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A two-step strategy for high-efficiency fluorescent dye removal from wastewater

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Conventional circulating activated sludge techniques (CASS) are time consuming (72 h) and energy intensive, all of which greatly limits their use. Although advanced oxidation techniques (e.g., photocatalysis, photoelectrocatalysis UV/•OH, and Electro-Fenton) can reduce the treatment time by several hours, the slow generation and fast coupling of electron and hole make the low degradation efficiency. In this work, an intact route using a two-step strategy is developed to eliminate organic dyes from wastewater in only a few minutes. The electron and hole exhibit “fast generation and slow coupling” by using the new technique via electrolytic discharge plasma (EDP) combined with a core-shell structure Au@SiO₂ nanocatalyst for [Rhodamine (RhB)/Eosin yellowish (EY)] dyes degradation in wastewater. Results demonstrate that the synergy of EDP and Au@SiO₂ nanocatalyst enhances degradation kinetics, and it is effective in degrading different concentrations of RhB and EY dyes in the range of 50–1.5 mg/L. Then, the Au@SiO₂ nanocatalyst (over 99%) and carbon impurities are filtered by a porous nanocomposite ultrafiltration membrane. Favorable contributions of the two-step strategy are further ascertained based on chemical oxygen demand (COD) and relative removal efficiency. This two-step strategy provides an unprecedented rapid approach for industrial wastewater treatment.

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INTRODUCTION

The amount of fresh water on Earth is limited under constant pressure. Preserving the quality of fresh water is important for drinking water supply, food production, and recreational water. Water quality can be compromised by the presence of pathogens, pesticides, PPCPs, heavy metals,^{1–3} which causes severe environmental problems due to complex chemical composition, toxicity, strong color, high chemical oxygen demand (COD), and low biodegradability.^{4–16} Many toxic and persistent substances, such as polycyclic aromatic hydrocarbons in dyestuffs wastewater, can weaken the ecosystem and place many species at risk of extinction. A simple and effective method to realize the rapid removal of fluorescent dyes from wastewater is thus highly desired.

Water treatment techniques, including organic matter degradation and water purification, are worldwide critical for addressing the problem of clean water shortages.¹ Although circulating activated sludge techniques (CASS) have been successfully used to refresh dye-containing wastewater in industrial-grade applications, low degradation efficiency, and extensive time consumption (more than 72 h) greatly limits their use. Over the past decades, extensive studies have focused on the development of advanced oxidation techniques for effective and efficient remediation of dyestuffs in wastewater, such as TiO₂ photocatalysis,¹⁴ photoelectrocatalysis,¹⁵ UV/HO₂,¹⁶ and Electro-Fenton.¹⁷ However, the advanced oxidation techniques still take several hours. The degradation efficiency of advanced oxidation techniques is often limited by slow transfer and subsequent fast recombination reactions of photoexcited electrons and holes.^{18–23} Achieving

highly efficient dye degradation in wastewater, especially in mere minutes, remains challenging.

Dielectric barrier discharge (DBD) technology has also attracted considerable interest in applications to remove organic contaminants from wastewater,^{8,20,24–26} considering fast removal rate and environmental compatibility. These features can be ascribed to many active radicals, such as •OH and •O, as well as multiple energies including strong UV light and local high temperatures generated in the DBD process. Although substantial progress has been made, the process still requires tens of minutes.²⁷ In addition, the high input voltage (1–40 kV) is not suitable for commercialization due to its high-energy consumption and relatively low degradation efficiency. Great concerns about the coupling process focus on the following three aspects in promoting industrial applications. The first is to develop a discharge technology driven by low input voltage (<220 V). The second is to further enhance the removal efficiency of organic contaminants by effectively preventing the recombination of electrons and holes. Finally, a suitable ultrafiltration membrane should be used to separate suspended nanomaterials from treated water.

