Original Article

Preparation of a Floating Photocatalyst *via* Electroless Ni-P-TiO₂ Composite Plating on Polypropylene Balls for Wastewater Treatment

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ABSTRACT

Application of photocatalysts is among the most promising methods to eliminate organic pollutants in wastewater. A photocatalytic reaction, which involves the generation of reactive radicals from the reaction on the photocatalyst's surface and their interaction with organic molecules, can degrade organic pollutants. Titanium dioxide (TiO₂) is a well-known photocatalyst because it has low toxicity and cost including high chemical stability. However, it cannot be efficiently activated in water because of the difficulty in adsorbing ultraviolet light. In this work, a floating photocatalyst was prepared by combining TiO₂, Ni-P plating, and a polypropylene (PP) hollow ball substrate. An Ni-P coating was electrolessly deposited on the PP hollow ball in the presence of TiO₂. The prepared photocatalyst was characterized using X-ray diffraction and scanning electron microscopy–energy-dispersive X-ray spectroscopy. The PP hollow ball substrate was sufficiently covered with the Ni-P coating and Ti was confirmed to be contained in the Ni-P coating. The obtained specimen floated when placed in aqueous solutions and its photocatalytic activity was confirmed through degradation of methylene blue. In addition, the Ni-P plating was found to protect PP from degrading by photocatalytic activity of the TiO₂.

Keywords: electroless Ni-P plating, photocatalysis, wastewater treatment, TiO₂

INTRODUCTION

Over the years, problems caused by wastewater produced from hospitals, industries, and our daily lives have continually increased. Particularly in the textile industries, wastewater containing chemicals applied during wet processes are generated, *i.e.* dyes, surfactants, soaps of metals, acids and alkalis- [1]. The hazardous contaminants in this wastewater have an impact on living things that consume the water resulting in diseases and weakening. Therefore, wastewater should be treated at onsite facilities to ensure remediation before release into the local environment. Various methods have been attempted to treat wastewater, including the usage of *Moringa oleifera* as a natural coagulant [2], the utilization of activated carbon for adsorbing metal ion contaminants [3,4], and removal of organic dyes using a photodegradation process [5,6]. Among these methods, the photodegradation

process may be more promising because it is green, economical, and low in energy and in toxic solvent consumption.

A highly efficient photocatalyst was applied to enhance the photodegradation ability, particularly titanium dioxide (TiO₂) [7]. Titanium dioxide is a broad band gap semiconductor having good chemical stability and low toxicity. In nature, TiO₂ presents three crystalline forms, anatase, rutile, and brookite, that exhibit different properties. The anatase form is considered the best photocatalyst because it has the largest band gap, approximately 3.23–3.59 eV, between the valence band and conduction band, while the rutile form has a gap of approximately 3.02–3.24 eV [8,9]. In the field of photocatalytic reactions, AEROXIDE® P25 TiO₂ powder produced from Evonik Industries is a commercial material extensively used for enhancing process ability. It contains approximately 70–80% w/w anatase and a small amount of rutile. According to the literature reported by Hurum *et al.*

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Received: June 29, 2018, Accepted: November 30, 2018, Published online: June 10, 2019

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Fig. 1 Basic principle of the photocatalytic activity of TiO₂ including the proposed model of a rutile antenna and subsequent charge separation rewritten from the report of Gray *et al.* [10].

[10], the mixed phase of the crystals results in the P25 TiO₂ having excellent photocatalytic activity because the rutile phase acts as an antenna for extending the photocatalytic activity into visible wavelengths and the structural arrangement of the same size of TiO₂ at the rutile-anatase interface [10]. The basic mechanism of the photocatalytic reaction occurring on the TiO₂ surface is shown in Fig. 1.

Although the nano-powdered TiO₂ exhibits great performance owing to its high specific surface area, it is difficult to separate it from the medium after usage and it cannot be easily reused. In addition, the sinking of TiO₂ powder in the medium drastically decreases the possibility of ultraviolet (UV) light contact, resulting in low photocatalytic activity. Therefore, TiO₂ film coated on substrates such as glass have been prepared to solve this problem [11]. Furthermore, hollow substrates that float on the medium may also be a promising means to overcome this drawback.

