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Formation of Stainless Steel Nanoballs via Submerged Glow-discharge Plasma and their Microstructural Analysis with Evaluation of Photocatalytic Activity

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Stainless steel has shown potential as a catalytic material in bulk form. However, it only becomes active in an aqueous acidic environment and elevated temperatures. This study aims to produce stainless steel nanoparticles that have high photocatalytic activity in a neutral medium and at room temperature and to elucidate the photocatalytic activity mechanism of the nanoparticles. Spherical, photocatalytic nanoparticles called “nanoballs” were synthesized by the submerged glow-discharge method. Stainless steel SUS316L grade wire was used as the cathode, platinum mesh was used as the anode while the electrolyte was potassium carbonate. The nanoballs were obtained after centrifuging and washing with water. The physical characteristics of the photocatalytic nanoballs were analysed by scanning electron microscopy, high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction. The nanoballs were mixed with methylene blue and irradiated with ultraviolet light for the evaluation of photocatalytic reaction. The photodecomposition samples were determined using UV-vis spectrometry. The by-products of the photodecomposition were evaluated using mass spectrometry. The results show that stainless steel nanoballs have photocatalytic activity when irradiated with ultraviolet light at room temperature. Submerged glow-discharge plasma method can synthesize nanoparticles rapidly using only metal wires as the electrode.

KEY WORDS: nanoparticles; stainless steel; nanoballs; photocatalysis; plasma discharge.

1. Introduction

Submerged glow-discharge plasma has been researched as a method of nanoparticles (nanoballs) synthesis method.^{1–14)} The discovery of formation of metallic nanoballs¹⁾ during plasma electrolysis has been documented.^{2–7)} The product that was obtained from the electrolyte plasma electrolysis was found to be uniformly-shaped spherical particles called “nanoballs”.¹⁾ Glow-discharge was chosen as the method for nanoballs synthesis because the predictability and ease of sustainable control of glow-discharge plasma. The advantages of submerged glow-discharge plasma for nanoballs synthesis are: (1) simple experimental setup,^{1,2,4,5)} (2) ease of control of nanoball sizes,^{1,2,11)} (3) ease of mass production because of relatively high yield,^{4,5)} and (4) use of easily available metallic wires as raw materials for nanoballs synthesis.^{1,2,4,5,11)}

As a result of glow-discharge plasma layer acting on the

surface of the cathode, which has very high temperature, melted nanoparticles was released from the cathode. As they enter the liquid region, they solidify into spherical nanoballs because of the surface tension of the electrolyte and the natural tendency to assume spherical shape.

During formation of nanoballs, some of the particles' surfaces were oxidized because of the high temperature environment or exposure to air after plasma treatment. Ti nanoballs in particular were found to have TiO₂ surface layers. Since TiO₂ is a photocatalytic material, the research aims to characterize the metallic nanoballs in terms of their photocatalytic performance.

These nanoballs were found to have photocatalytic ability when irradiated with ultraviolet (UV) light. Other than semiconductor materials such as TiO₂ and ZnO nanoballs, SUS316L nanoballs which are not semiconductor materials were found to have photocatalytic ability as well at room temperature.^{2,3)} However, the mechanism or driving force behind the photocatalytic ability of SUS316L nanoballs was unclear.³⁾ In comparison, a previous study has shown the catalytic activity of SUS316L stainless steel reactor wall in

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an aqueous acidic environment and elevated temperature,³²⁾ whereas the SUS316L nanoballs showed photocatalytic activity in a neutral dye solution and at room temperature. Therefore, this paper aims to elucidate the photocatalytic activity mechanism of SUS316L via microstructural analysis and free radicals detection.

