasonic treatment are shown in Fig. 4. The EDS results in Fig. 4b, c indicate that the surface was covered with irregular TiO_2 clusters and contained about 20–33 wt% of Ti. The crystal phase of the immobilized TiO_2 was investigated by Raman spectroscopy. The Raman spectra of virgin PMMA and immobilized TiO_2/PMMA chip are shown in Fig. 5. In the immobilized TiO_2/PMMA chip, the frequencies of Raman bands are identified as follows: 147.3 and 628.8 cm^{-1} (E_g), 392.8 and 513.14 cm^{-1} (B_{1g}), 515.2 cm^{-1} (A_{1g}). These data indicated that the surface of immobilized TiO_2 shows the anatase characterization [26].

Photodegradation test

The photocatalytic water treatment experiment of our immobilized TiO_2 was carried out as follows. First,

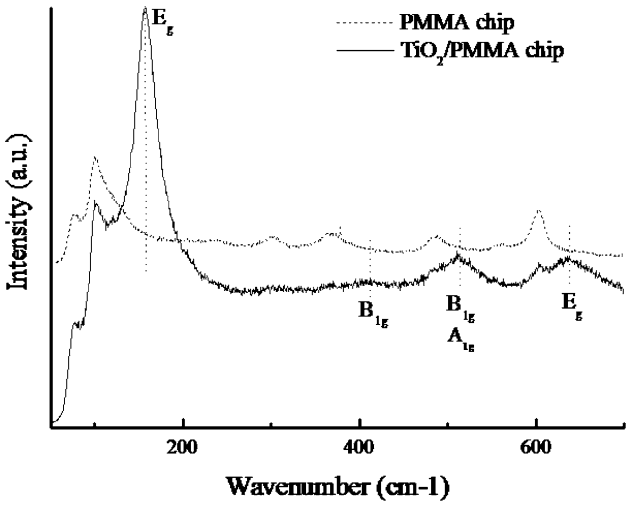


Fig. 5 Raman spectra of the PMMA chip and TiO_2/PMMA chip after ultrasonic treatment

300 mL of aqueous solution with 5 ppm methylene blue (MB) was prepared. Several immobilized TiO_2/PMMA chips were placed in this solution and irradiated by UV. The UV light was applied with a wavelength of 365 nm and a light intensity of 13 W. The total irradiation time was 6 h. An aliquot sample was taken for analysis every 1 h, and the results are shown in Fig. 6. From the results of Fig. 6, it can be seen that the immobilized TiO_2 sample prepared by our novel method has significant removal efficiency of the target compound to over 80% after 4 h.

Conclusion

A novel technology for the simultaneous synthesis and immobilization of TiO_2 nano-particles on the surface of

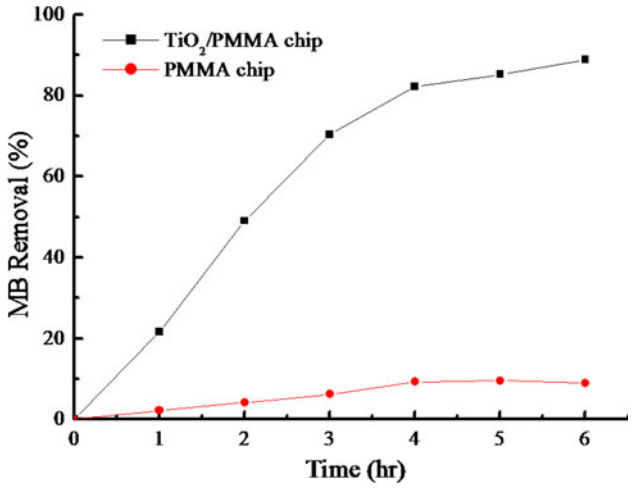


Fig. 6 Photodegradation of methylene blue in aqueous solution containing PMMA chips with or witohut immobilized TiO_2, with a TIP:IPA:IL:H_2O = 1:3:1:100 M ratio under UV irradiation

polymer materials by the sol–gel method under IL/MW conditions is reported. Combining with the multiple characteristics of IL, including structure-ordering, high microwave absorption ability, and lower temperature anatase crystallization, TiO_2 nano-particles can be effectively immobilized on a polymer surface under ambient conditions in a short time. The roughness of the polymer surface is an important factor for the effective immobilization. The surface roughness primarily results from the softening and swelling effect of an alcohol, such as IPA, on the polymer during microwave irradiation. In our water treatment experiment, the resulting immobilized TiO_2 sample exhibits significant removal efficiency of the target compound efficiency.

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