Polypropylene (PP) is among the abundant polyolefins widely used in the world because it has high chemical resistance, low density, and high tensile strength [12]. Polypropylene has been widely used in many applications such as packaging, toys, bottles, and automotive components. Because of its very low density (approximately 0.91 g/cm³ [13]) and good mechanical properties, PP was chosen to be used as a substrate for creating a floating TiO₂ photocatalyst in this study. However, Garcia *et al.* [14] have reported the degradation of TiO₂ nanoparticles incorporated into PP film

Fig. 2 Mechanism of the photo-oxidative degradation of PP in the presence of a hydroxyl radical generated from the photocatalysis on the TiO₂ surface. This figure is modified from the previous work reported by Garcia *et al.* [14].

under xenon lamp radiation. They found that the film lost its weight and some carbonyl groups were generated [14]. The proposed mechanism for the photodegradation of PP film is shown in Fig. 2. The photo-oxidative degradation occurring on the TiO₂ surface caused a chain scission, a reduction in chain size, and generation of some chromophores on the polymer surface leading to a higher photodegradation ability resulting in crack formation as well as a decrease in mechanical properties [15,16]. These observations agreed with

the results reported by Curcio *et al.* [17]. The pro-oxidant additive in PP, however, acts as an initiator for photo-oxidative degradation leading to a decrease in melting point and chain scission of PP polymer chains causing damage to the substrate [1]. To solve this problem, a coating of a protective layer on the PP substrate was ruminated for avoiding the direct attachment between TiO₂ nanoparticles and the PP substrate. An electroless Ni-P coating on PP has received considerable attention due to its outstanding properties such as excellent corrosion and fouling resistance [18], high hardness and wear resistance [19], as well as low cost and manufacturing ease [20]. The basic component for the electroless bath includes a metal ion source, a reducing agent, complexing agent (s), a bath stabilizer, and a pH-adjusting solution. Generally, for electroless deposition, metal ions are reduced to metal by the reducing agents. The reducing agents act as electron donors; meanwhile, the metal ions act as electron acceptors. There have been reports that the codeposition of composite materials such as SiC, TiO₂, Al₂O₃, and diamond can improve the mechanical and physical properties of coatings compared to the electroless Ni-P coating [21,22], termed electroless composite coatings. An electroless Ni-P composite coating has been widely applied in several fields, for example, during the rapid water-oil separating process [23].

In the present work, we report the preparation of a floating electroless Ni-P-TiO₂ composite plated on PP balls (NiPTi-PP) for use as a photocatalyst in wastewater treatment. The effects of pH and the amount of TiO₂ nanoparticles in the plating bath on the incorporation ability of TiO₂ on the PP surface were studied. The Ni-P-TiO₂ composite coatings were investigated using X-ray diffraction (XRD) and scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX) techniques. The photocatalytic activity of TiO₂ was also studied using methylene blue (MB) as an organic dye model.

MATERIALS AND METHODS

Materials

A polypropylene (PP) ball with a diameter of 3.2 mm was purchased from AS ONE Co., Japan. Nickel (II) chloride hexahydrate (NiCl₂·6H₂O), tri-sodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O), sodium phosphinate monohydrate (NaH₂PO₂·H₂O), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), o-xylene (C₆H₄(CH₃)₂) and chromium (VI) oxide (CrO₃) were purchased from Nacalai Tesque, Inc., (Kyoto, Japan). An alkaline solution (EC-B), a conditioner (PB-119S), and a catalyzer (CT-580) were commercial chemicals

provided by JCU Co., (Tokyo, Japan). Methylene blue was purchased from Chameleon Reagent, Japan. AEROXIDE® P25 TiO₂ was purchased from Evonik Industries AG, (Essen, Germany). Titanium Tetraisopropoxide (TTIP) was purchased from Wako Pure Chemical Industries, Ltd., (Osaka, Japan). All chemicals were used without further purification.

