Exploring the cooperation effect of DBD byproducts and Ag/TiO$_2$ catalyst for water treatment in an APPJ system

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Abstract
In this paper, the collective effects of combining heterogeneous Ag/TiO$_2$ nanocomposite catalyst with the byproducts (primarily the irradiation and the O$_3$ species) of an atmospheric pressure plasma jet (APPJ) system on the degradation of methyl orange (MO) were explored. The heterostructured Ag/TiO$_2$ nanocomposite was achieved via decorating the Ag quantum dots (QDs) on the commercially available TiO$_2$ catalyst (P25) through a hydrothermal method. The x-ray diffraction analysis of the nanocomposite catalyst showed the diffraction peaks at 44.3°, 64.4°, and 77.5°, corresponding to the Ag planes of (200), (220) and (311), respectively. The high resolution transmission electron microscope characterization of the nanocomposite catalyst indicated that the Ag QDs with an average diameter of 5 nm were homogeneously distributed on the P25 surface. The experimental results on the MO photodegradation showed that the APPJ irradiation had a marginal effect on the cleavage of the MO molecules. When the Ag/TiO$_2$ nanocomposite catalyst was used, the photodegradation rate of MO increased about 5 times. When both the APPJ byproducts and the Ag/TiO$_2$ nanocomposite catalyst were used, however, over 90% of the MO in the tested solution was cleaved within 15 min, and the energy efficiency was about 0.6 g/kW h. Moreover, an optimal Ag dosage value was determined (6 wt%). The catalytic results indicated that combining the DBD plasma byproducts with heterogeneous nanocomposite catalysts may be an effect protocol for decreasing the application cost of the DBD system and mitigating the environment pollution by organic dyes in the textile industry.

Keywords: APPJ, plasma byproduct, heterostructured catalyst, organic wastewater treatment

(Some figures may appear in colour only in the online journal)

1. Introduction
The textile industry is one of the vital components of the economy in China. Approximately one billion tons of textile wastewater are produced by the textile industry, which need to be deeply treated, particularly the organic dyes as these aromatic amines are potential carcinogens and account for roughly 15% of the total world wastewater generated during the dyeing process [1]. Moreover, technological developments have led to the use of chemically synthesized dyes and auxiliaries, which further complicates the textile wastewater treatment processes as these synthetic species are particularly difficult for the ecosystems to handle. Therefore, it is necessary to explore effective protocols for eliminating dyes from the wastewater before it is discharged into the natural water resources. Methods including the biological treatment...
processes [2], adsorption [3], and physical-chemical treatments [4] are used for such purposes. However, these processes are typically associated with drawbacks such as being time consuming, inefficient, energy deficient, and prone to creating secondary pollution [5].

Recently, various advanced oxidation processes (AOPs) have been developed for dye treatment and the hydroxyl radicals (OH) generated by these AOPs have been shown to efficiently promote the degradation of organic dye pollutants [6–8]. Among these AOPs, a non-thermal plasma (NTP) technology has attracted increasing attention owing to its environmentally friendly nature and excellent oxidation performance. However, the NTP technology is generally associated with drawbacks including low energy efficiency and mineralization [9, 10], and such drawbacks limit the wide application of NTP technology. A promising method to overcome such drawbacks is to combine the NTP technology with nano catalysts [11].

Among the various non-noble metal oxide catalysts, the TiO2 nanoparticles are highly attractive as they are commercially readily available. However, TiO2 nanoparticles alone would require ultraviolet (UV) excitation in order to generate the electrons/hole (e−/h+) pairs (main active species for dye treatment) and the fast electron and hole recombination rate is a major concern. On the other hand, silver has been demonstrated to possess remarkable catalytic activity [12], and it can significantly suppress the recombination of the e−/h+ pairs thanks to its strong electron trapping ability. Thus, modifying the commonly available TiO2 nanoparticle catalyst by decorating with Ag nano quantum dots (QDs) may significantly enhance the catalytic performance owing to the quantum enhancement effect [13]. Moreover, the UV visible light and the oxidative species are the byproducts of the NTP plasma, naturally it will be of interest to combine all these components discussed above and evaluate the performances in terms of organic dye removal.