2. Materials and Experimental Methods

2.1. Submerged Glow-discharge Plasma

The experimental setup for nanoparticles synthesis was described in our previous work.⁴⁾ A platinum wire of 1 000 mm in length, 0.5 mm in diameter was used as the anode; this wire was bent and fixed onto a semicircular glass frame measuring 45 mm in height and 60 mm in width. A stainless steel wire (SUS316L, Fe: 65–72%, Cr: 16.0–18.0%, Ni: 10.0–14.0%, Mo: 2.0–3.0%, C: 0.030%, Mn: 2.0%) of 1.0 mm in diameter (Nilaco, Tokyo, Japan) was used as the cathode. A glass tube and silicone tubing was used as insulation to obtain an exposed length of 20 mm; the exposed part functioned as the net actual electrode. The electrolyte was a 300 ml solution of 0.1 mol K_2CO_3 with 99.5% purity. The anode and cathode were dipped in solution of 10% sulphuric acid for a few seconds and then washed with purified water. The electrolyte was warmed from room temperature until 90° Celcius using a hotplate stirrer, then electric current was applied until plasma forms under constant-voltage control (DC power supply: Takasago GP0250-10R). Then the voltage was fixed at a constant value for 3 hours. The sustained voltages for the electrodes were 130 V, while the current was around 0.1 A.

Figure 1 shows the typical voltage-current graphs during synthesis of SUS nanoballs using SUS316L wire. The glow-discharge voltage for nanoballs production depends on the material; metals with higher melting temperature require higher voltages to initiate glow-discharge. Based on the voltage-current graphs, the ideal voltage for nanoballs synthesis can be predicted for maximum nanoball yield. The ideal glow discharge voltage can be predicted when the current begins to plateau as the voltage was increased after maximum current was achieved.

After submerged glow-discharge plasma, the products were collected via centrifuging and washing with purified water to remove the electrolyte. The nanoballs were freeze-

dried for 12 hours to convert the nanoballs into powder form. Scanning electron microscope-energy dispersive spectroscopy (SEM-EDS, JEOL JSM7001FA FE-SEM) was used to identify the elemental composition and mapping of each type of nanoball, using 15 kV accelerating voltage. TEM images were taken using an H-700 (Hitachi High-Technologies, Japan) and TitanG3 60–300 S/TEM (FEI, Oregon, USA) TEM at an operating voltage of 150 kV and 300 kV, respectively. The aqueous solution containing the nanoballs was deposited onto a Quantifoil grid (a type of perforated support foil) for TEM observation. Size distribution software (Mac-View ver.4, Mountech Co. Ltd.) was used to estimate the nanoballs size distribution. X-ray diffraction (XRD, Rigaku Miniflex, Cu-K α source) was used to identify the oxides present and crystal structures of the nanoballs by comparing the XRD patterns with the built-in database. Brunauer-Emmet-Teller (BET, Quantachrome Instruments Autosorb 6) method was used to measure the nanoballs' surface area and average size.

2.2. Photocatalytic Test Using MB and UV

The photocatalytic ability of the nanoballs was determined by the decomposition of methylene blue (MB). MB, a type of AZO dye, has been used commonly as an indicator of photocatalytic performance of photocatalytically active nanomaterials.^{19–29)} MB ($C_{16}H_{18}N_3SCl$, molecular weight is 319.9 g/mol) is toxic if swallowed. It is usually used as a dye in textile industry and as the reagent in 'blue bottle' experiments. The decomposition pathways of MB have been extensively documented.^{4,5,19–29)} Identification of the intermediate products (by-products) that appear during decomposition is important, because it can help identify the decomposition pathway. Generally, photocatalytic materials act to oxidize the dye, while mineralization of carbon and hydrogen heteroatoms occurs at the same time. Apart from intermediate products such as Azure A, Azure B and phenol, decomposition of MB produces CO_2 , NH_4^+ , NO_3^- and SO_4^{2-} heteroatoms. The intermediate products can be detected using mass spectrometry, while the overall concentration of MB solution can be measured using photoabsorbance test.

An aqueous solution of MB and nanoballs was exposed to UV irradiation for 24 hours while enclosed inside a dark chamber. The distance between MB cell and UV light was 200 mm. The UV light was emitted at 354 nm wavelength, and the power of the UV lamp was 100 W. The initial concentration of MB was 0.1 g/1 000 ml and the concentration of nanoballs in MB was 0.1 g/5 ml. Ultra-violet/visible (UV/VIS) spectrophotometer (Jasco V-630) was used to measure the relative concentration of MB before and after the photocatalysis test.