Preparation of an electroless Ni-P-TiO₂ composite plated on PP balls (NiPTi-PP balls)

The surface of the PP balls, the substrate, was pre-treated prior to electroless plating in the composite bath. Because the low density (0.91 g/cm³) of the PP balls made them float, they were constantly stirred in all solutions to ensure homogeneous contact with their surfaces. The pretreatment of PP surface was performed as follows;

Firstly, the organic solvent on PP balls was removed by washing the PP balls in an EC-B solution at 40°C for 3 min. Secondly, they were soaked in o-xylene at 70°C for 30 min in order to weaken the PP surface and further making the surface roughness by pickling in a solution containing 300 g/L CrO₃ and 200 mL/L H₂SO₄ at 70°C for 10 min. Then, the balls were roughed again in the PB-119S followed by activating in a CT-580 solution and accelerated in a 20% v/v H₂SO₄ solution at 40°C for 3 min during all steps. Note that the balls were thoroughly washed with distilled water before passing on to each step.

The bath composition and plating parameters performed in this work are listed in **Table 1**. Before plating, the composite was sonicated at room temperature for 1 h. The pretreated PP balls were placed into the bath under magnetic stirring at 500 rpm. The conventional electroless Ni-P coating (NiP-PP) was also prepared for comparison to the same bath composition and parameters except for the addition of P25 TiO₂ powder. The pH value of the plating bath was adjusted using diluted NaOH solution and H₂SO₄ solution. After plating, the specimens were rinsed and further stirred in distilled water for 5 min to remove the poor attachment of the TiO₂. Finally, they were air-dried and maintained for further characterization.

Characterization of the coatings

The surface morphology and the cross section of the coatings was observed using a JSM-6330F SEM provided by JEOL, (Tokyo, Japan). An EDX attachment was employed for elemental chemical analysis. The structure of the coatings was investigated using XRD carried out on a diffractometer (UltimaIV, Rigaku Co., Akishima, Japan) equipped with a Cu-K α radiation source ($\lambda = 1.5405 \times 10^{-10}$ m). The

Table 1 Bath composition and plating parameters for electroless NiPTi-PP plating.

Bath compositions and plating parameters	Quantity
NiCl ₂ ·6H ₂ O	18.328 g/L
NaH ₂ PO ₄ ·H ₂ O	48.18 g/L
C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O	45.579 g/L
P25 TiO ₂ powder	0, 15, 30, 45, 60 g/L
Temperature	80 ± 2°C
pH value	5.0, 6.0, 7.0, 8.0, 9.0 ± 0.02
Plating time	20 min

acceleration voltage, acceleration current, scanning rate, and measured 2θ range were 40 kV, 30 mA, 2.0°/min, and $20^\circ \leq 2\theta \leq 60^\circ$, respectively.

Photocatalytic activity test of NiPTi-PP balls

The photocatalytic activity of the specimen was evaluated using their photodegradation ability against an MB solution of 2 mg/L. A 22-W UV lamp (254 nm), which was purchased from AS ONE Corporation (Osaka, Japan), was utilized as the light source. The MB solution was poured into a container and the distance between the lamp and the liquid was 5 cm. The photodegradation of the dyes begin after their sufficient adsorption on a photocatalyst in darkness. During a typical procedure, 10 balls of NiPTi-PP were floated in 10 mL of MB solution. The MB solution was stirred in the dark for 30 min to reach an adsorption/desorption equilibrium. Before each irradiation interval, the UV lamp was turned on for 3 min to achieve a constant level of radiation intensity of UV light. Then, the MB solution in the presence of NiPTi-PP balls was placed under the irradiation of UV light for 2 h. The depth of the MB solution was 1.5 cm. After a given time, the irradiated MB solution was subjected to a UV-2450 spectrophotometer (Shimadzu Co., Japan) for UV-vis analysis. The MB concentration was determined at a wavelength of 664 nm. The photocatalytic activity of NiPTi-PP was observed *via* the calculation of the residual MB concentration. The photodegradation test was repeated 3 times for each condition to ensure its accuracy and their statistical significance was validated by performing analysis of variance (one-way ANOVA).