In this work, a two-step strategy has been designed to eliminate nonbiodegradable and toxic fluorescent dyes from wastewater with high efficiency and good quality. Rhodamine (RhB) and Eosin yellowish (EY) dyes were selected to test the feasibility and utilization of the system. In the first step, fluorescent dye degradation was carried out via the electrolytic discharge plasma (EDP) process in K₂S₂O₈ electrolyte integrated with an Au@SiO₂ nanocatalyst, as shown in Fig. 1a. This combined system provides a synergic function of active species and multiple energy fields,

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causing full degradation of dyes in organic solutions within only a few minutes. The high efficiency and superior effectiveness of this method prove that the coupling process can effectively prevent the recombination of electrons and holes and accelerate the redox reaction. Then, Au@SiO₂ nanoparticles and carbon impurities were filtered through a porous composite membrane in the second step (see Fig. 1b). Herein, a porous composite membrane was fabricated by solid-state sintering with high porosity containing micro- and nano-sized pores. The porous composite membrane with dual-scaled porous structure and Al₂O₃ bulges was found to effectively separate nano-Au@SiO₂ and carbon impurities from the solutions. Therefore, full removal of fluorescent dyes from wastewater can be realized by using this novel two-step strategy. The detailed effects of plasma, K₂S₂O₈ electrolyte, Au@SiO₂ nanocatalysis, and porous composite membrane are also discussed in this work.

Fig. 1 Schematic illustration of an innovative two-step method to eliminate fluorescent dyes from wastewater. **a** Step 1: rapid degradation of fluorescent dyes by EDP in K₂S₂O₈ electrolyte combined with nano-Au@SiO₂ photocatalyst. **b** Step 2: effective removal of Au@SiO₂ nanoparticles and carbon impurities from water via porous composite membrane

RESULTS AND DISCUSSION

Plasma formation and dye degradation

A typical current–voltage curve of the EDP process in the K₂S₂O₈ electrolyte using simulated organic wastewaters is shown in Fig. 2a. As expected, the EDP process can be divided into three parts: normal electrolysis (Region I), plasma electrolysis (Region II), and overload (Region III). In Region I, with a voltage lower than 100 V, the cathodic current density initially rose with an increase in voltage, and many bubbles overflowed around the anode and cathode; conventional water electrolysis thus appeared. Then, the cathodic current density began to decline as the voltage continued to rise from 50 V, indicating the onset of plasma discharge with tiny spots on the cathode surface. When the voltage reached ~100 V, corresponding to the onset of Region II, a minimum value of cathodic current density appeared and a large amount of plasma was generated on the cathode surface. As the input voltage rose up to 150 V, liquid electrolysis plasma became sustainable and stable. Results also showed that the point discharge existed at the edge or tip of steel wire on the cathode. Similar phenomena were found in the literature on the microwave plasma discharge process,^{28,29} indicating that uneven plasma discharge can lead to heterogeneous distribution of surface electric field, temperature, and gas flow. Therefore, a pulsed power should be adopted to alleviate the disadvantage associated with point discharge. In Region III, the steel wire serving as a cathode began to melt due to local high temperature when the voltage exceeded 150 V.

To generate and optimize the plasma effect on fluorescent dye degradation, suitable parameters of the EDP process needed to be determined at the pulsed frequency of 4000 Hz (on/off switch time = 3 μs: 2 μs) as shown in Fig. 2b. Continuous and stable plasma electrolysis only occurred when the voltage and duty cycle were within a suitable zone (i.e., Region II). Moreover, the duty cycle could be appropriately reduced with an increase of input voltage to maintain stable plasma electrolysis in Region II.