A mechanism that allows photocatalytic materials to decompose pollutants is by releasing hydroxyl radicals when irradiated with light. Hydroxyl radicals, which have powerful oxidising properties, are generated during photocatalytic reaction.^{40–42)} P-nitrosodimethylaniline (PNDA) was used as the hydroxyl radicals probe compound. PNDA is selectively oxidized only by hydroxyl radicals, and does not react with superoxide anions and other oxidizing compounds that contribute little to the photocatalytic process.⁴⁰⁾ Therefore, to determine the amount of hydroxyl radicals

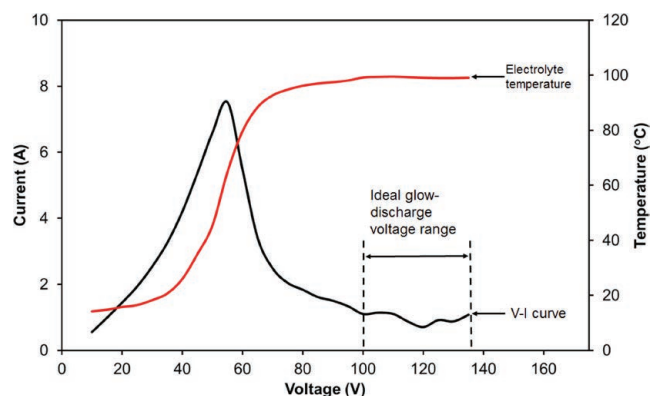


Fig. 1. Voltage-current and voltage-temperature curves for glow-discharge plasma for SUS316L. (Online version in color.)

generated by the nanoballs, the photobleaching of PNDA was measured using UV/VIS spectrometry and the change in absorption peak at $\lambda = 440$ nm was observed.

3. Experimental Results and Discussions

3.1. Physical Characteristics of Nanoballs

Figure 2 shows the SEM image of the SUS316L nanoballs that were synthesized using glow discharge plasma process. The nanoballs were washed using deionized water and centrifuged to remove the electrolytes. The morphology can be described as being uniformly spherical and nano-sized. The diameters of the nanoballs are within a relatively wide range of 10 nm to 1 μ m.

Figure 3 shows the SEM-EDS spectra for SUS316L wire and nanoballs. The SUS316L wire is composed of mainly Fe, Ni and Cr, which are consistent with its specifications. The wire contains O in negligible amount. In case of the nanoballs that were synthesized using SUS316L wire, O atoms can be observed in the SEM-EDS spectrum, in addition to the Fe, Ni and Cr. Besides that, Zn was also detected. However this was because the SUS316L nanoballs were dropped onto a Zn sheet that was subsequently used for the SEM-EDS analysis. The detection of Si was likely caused by the silicone tubing that was used to protect the upper part of the SUS316L wire during glow-discharge. The results indicate that the surfaces of the nanoballs consisted

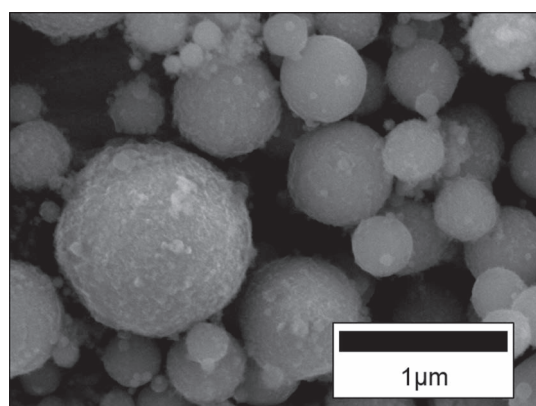


Fig. 2. SEM images of SUS316L nanoballs.

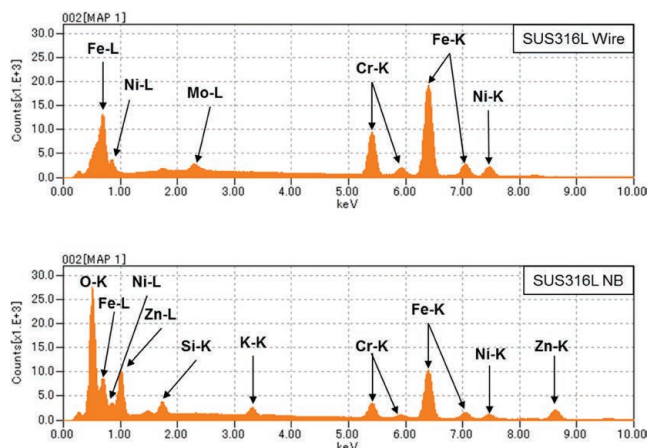


Fig. 3. SEM-EDS spectrum of SUS316L wire and SUS316L nanoballs. (Online version in color.)

of oxide species.