In this work, an atmospheric pressure plasma jet (APPJ) system to simulate the NTP byproducts was designed and the cooperation between the APPJ and the Ag/TiO2 nanocomposite catalysts for the methyl orange (MO) degradation was evaluated. The effects of the discharge power, the catalyst loading, the gas flow rate, and the Ag dosage on the cleavage of the MO molecules were explored.

2. Experimental section

2.1. Ag/TiO2 nanocomposite catalyst preparation

1.0 g of the TiO2 nanoparticles (Analytical grade, Yongda Co. Ltd., China) and various desired amounts of AgNO3 (analytical grade, Yuhan Co. Ltd., China) (corresponding 2–8 wt% Ag dosages,) were dispersed into 200 ml ethyl alcohol and sonicated for 10 min at room temperature. The prepared solutions were then transferred to the polyfluorotetraethylene-lined autoclaves (125 ml) and kept in a muffle furnace at 225 °C for 2 h (with a heating rate of about 2 °C min−1 to increase the temperature from room temperature to 225 °C).

At the end of the hydrothermal reaction, solid contents were obtained and sequentially washed with ethanol and deionized water three times. Finally, the washed products were dried at 550 °C for 2 h in static air.

2.2. Catalyst characterization

The morphological characterization of the synthesized Ag/TiO2 nanocomposite catalysts was performed with a JSM-6700F field-emission scanning electron microscope (JEOL, Japan) and a transmission electron microscope (TEM, JEOL, Japan). The crystalline phases of samples were examined by x-ray diffraction (XRD, Thermo Fisher Scientific, USA) using a Cu Kα radiation source at 35 kV. The diffraction patterns were taken in the 2θ range of 20°–90° at a scan speed of 2.0° per minute and a step width of 0.02°.

2.3. APPJ system

The APPJ apparatus used for estimating the cooperation of plasma byproducts and Ag/TiO2 for the dye degradation, as shown in figure 1, was similar to that reported in our former work [14]. Briefly, a copper tube centered in a quartz tube (inner diameter: 8 mm, wall thickness: 1.5 mm) acted as one electrode, and the dye solution contained in the outer layer of the quartz tube (inner diameter: 100 mm) was the second electrode. Both electrodes were connected to an AC power with a maximum peak voltage of 30 kV at adjustable frequencies ranging from 8 to 30 kHz. The O3 concentration and active species generated in the APPJ system were measured with an ozone analyzer (GT901, Keernuo Tech. Co. China) and optical emission spectrum (OES) over a wavelength range of 200–800 nm (Andor, Sr-500i-A, USA). The downstream gas of APPJ was transformed to a water tank (outer electrode) by a PET tube and bubbled in the dye solution with a gas distributor. The photodegradation of the MO molecules in the tested dye solutions (10 mg l−1) was analyzed with a UV–vis spectrophotometer (PerkinElmer, USA). It should be noted that the flow rate of Ar and O2 in the treatment process of the MO solution was 0.4 and 0.1 m3 h−1, and the applied discharge power was 70 W.

3. Results and discussion

Figure 2(a) shows the relationship between the O3 concentration (oxygen flow rate: 0.1 m3 h−1) and the Ar flow rates with a discharge power of 60 W. Data depicted in figure 2(a) showed that the O3 concentration increased from 30 to 62 ppm as the Ar flow rate increased from 0.1 to 0.4 m3 h−1. Such an observation was attributed to the fact that a higher concentration of Ar ions generated in the APPJ system would induce a higher density of electrons. Another potential explanation was that the increased Ar flow rate would induce increased collision between O2 molecules and the electrons and in turn generate a higher concentration of O3 [15]. Figure 2(b) presents the OES of the Ar/O2 plasma, and the N2 peaks at 265, 315, 337, 357 and 380 nm were mainly
attributed to the ionization of the air at the APPJ boundary. Moreover, the emission at 309 nm in figure 2(b) indicated the presence of reactive OH species, potentially formed by the reaction of the excited O ions with the water vapor (H₂O + O⁺ → 2OH) and the electron impact dissociation (H₂O + e⁻ → H + OH + e⁻) [16].