The UV–vis spectroscopic method was used to evaluate the remaining concentrations of RhB and EY in organic solutions after EDP degradation. Figure 3 depicts the relationship between RhB/EY concentration and EDP processing time, reflecting the effect of K₂S₂O₈ electrolyte on dye degradation. Full degradation of 50 mg/L of RhB fluorescent dye via EDP in 1 g/L K₂S₂O₈ electrolyte took ~1500 s. As increased the concentrations of K₂S₂O₈ into 2 g/L, the degradation efficiency of RhB fluorescent dye rapidly increased, taking ~900 s to completely degrade the 50 mg/L RhB fluorescent dye. Therefore, K₂S₂O₈ electrolyte appeared to play a positive role in RhB degradation.

In the case of EY degradation, the initial concentration of 50 mg/L in EY-containing wastewater rapidly declined with EDP processing time until <5 mg/L EY remained in the organic

Fig. 2 **a** Current–voltage characteristics during the EDP process in the K₂S₂O₈ electrolyte using simulated organic wastewaters; and **b** suitable parameters of EDP for dye degradation at a pulsed frequency of 4000 Hz (on/off switch time = 3 μs: 2 μs)

Fig. 3 Degradation durations of **a** RhB and **b** EY dyes using electric discharge plasma in 1 and 2 g/L K₂S₂O₈ electrolytes, respectively

solution. When using a lower concentration of K₂S₂O₈ electrolyte, much more time was needed to degrade the EY dye with a concentration below 5 mg/L in the organic solution. Thus, the total EDP processing time was ~1500 s to degrade 50 mg/L of EY dye in 1 g/L K₂S₂O₈ electrolyte. An obvious reduction in EDP processing time occurred with 2 g/L K₂S₂O₈ electrolyte, taking 600 s to completely degrade 50 mg/L EY dye.

The basic mechanism to degrade fluorescent dyes using EDP involved plasma formation, which leads to local high temperature, strong UV light, intense shockwaves, and the formation of chemically active species, such as •OH, •H, •O, •OH, •HO₂, H₂O₂, O₃, and others. Van et al. considered the core temperature of discharges up to 6800–9500 K with high-energy plasma fed into the solution.³⁰ Thus, high-energy discharge in contact with liquids can dissociate/ionize water molecules into hydroxyl radicals (•OH) and hydrogen radicals (•H), which may then interact to form H₂O₂, •HO₂, and H₂. These radicals can diffuse in the surrounding liquid and be used to remove dissolved contaminants. In particular, •OH can oxidize any organic molecule into carbon dioxide in a non-selective manner. Moreover, O atoms (•O), which can be generated via dissociation of O₂, boost the production rate of •OH and react directly with contaminants. Ozone (O₃), a strong oxidizing agent for wastewater treatment, can also be formed due to the reaction between •O and O₂. A series of active reactions and interactions thereby occur during the formation and extinction of high-energy plasma according to the following equations:

Consequently, fluorescent dyes in wastewater can be degraded through effective oxidation of dissolved organic molecules. UV

irradiation and shockwaves also favor the •OH generation and the degradation of organic compounds in the pulsed discharge process.

In this study, K₂S₂O₈ electrolyte was used during EDP, producing a one-electron sulfate radical (•SO₄²⁻) with strong oxidation ability through the following reaction:

In particular, UV light obtained from the pulsed discharge can efficiently generate •SO₄²⁻. The sulfate radical •SO₄²⁻ (*E*₀ = 26 V vs NHE) has a similarly high standard redox potential as •OH (*E*₀ = 2.73 V vs NHE), suggesting enhanced oxidation capability and accelerated dye degradation in the EDP process. For RhB and EY fluorescent dyes, a higher concentration of K₂S₂O₈ in the organic solutions exhibited faster degradation kinetics. This finding suggests that both RhB and EY fluorescent dyes were highly reactive with •SO₄²⁻. In addition to using K₂S₂O₈ in the atrazine degradation as in Luo, et al.,³¹ the present work further confirms the effectiveness of K₂S₂O₈ electrolyte in remediating RhB- and EY-containing wastewaters during EDP.