This oxide surface has an important role in photocatalysis, since they are reactive towards UV light to release hydroxyl radicals. Since the oxide layer on the nanoballs has been identified, further investigation of the cross-sections of the nanoballs is needed. Also, the microstructure between the oxide surface and the nanoball bulk volume is of interest, to determine the growth mechanism of the oxide surface.

Figure 4 shows the XRD pattern for the SUS316L wire used as the cathode for nanoballs synthesis and the nanoballs that were produced. In terms of peak intensities, Fe (austenitic, ICDD: 01-081-8770) was the main compound detected in the wire. Meanwhile, in addition to austenitic Fe, metal oxides such as Fe_2O_3 (ICDD: 01-072-6230) and Fe_3O_4 (spinel, ICDD: 01-078-3149) were detected in the SUS316L nanoballs specimen. The presence of Fe_2O_3 and Fe_3O_4 in SUS316L nanoballs contribute to its photocatalytic effect.^{30–39} The bandgaps of both Fe_2O_3 and Fe_3O_4 are 2.2 eV. Their low bandgap allows them to be photoexcited by UV light and potentially by visible light as well. As a comparison, the bandgap of anatase TiO_2 is 3.0 eV, which is much higher than that of Fe_2O_3 and Fe_3O_4 , and thus can only be photoexcited by UV light.

The TEM images of the 316L nanoballs are shown in **Figs. 5 and 6**. The nanoballs are uniformly spherical and are nanosized, which was consistent with the observations by SEM. Additionally, particle size distribution and BET method was used to determine the sizes of the synthesized nanoballs. Figure 5 shows the high-resolution transmission electron microscope (HRTEM) image of a SUS316L nanoball. In this particular nanoball, the spinel structure can be observed near the surface of the nanoball where the lattice constant was measured as 0.16 nm. This shows that the oxides with spinel structure were present in SUS316L nanoballs.

Figure 6 shows the STEM-HAADF and TEM-EDS image of SUS316L nanoballs. The individual nanoballs have different oxide compositions. This shows that the nanoballs made using SUS316L wire were reconstituted into different types of metal oxides. This result was reflected in the SEM-EDS and XRD results as well, where the different metal oxides were clearly distinguished.

Table 1 shows the elemental composition of SUS316L nanoballs measured using TEM-EDS. The measurements were taken at the center and the surface of the nanoball.

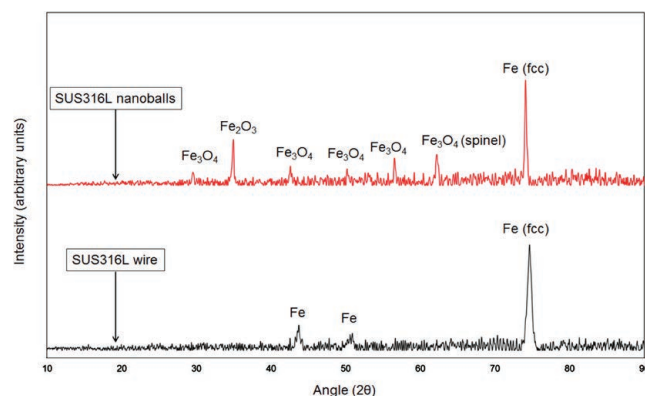


Fig. 4. XRD pattern of SUS316L wire and nanoballs showing the oxide species present. (Online version in color.)