The crystalline phases of the synthesized Ag/TiO₂ nanocomposites were characterized by XRD measurements, and the results were shown in figure 3. For the original TiO₂ (P25, line a), the peaks at 2θ values of 25.5°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3°, and 75.0° were indexed to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of the anatase TiO₂ in P25, respectively. Characteristic diffraction peaks at 27.4°, 36.1°, and 41.2° corresponding to the (110), (101), and (111) faces of the rutile TiO₂ in P25 [17] were also observed. When the Ag QDs decorated the TiO₂ nanoparticles, characteristic peaks were observed at 44.4°, 64.4°, and 77.4°, corresponding to the cubic phase (JCPDS 03-0921) of the silver, as shown in lines (b)–(e) of figure 3. It should be noted that the peak intensity at 38.3° (assigned to the (111) plane of the Ag) increased when the Ag amount dotted on the TiO₂ surface increased. The Debye–Scherrer equation was used to analyze the most intensive peak of the spectrum and the diameter of the Ag QDs was calculated to be around 5 nm.

Figure 4 shows the morphology of the Ag/TiO₂ nanocomposite with different Ag dosages, and the diameter of TiO₂ nanoparticles was in the range of 60–130 nm. It should be noted that the surface structure of TiO₂, as shown in Figures 4(a)–(d), was relatively independent on the calcination temperature. For the dosages (ranging from 2.0 to 8.0 wt%) of Ag content used in this work, consistently homogenous dispersion of the Ag QDs on the TiO₂
nanoparticles was achieved. Moreover, under the experimental conditions employed in this work, no apparent aggregation of the Ag QDs was observed, indicating that the synthetic routine employed in this work was effective and consistent in terms of producing well defined Ag/TiO$_2$ nanocomposite catalysts. In order to further illustrate the distribution of the Ag QDs on the TiO$_2$ surface, the samples were also analyzed with a TEM instrument. Figure 5 shows the high resolution TEM images of the Ag/TiO$_2$ samples and the results showed no apparent increase in the size of the Ag QDs (about 4.0 nm, fairly consistent with the value calculated using the XRD data shown in figure 3) when the Ag dosage increased from 4.0 to 8.0 wt%. The adhesion of the Ag QDs to the TiO$_2$ nanoparticles was evaluated by sonicating the

Figure 3. XRD patterns of TiO$_2$ dotted with different Ag contents. Line a: Original TiO$_2$, Line b: 2 wt%, Line c: 4 wt%, Line d: 6 wt%, Line e: 8 wt%.

Figure 4. SEM images of Ag/TiO$_2$ with different Ag contents: (a) 2 wt%, (b) 4 wt%, (c) 6 wt%, (d) 8 wt%.
synthesized Ag/TiO₂ nanocomposite for 30 min and the TEM images were very similar (before and after sonication), indicating strong adhesion between the Ag QDs and the TiO₂ nanoparticles. Such a phenomenon corresponded to a high stability in the heterogeneous structure, especially in the catalytic process.

Figure 6 shows the effects of the treatment time and the APPJ discharge power on the MO cleavage performance with 6 wt% Ag/TiO₂ (indicated by the absorbance peaks at 464 nm). The data depicted in figure 6(a) shows that a discharge power of 30 W and a duration of 15 min would result in about 60% of MO removal, whereas a discharge power of 50 W would completely cleave the MO contents within 12 min (figure 6(b)). Furthermore, the treatment time needed for complete cleavage of the same amount of MO contents decreased with the further increase in the discharge power (9 and 6 min for 70 and 100 W, as shown in figures 6(c) and (d), respectively). Such observations were attributed to the increased concentrations of O₃ when higher discharge powers were used in the APPJ system. In addition, it should be noted that when high power was used, the micro-filaments at the end of the inner electrode could turn into micro-arcs at a higher cruising frequency. Consequently, more vortices would be produced which could transform the flow pattern at

![Figure 5. TEM images of Ag/TiO₂: (a) 4 wt% Ag; (b) 8 wt% Ag.](image)

![Figure 6. The UV–vis spectra of MO treated by 6% Ag/TiO₂ with different powers. (a) 30 W, (b) 50 W, (c) 70 W, (d) 100 W.](image)
the outlet from laminar to turbulent [18]. Such an effect would further enhance the contact between the MO molecules and the O₃ species, naturally leading to better MO cleavage performances.