Protection of PP substrate from photodegradation taking place on TiO₂ surface

In order to investigate whether the Ni-P plating could protect the degradation of PP ball caused by the photocatalysis on TiO₂ surface or not, the UV experiment of three specimens was carried out. All specimens were pretreated

to make the surface roughness with the same procedure as the preparation of NiPTi-PP balls that was described previously until soaking in the PB-119S solution. The pretreated balls were called “PP ball without any coatings”. To study the effect of TiO₂ on the degradation of PP ball, the pretreated PP ball was dipped into TiO₂ precursor sol (ITTIP:100H₂O:3EtOH:0.2HCl) for 5 times and dried in the oven at 110°C for 12 h to obtain TiO₂ film-coated PP ball. Finally, TiO₂ film coated on Ni-P-plated PP ball was prepared to confirm the protection of PP degradation from TiO₂. The pretreated PP ball was electrolessly plated in Ni-P solution bath with the same condition as NiPTi-PP ball except for the introduction of P25-TiO₂ powder. Then it was dipped into TiO₂ precursor sol using the same procedure that was used to prepare TiO₂ film-coated PP ball.

For UV experiment, all specimens were put into distilled water and further exposed to UV light for 6 h. The appearance as well as surface morphology of all specimens before and after UV irradiation were observed by SEM.

RESULTS AND DISCUSSION

It is noted that successful electroless composite plating depends on various factors, for example, electroless bath composition concentration, bath temperature, bath pH, compatibility of the particles with the metal matrix, etc. In the present work, we varied the pH and the amount of P25 TiO₂ nanopowder dispersed in the bath and studied the effects on the composite coatings on the PP balls.

Figure 3 shows the average weight percentage of Ni, P, and TiO₂ on the surface of different composite coating balls analyzed *via* EDX. Three balls were analyzed for each condition. It was found that the surface of the coatings had higher P content (more than 10% w/w). Ni-P coatings with higher P content are reported to have more corrosion resistance against neutral or acidic environments than those with a lower P content [24]. This characteristic is beneficial for ap-

Fig. 3 Surface compositions of different electroless Ni-P-TiO₂ composite balls prepared under various pH conditions. Error bars indicate the standard deviation of data.

Fig. 4 SEM/EDX images in mapping mode of the electroless Ni-P-TiO₂ coating on the PP ball presenting the presence of (a) P, (b) Ni, and (c) Ti.

plication in wastewater treatment. From **Fig. 3**, it can be seen that the Ni and P contents slightly decrease with increasing pH value while the TiO₂ content increases with increasing pH value. The increased incorporation of TiO₂ on the surface coatings might be due to the electrostatic adsorption between the cationic Ni ion and the negatively charged TiO₂ particles. According to the point of zero charge of TiO₂ which is at approximately pH 5.8–6.8 [25], TiO₂ exhibits a positive charge at a pH below 5.8 and a negative charge at a pH above 6.8. Therefore, the incorporation of TiO₂ at a high pH up to pH 9 was probably enhanced because the cationic Ni ions were attracted to the negatively charged TiO₂ nanoparticles [26]. To test the significant difference in pH ranges, one-way ANOVA was applied for statistical analysis. For % of Ni and P on PP balls, the results showed an insignificant difference among pH ranges with $P > 0.05$. Meanwhile, in case of %Ti, the P

value was less than 0.05 indicating there is a significant difference among pH ranges. The uniform distribution of TiO₂ on the coating surface was evidenced *via* SEM-EDX analysis in the mapping mode; the images are shown in **Fig. 4**.