Characteristics and effect of Au@SiO₂ nanocatalyst

The phase formation and microstructure features of the as-prepared Au@SiO₂ nanoparticles are shown in Fig. 4. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Fig. 4a, c present a monodisperse morphology and uniform distribution of core-shell Au@SiO₂ nanoparticles with an average particle diameter of 310 nm. N₂ sorption-desorption analysis of Au@SiO₂ (see Fig. 4b) exhibits a type IV isotherm with a total surface area of 886.89 m²/g and an average pore diameter of 4.1 nm. Energy dispersion spectrometry map scans from the TEM image, as displayed in Fig. 4d, confirm that nanoparticles mainly consisted of Si, O, and Au. The results demonstrate that the nano-Au@SiO₂ photocatalyst with core-shell structure can be prepared successfully.

For enhancing the efficiency of plasma oxidations towards dye degradation, nano-Au@SiO₂ photocatalysis was combined with EDP in 2 g/L K₂S₂O₈ solution. Figure 5 compares the processing time to degrade 50 mg/L RhB and EY dyes in simulated wastewaters with and without the addition of 2 mg/L Au@SiO₂ catalysts. The catalytic EDP process reduced the processing time to 360 s from 900 s of a simple EDP process for full degradation of 50 mg/L RhB dye. Similarly, the combination of nano-Au@SiO₂ photocatalysis and EDP degraded 50 mg/L EY dyes after treatment of 360 s. Moreover, the addition of the Au@SiO₂ nanocatalysts seemed more effective in shortening the processing time for low EY dye concentrations.

Fig. 4 **a** SEM image; **b** N₂ sorption-isotherm (inset: pore size distribution); **c** TEM image; and **d** EDS spectrum fully scanning on the TEM image for as-prepared Au@SiO₂ nanoparticles

Fig. 5 Degradation durations of **a** RhB and **b** EY dyes through the coupling process of electric discharge plasma and Au@SiO₂ nano-catalysis, respectively

To further confirm degradation quality, fluorescence spectra for RhB and EY dyes after coupling processing for 360 s respectively shown in Fig. 6a, b. For comparison, the standard linear relationships of fluorescence intensity vs. concentrations of RhB/EY are given in Fig. 6c, d. The small emission peak around 575 nm for RhB dye, as shown in Fig. 6a, demonstrates that only a tiny amount of RhB remained in the solution after coupling processing for 360 s. Similar results for EY dyes can be observed in Fig. 6b. Hence, the integration of nano-Au@SiO₂ photocatalysis and EDP demonstrated a high-quality, synergic effect for complete removal of RhB and EY dyes. In comparison with CASS processing of 72 h, a milestone in degradation kinetics and quality was reached by removing a high concentration of fluorescent dyes from wastewater in only 6 min.

In addition, the effect of the catalytic EDP process on the remediation of simulated wastewaters with initially low

concentrations of RhB (3 mg/L) and EY (1.5 mg/L) were respectively studied. Figure 7 depicts fluorescence spectra for RhB and EY dyes in organic solutions along with coupling degradation processing time. Compared with the standard curve of fluorescence intensity in Fig. 6c, 3 mg/L of RhB dyes in the simulated organic solution were completely degraded within 3 min as shown in Fig. 7a. In the case of 1.5 mg/L EY dyes in organic solution, Fig. 7b shows nearly no peak around 540 nm in the fluorescence spectra after the combined treatment of <3 min. Thus, <3 min was needed to fully degrade EY dyes with an initial concentration of 1.5 mg/L in the organic solution. Therefore, the coupling system of nano-Au@SiO₂ catalyst and EDP can be used successfully, with high efficiency and good quality, to degrade low dye concentrations in wastewater.