The MO mitigation was further illustrated by the C/C₀ versus treatment time under various discharge powers when Ag/TiO₂ nanocomposite catalysts were incorporated, as shown in figure 7. Figure 7(a) shows that 57%, 78%, and 85% cleavage of the MO contents in the tested solution were achieved after treating for 15 min under discharge powers of 30, 50, and 70 W respectively. It should be noted that further increasing the discharge power to 100 W would result in no observable increase in MO cleavage after 6 min of treatment. While the exact cause of this observation was yet to be determined, it was hypothesized that MO might be mineralized on the Ag/TiO₂ nanocomposite catalysts under a high

Figure 7. The concentration conversion and degradation efficiency of MO treated by 6 wt% Ag/TiO₂ with different discharge power.

Figure 8. Radiation from the discharge region for MO degradation without O₃: (a) without catalysts, (b) TiO₂, (c) TiO₂ dotted with 6 wt% Ag, (d) the degradation efficiency with different treating conditions.
discharge power, and thus block the access of the MO molecules in the solution to the active sites of the catalyst, resulting in a lower than expected MO cleavage performance. Figure 7(b) shows the correlation between the discharge power and the MO degradation performance, and it clearly shows that an optimal discharge power may exist.

In order to demonstrate the necessity of the O3 and the catalyst for MO cleavage, the roles of O3 and Ag/TiO2 for dye degradation were investigated. Figure 8(a) shows the effect of APPJ radiation on the MO degradation without O3 and catalyst, and negligible change in the maximum peak at 464 nm was observed, indicating that the APPJ radiation cannot effectively cleave the MO molecules. When the TiO2 catalyst was added in the dye solution, the degradation rate of MO increased noticeably, as shown in figure 8(b). Moreover, when the Ag/TiO2 nanocomposite catalyst was used, as shown in figure 8(c), considerable enhancement in terms of MO cleavage performance was achieved, as compared with that achieved by TiO2 catalyst. The comparison amongst figures 8(a)–(c) was better illustrated by figure 8(d). The enhancement in the MO cleavage performance by the incorporation of the Ag QDs was attributed to the function of the heterojunctions [19]. It should be noted that when no O3 species presented, the MO cleavage performance was generally poor for the experiments conducted using the conditions given in figure 8.

In order to determine the optimized dosage content of Ag QDs, the MO cleavage performances of the Ag/TiO2 nanocomposite catalysts with various Ag dosages were evaluated. Figure 9(a) shows the effect of the Ag dosage on the catalytic activity of heterostructured Ag/TiO2, and the degradation rate of the MO dye increased apparently with the increase of Ag dosage. Moreover, when the 6.0 wt% Ag dosage was used, nearly 90% of the MO molecules were cleaved (represented by the disappearance of the absorbance peak at 464 nm) after a treatment time of 15 min, which was better illustrated in figure 9(b). Further increase in the Ag dosage would result in no measurable improvement in the MO cleavage, indicating that a 6.0 wt% Ag dosage would be an optimal condition when synthesizing the Ag/TiO2 nanocomposite catalyst. It should be noted that the peak at 275 nm attributed to the aromatic ring also decreased obviously, and it indicates that the mineralization of the MO molecules on the Ag/TiO2 nanocomposite catalysts by the APPJ byproducts was achieved. Therefore, the APPJ system is a perfect device for simulating the collective action of UV–visible light, O3 and catalyst for the organic-molecules mineralization.

4. Conclusion

In summary, a heterogeneous nanocomposite catalyst based on the TiO2 nanoparticles decorated with the Ag QDs was synthesized, and the combination of the synthesized catalyst and the byproducts of an APPJ system was evaluated for the mitigation of organic dyes in the textile wastewater. The effect of irradiation light generated by APPJ on the MO degradation can be neglected. However, the degradation efficiency of O3 for MO cleavage was about 55%. An optimal Ag dosage of 6.0 wt% was determined, and nearly 90% of the MO in solution was cleaved under the collective function of O3, UV–visible light, and 6 wt% Ag/TiO2 nanocomposite catalyst. The experimental results indicated that the combination of the Ag/TiO2 nanocomposite catalyst with the byproducts of the DBD system is a promising protocol when organic dye treatment of the wastewater is concerned in the textile industry.

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