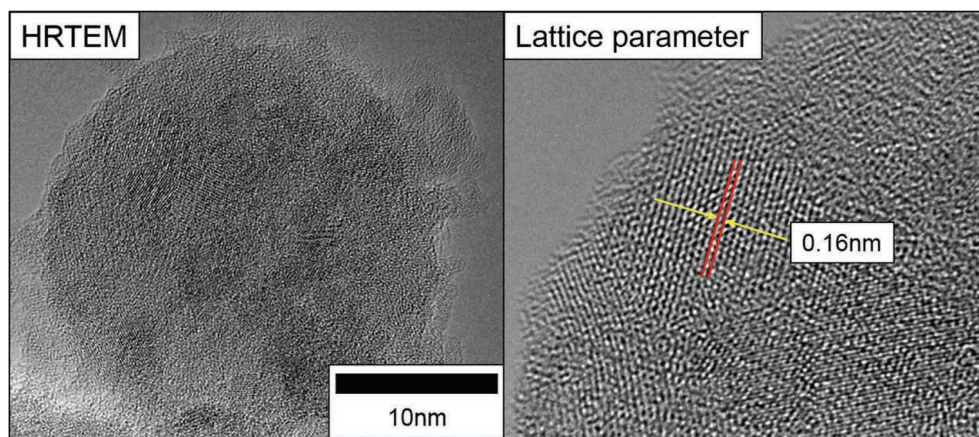


Fig. 5. TEM image of SUS316L nanoball showing HRTEM and lattice parameter of its surface which corresponds to spinel structure. (Online version in color.)

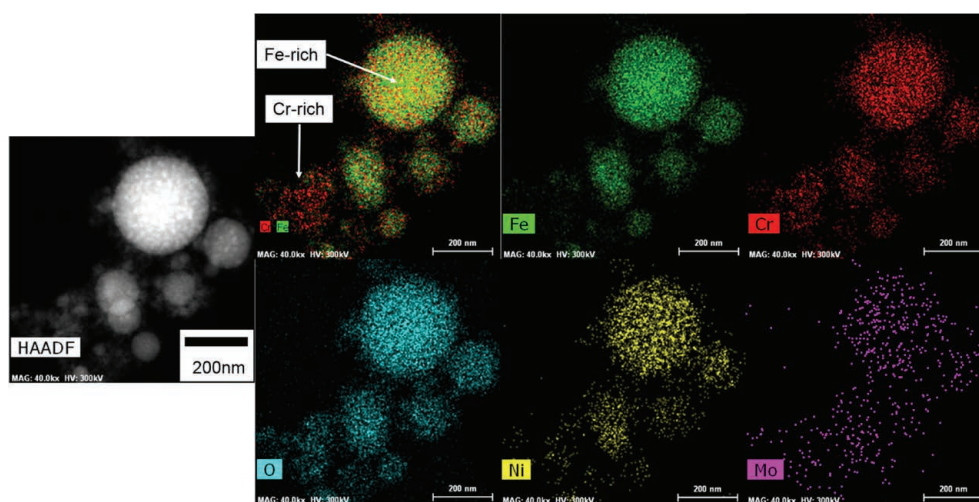


Fig. 6. TEM-EDS image of SUS316L nanoballs showing the presence of distinct metallic oxide species such as iron oxide, chromium oxide and nickel oxide. (Online version in color.)

Table 1. TEM-EDS elemental composition of SUS316L nanoballs.

Element	Mole percent (%)	
	Nanoball surface	Nanoball center
Fe	51	23
Cr	9	9
Mn	1	1
O	38	66
Mo	1	1
Total	100	100

Table 2. Yield of nanoballs after three hours of continuous glow-discharge using SUS316L wire. Surface area and total pore volume of the nanoballs measured using BET. Average surface area and diameter for individual nanoballs were measured using TEM images.

Properties	SUS316L nanoball
Mass (g)	0.017
Surface area (m ² /g)	40.94
Total pore volume (cm ³ /g)	0.06587
Average surface area (nm ² /g)	3 861.37
Average particle diameter (nm)	67.06

Apparently the oxide content at the center is significantly higher than the oxide content at the surface. This would explain the lack of a passivation layer on the nanoball surface.

Table 2 shows the results of surface area and pore size measurements performed using BET method. The table shows the results of BET measurements, where the surface area and pore volumes of SUS316L nanoballs were measured. The mass was obtained by measuring the mass of the SUS316L wire before and after plasma synthesis; the mass of the nanoballs was obtained by measuring the mass

of the wire after plasma synthesis and subtracting it from the mass of the wire before synthesis. The nanoballs surface area and pore sizes were sufficient for photocatalytic reaction. However, further optimization of nanoballs synthesis is needed to produce smaller sized nanoballs with larger surface area; submerged glow-discharge plasma process has good potential to produce nanoballs with large surface area. This will further increase the photocatalytic activity of the nanoballs. Besides that, the average surface area and particle size in term of their diameters are also shown in Table 2. The values were obtained by manually measuring

the nanoballs diameter using the TEM image of SUS316L and subsequently calculating their average surface areas and diameters. The discrepancy between the BET and TEM measured surface areas indicates the existence of fine roughness or pores that was not detected with TEM.