The contribution of Au@SiO₂ nanocatalysis for dye removal in the EDP system mainly lies in three main points. (1) Au@SiO₂

Fig. 6 **a, b** Fluorescence spectra of RhB- and EY-containing wastewaters treated after coupling processing for 6 min; and **c, d** standard linear relationships of fluorescence intensity as a function of RhB/EY concentrations in organic solutions

Fig. 7 Fluorescence spectra of organic solutions containing **a** 3 mg/L RhB and **b** 1.5 mg/L EY dyes after coupling treatment for different processing times

nanocatalysts as core-shell composites offer advantages in separating electrons and holes. Using Au@SiO₂ nanocatalysis, an electron-hole pair forms during the EDP processing. Once the excited charges reach the surface of the Au@SiO₂ nanocatalysis, they can participate in surface redox reactions with adsorbed donor or acceptor molecules. (2) The electron transport pathway is typically sufficiently fast, especially when Au nanoparticles (Au core), is used as catalysts. Au core acts as electron sinks, suppressing the electrons across the interface of core and shell. To prevent recombination, the holes are confined inside the nanostructure (mesoporous SiO₂ shell) acting as a hole trap, which are preferably away from the electrons. Alternatively, the holes are scavenged by a sacrificial agent.

According to the redox shuttle mechanism identified by Thomas et al.,³² photogenic electrons are transferred to the surface of metal and captured by the Schottky barrier, while the holes are confined to the interior nanostructure acting as a hole trap to prevent recombination. Thus, the photocatalytic reaction can facilitate the separation of electrons and holes, producing more active species such as $\cdot OH$. The addition of Au@SiO₂ nanocatalysts with a core-shell structure can enhance charge separation,^{30,32–37} allowing for more efficient use of active species and multiple energies generated during EDP. Hence, the favorable effect of EDP integrated with a nano-Au@SiO₂ photocatalyst appears for fluorescence dye degradation in liquid media.

Fig. 8 **a** XRD patterns after different heat-treatment steps; **b** FESEM image and **c** pore diameter for as-prepared porous composite; **d** filtration efficiency of porous composite ultrafiltration membrane when increasing the number of filters

Microstructure and filtration of porous composite ultrafiltration membrane

The separation of nanocatalysis nanoparticles from the EDP system remains challenging due to their small particle size.^{38–40} In this work, a porous composite ultrafiltration membrane has been developed to overcome this problem. Figure 8 shows the phase composition, surface morphology, and pore structure of the porous composite ultrafiltration membrane obtained after three-step sintering. The X-ray diffraction patterns confirm reactions between Al and Ti at 600 °C, as well as between Al and Nb at 900 °C. After sintering at 1350 °C, nano- Y_2O_3 powder was found to exert a significant impact on phase compositions of the composite based on the appearance of Y and $\alpha\text{-Al}_2\text{O}_3$. Therefore, the porous composite obtained at 1350 °C were mainly composed of Ti_3Al , TiAl, Nb_2Al , Y, and Al_2O_3 , and both Y and Nb_2Al appeared as soluble solids in the interior of the matrix. The field emission SEM image shows that the porous composite ultrafiltration membrane possessed a micro–nano pore structure and contained Al_2O_3 bulge, which could be beneficial in separating nanocatalysts and other nanopollutants from water. The pore size distribution of porous composite analyzed via mercury intrusion porosimetry is displayed in Fig. 8c. Results indicate that the porosity and density of the porous composite ultrafiltration membrane was 34.2% and 3.718 g/cm^3 , respectively. Two peak positions in pore volume appeared for the porous composite ultrafiltration membrane; the larger peak corresponded to a pore diameter of 3–10 μm , and a smaller peak occurred around an approximate pore diameter of 200 nm. This wide pore-diameter distribution demonstrates the dual-scaled porous structure and high porosity of the porous composite ultrafiltration membrane. Therefore, it is expected to

offer sufficient space to separate Au@SiO_2 nanoparticles and carbon impurities from water.