The co-deposition of TiO₂ is also expected to be influenced by the amount of TiO₂ particles in the plating bath as reported by several groups using a plate as the substrate [26,27]. Thus, the TiO₂ concentration in the electroless plating bath should also be a crucial factor for composite plating. The elemental composition of coatings prepared at pH 9 with a different P25 TiO₂ nanoparticle concentration was determined using SEM-EDX, as shown in **Fig. 5**. It can be seen that the TiO₂ content increased with increasing TiO₂ concentration in the plating bath until 45 g/L. At 60 g/L, the TiO₂ content on the surface coatings decreased perhaps because of the repulsion between the negatively charged TiO₂ nanoparticles at the

Fig. 5 Surface compositions of different electroless Ni-P-TiO₂ composite coating balls prepared at various P25 TiO₂ concentrations. Error bars indicate the standard deviation of data.

Fig. 6 Surface morphology of electroless Ni-P and Ni-P-TiO₂ composite coatings of different TiO₂ concentrations: (a) 0, (b) 15, (c) 30, and (d) 45 g/L.

high TiO₂ concentration.

The surface morphology of the electroless Ni-P and Ni-P-TiO₂ coatings prepared using various TiO₂ concentrations were evaluated using SEM-EDX as shown in **Fig. 6**. The pure Ni-P coating shows a surface comprising well-bonded granules without any gaps as can be seen in **Fig 6 (a)**. In

the presence of TiO₂ nanoparticles, the coarser surfaces with some submicro-sized granules are apparent. By increasing the TiO₂ concentration, the boundary of the granules becomes unclear and the surface roughness of the coatings seemed to decrease. The smoother surface coatings are shown in **Fig. 6 (b-d)**.

From the aforementioned results, the adequate condition for preparing NiPTi-PP ball was found to be an Ni-P solution containing P25 TiO₂ nanoparticles at 45 g/L and a pH of 9. A cross-sectional image of the NiPTi-PP ball is shown in **Fig. 7 (a)**. The SEM/EDX images obviously show the presence of uniformly distributed Ni, P, and TiO₂ particles as shown in **Fig. 7 (b), (c), and (d)**, respectively. The cross-sectional image at the high magnification of the prepared NiPTi-PP ball is shown in **Fig. 8**. The white region was found to be the Ni-P-TiO₂ layer. Voids between the Ni-P-TiO₂ layer and the resin were observed, indicating the relatively strong adhesion of the coating on the PP ball. The thickness of the composite layer was found to be approximately 1.6 μm. From these observations, it can be summarized that the Ni-P-TiO₂ composite was successfully plated on the PP ball with a good adhesion between the composite layer and PP substrate. Furthermore, the P25 TiO₂ was also uniformly deposited in the Ni-P layer.

Figure 9 shows the XRD patterns of PP, as deposited Ni-P and Ni-P-TiO₂ composite coatings. The broad diffraction peaks at around 44–47° shown in **Fig. 9 (b) and (c)** were

Fig. 7 Cross-sectional images in mapping mode of (a) NiP-Ti-PP ball, (b) Ni, (c) P, and (d) Ti.

attributed to an amorphous Ni-P coating. Platings with amorphous structure have been reported to show better corrosion resistance than that of polycrystalline ones [24], implying that this plating is promising for application in wastewater treatment under severe conditions. Peaks of P25 TiO₂ are also shown in **Fig. 9 (a)**, although some peaks overlapped the peaks of PP and metallic Ni. The XRD results are in agreement with the SEM-EDX results, as the P25 TiO₂ nanoparticles were embedded in the Ni matrix during the electroless deposition.

In order to evaluate the photocatalytic activity of the NiPTi-PP ball, MB was chosen to be a model during the degradation process. The photodegradation started after the

Fig. 8 Cross-sectional SEM image of NiPTi-PP ball.