3.2. Photoabsorbance Test Results Using MB and PNDA

Figure 7 shows the images of the MB dye solution during the photocatalytic effect test on SUS316L nanoballs. Every six hours, a photograph of the cuvette containing the MB and nanoball mixture was taken. This was to provide visual proof on the degradation of MB dye solution. The photocatalytic degradation was observed through the loss of MB color; as the dye faded, the blue color of the dye disappeared causing the dye solution to gradually become transparent.

Figure 8 shows the photoabsorbance results of MB photodecomposition while being mixed with SUS316L nanoballs under UV irradiation. The characteristic peak of MB is at $\lambda = 660$ nm. The decomposition of MB was confirmed in the photoabsorbance test of SUS316L nanoballs, as shown in Fig. 8. **Figure 9** shows the photodecomposition trend of MB under the conditions of (i) without nanoballs or UV irradiation, (ii) with nanoballs only, and (iii) with nanoballs and UV irradiation. For cases (i) and (ii), the MB dye solution did not fade after 72 hours. These cases suggested that MB does not undergo degradation without any nanoballs and UV irradiation. The presence of only nanoballs without UV irradiation did not cause any loss of MB color, showing that the nanoballs did not interact with MB. In case (iii), dur-

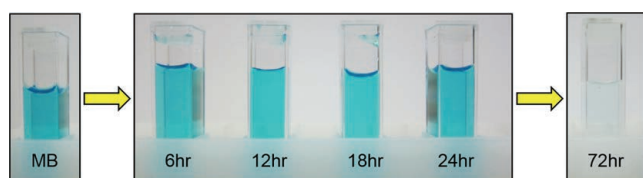


Fig. 7. Photocatalytic test photos of the mixture of MB solution in SUS316L nanoballs under UV light irradiation. (Online version in color.)

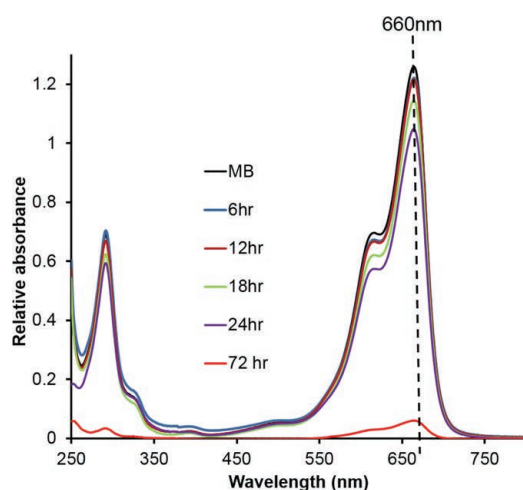


Fig. 8. Photoabsorbance spectra for MB photodecomposition in presence of SUS316L nanoballs under UV light irradiation, showing the characteristic absorbance peaks at 270 nm and 660 nm. (Online version in color.)

ing the first 24 hours of UV irradiation in presence of nanoballs, MB dye solution did not significantly fade. However, the dye solution became transparent after 72 hours of continuous UV irradiation. This showed that SUS316L nanoballs were able to decompose the MB dye solution in presence of UV light. The loss of absorbance at the MB characteristic peak was observed, where it was reduced to baseline level after 72 hours of UV irradiation. We suggest that the MB was oxidized into sulfoxide compound before decomposing into lighter by-products.³⁾ During this time, there was not much hydroxyl radicals being generated. As a result, MB was oxidized during the first 24 hours of UV irradiation, then afterwards due to the greater generation of hydroxyl radicals, gradually decomposing until baseline level. Therefore, these results indicate that SUS316L nanoballs have photocatalytic activity when irradiated with UV light.