thorough adsorption of MB onto the photocatalyst in darkness. **Figure 10** shows the residual MB after UV irradiation for 2 h. The error bars indicate the standard deviation calculated from triplicate runs. In the presence of the NiPTi-PP balls without UV light, the MB concentration decreased to approximately 90%. It was assumed that the MB was adsorbed on the NiPTi-PP balls because of its rough surface. Under UV irradiation without the NiPTi-PP balls, the MB concentration further decreased to approximately 86%. Nonetheless, when the NiPTi-PP balls were incorporated into the system under UV irradiation, the MB concentration further decreased to 29%. The difference among the three conditions were found to be significant according to one-way ANOVA ($P < 0.05$). This must have been because of the photocatalytic mechanism on the TiO₂ surface. Additionally, Zhu *et al.* [28] have investigated on the removal of organic dyes based on photodegradation of Ni/NiO/TiO₂ composite thin films under solar light irradiation. They found that Ni/NiO can enhance the photocatalytic activity of TiO₂ by acting as a bridge to transfer the photogenerated e⁻ and h⁺ to a different part of the photocatalyst leading to the inhibition of

Fig. 9 XRD patterns of (a) NiPTi-PP specimens, (b) NiP-PP, and (c) pristine PP.

Fig. 10 Photocatalytic activity test of NiPTi-PP balls based on the degradation of 2 mg/L MB solution under UV irradiation for 2 h.

Fig. 11 Photograph of (a) NiPTi-PP and (b) pristine PP balls floating on water.

the recombination of photogenerated e^- and h^+ . Perhaps, the Ni-P plating in our study may also have acted as an inhibitor of recombination of e^- and h^+ to improve the efficiency of TiO_2 ; however, further investigation is necessary to confirm this effect.

To confirm its floatability, the NiPTi-PP and pristine PP balls were injected into the water, as respectively shown in **Fig. 11 (a) and (b)**. Although the PP ball was coated with an Ni-P- TiO_2 composite layer, it still possessed a floating ability on the water which would be beneficial in a wastewater treatment application. This implies that a thin plating with a light weight was successfully obtained.

Finally, the protection of PP from photodegradation by TiO_2 was considered. **Figure 12** shows the appearance of specimens before and after UV irradiation for 6 h. A change in color is clearly observed for the TiO_2 coated on PP ball,

Fig. 12 Color change of specimens before (a, b, c) and after (d, e, f) UV irradiation for 6 h. (a,d) PP balls, (b,e) TiO_2 film-coated PP balls, (c,f) TiO_2 film-coated NiP-PP balls.

while the other two showed no obvious difference. The SEM images of the cross section of each specimen before and after UV irradiation are shown in **Fig. 13**. Comparison with the specimens before UV irradiation (**Fig. 13 (a), (b) and (c)**), the interface between PP and TiO_2 of the TiO_2 film-coated PP ball after UV irradiation was found to become rough (**Fig. 13 (e)**) while specimens without TiO_2 (**Fig. 13 (d)**) and with TiO_2 -coated Ni-P platings (**Fig. 13 (f)**) remained smooth, as can be seen in the dashed-line box. This probably implies that the Ni-P plating has the ability to protect the PP substrate from the photocatalytic activity of TiO_2 .

CONCLUSIONS

A floating photocatalyst was successfully prepared *via* electroless Ni-P- TiO_2 composite plating on a PP hollow ball. The pH of the plating bath and the TiO_2 concentration was found to affect the incorporation of TiO_2 . The incorporation of TiO_2 increased with increasing pH and TiO_2 concentration of the plating bath. The as-deposited Ni-P- TiO_2 coating obtained at higher pH values showed a higher P content with amorphous structure, which are expected to show better corrosion resistance than that of equivalent polycrystalline ones, essential for application in wastewater treatment under severe conditions. The floating Ni-P- TiO_2 photocatalyst showed photocatalytic activity and degraded MB under UV irradiation. In addition, the Ni-P plating was confirmed to protect PP from photodegradation by the photocatalyst, TiO_2 . Therefore, the prepared floating PP ball with a Ni-P- TiO_2 composite plating can be used as a photocatalyst during the wastewater treatment process and can be easily separated after usage.

Fig. 13 SEM images of the cross section of specimens before (a, b, c) and after (d, e, f) UV irradiation for 6 h. (a,d) PP balls, (b,e) TiO₂ film-coated PP balls, (c,f) TiO₂ film-coated NiP-PP balls.

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