Figure 10 shows the photoabsorbance test results of PNDA photodecomposition in presence of the nanoballs under UV irradiation. The characteristic absorption peak for PNDA is at $\lambda = 440$ nm. The loss of absorbance at the characteristic peak was rather slow during the first 24 hours of UV irradiation. However, the decrease was rapid between 24 hours and 72 hours of irradiation. Since the absorbance

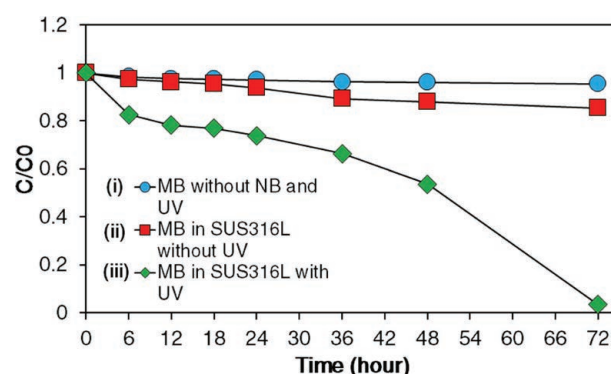


Fig. 9. Photodecomposition behaviour of MB without nanoballs (NB) and UV, in SUS316L NB only and in SUS316L NB and UV irradiation. C_0 is the initial concentration of MB, while C is the concentration of MB measured at a predetermined time interval during UV irradiation. (Online version in color.)

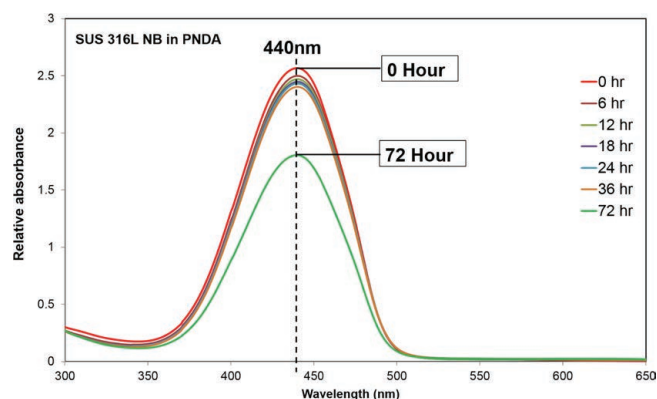


Fig. 10. Photoabsorbance spectra of PNDA during UV irradiation showing its characteristic absorbance peak at $\lambda = 440$ nm. The decrease of PNDA characteristic peak indicates the generation of hydroxyl radicals. (Online version in color.)

loss at the characteristic peak for PNDA was observed, it is suggested that significant amount of hydroxyl radicals were generated between 24 to 72 hours of UV irradiation, which allows for the MB to decompose in SUS316L nanoballs during that period of time.

The results of MB and PNDA photodegradation showed a significant finding. In both cases, the loss of MB and PNDA characteristic peaks occurred after 24 hours of UV irradiation. We can observe that SUS316L nanoballs become photocatalytically active after 24 hours of continuous UV irradiation.

Based on the results, we suggest that the SUS316L nanoballs showed photocatalytic activity because of the presence of various oxide species such as Fe_2O_3 and Fe_3O_4 (spinel). Although Fe_2O_3 had a narrow bandgap, the high recombination rate of the active radical species caused low photocatalytic activity during the first 24 hours of UV irradiation. However, the hydroxyl radicals generation then increased after 24 hours, which was shown in the PNDA decomposition analysis. As a result, the SUS316L nanoballs exhibited an increased photocatalytic activity after 24 hours of UV irradiation and subsequently decomposes the MB dye solution.

4. Conclusions

Using SUS316L wire as the cathode, stainless steel nanoballs were synthesized via submerged glow-discharge plasma. The photocatalytic activity and the mechanism of stainless steel nanoballs photocatalytic activity were described. Stainless steel nanoballs were found to have photocatalytic activity when irradiated with UV light at room temperature. The physical characteristics of the stainless steel nanoballs were investigated. They were nanosized (typically 10 nm to 200 nm in diameter) and uniformly spherical. Submerged glow-discharge plasma has the advantage of being able to synthesize multialloy nanoparticles. The surface of the nanoballs consisted of various oxide species; the combination of these species contributed to the photocatalytic activity of stainless steel nanoballs. Using submerged glow-discharge plasma, photocatalytic nanoballs can be synthesized easily and inexpensively as demand for new photocatalytic materials increase.

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