After respective degradation of RhB and EY, organic solutions containing Au@SiO_2 nanoparticles and carbon impurities were filtrated through the porous composite ultrafiltration membrane. The filtration efficiency of the porous composite ultrafiltration membrane (η_s) is defined by:

$$\eta_s = [(m_0 - m_f)/m_0] \times 100\%$$

where m_0 and m_f are the mass of the organic solutions treated by EDP and Au@SiO_2 photocatalyst before and after filtration, respectively. Combined with the concentration measurement of Au@SiO_2 nanoparticles in solution through ICP-OES, the dual-scaled porous composite ultrafiltration membrane achieved a filtration efficiency of 99.35% for removal of the Au@SiO_2 photocatalyst. The excellent utilization of the porous composite ultrafiltration membrane can be ascribed to the dual-scaled porous structure and high porosity. In particular, Al_2O_3 bulges embedded into the membrane matrix and nanoscale pores could effectively block the passage of nano- Au@SiO_2 and carbon impurities. In addition, 60 bottles of 100 mL organic solution containing Au@SiO_2 nanoparticles and carbon impurities after individual degradation of RhB and EY were investigated to assess the regeneration capability of the porous composite ultrafiltration membrane. As shown in Fig. 8d, porous composite ultrafiltration membrane was reused for 60 times to filtrate the 100 mL organic solutions containing Au@SiO_2 nanoparticles and carbon impurities after a filtration interval of ten times for 10 min with ultrasonic-assisted cleaning in purified water (10 min). Results show that porous composite ultrafiltration membrane achieved high

Fig. 9 Photos of simulated wastewaters with **a** RhB or **b** EY dyes before and after treatment via the two-step method. Step 1: combined process of EDP and Au@SiO₂ photocatalyst; and Step 2: filtration process through the porous composite membrane

filtration efficiencies of 99.46% (after being filtered 10 times), 99.42% (after being filtered 20 times), 99.28% (after being filtered 30 times), 99.36% (after being filtered 40 times), 99.31% (after being filtered 50 times), and 99.25% (after being filtered 60 times).

Dye removal after two-step strategy

To further illustrate the high efficiency and excellent utilization of the entire strategy with the two-step method, Fig. 9 shows photographs of the initially simulated wastewater with RhB or EY dyes. Wastewater was treated with a combination of EDP and Au@SiO₂ photocatalyst, and then the solution was filtered through the porous composite membrane. The initially RhB- and EY-containing wastewaters respectively turned into crimson and yellow. After the coupling process with EDP and Au@SiO₂ photocatalyst, both solutions became muddy in a few minutes. This pattern can be explained by the suspension of Au@SiO₂ nanoparticles and carbon impurities in the solutions after the degradation of RhB and EY dyes. Finally, the solutions became clear and transparent after filtration through porous composite ultrafiltration membrane.

The COD values of RhB- and EY-containing wastewaters solutions before and after the two-step treatment are given in Table 1. For RhB dye, COD value declined to 0.112 mg/L from 276.6 mg/L after the two-step strategy, resulting in a COD removal efficiency of 99.96%. Similar results were achieved for EY dye, which demonstrated a COD removal efficiency of 99.95%. These results confirm that the proposed two-step strategy can efficiently and effectively eliminate fluorescent dyes from wastewater, providing encouraging prospects for industrial wastewater treatment.

This work focused on a two-step strategy including degradation and filtration for complete and effective removal of nonbiodegradable and toxic fluorescent dyes from wastewaters. During RhB and EY dye degradation, a nano-Au@SiO₂ photocatalyst was added into the plasma discharge system, and degradation kinetics increased substantially. The RhB and EY dyes with high concentration of 50 mg/L in organic solutions only took 6 min to be fully degraded. For 3 mg/L of RhB dye and 1.5 mg/L of EY dye, full degradation occurred within <5 and 3 min, respectively. The high efficiency and good quality substantiate the synergistic advantages of the EDP process and Au@SiO₂ photocatalysis for dye degradation in wastewater. Based on the existence of Au@SiO₂ nanoparticles and carbon impurities in the solutions after degradation, a porous composite membrane possessing a dual-scaled porous structure was designed for filtration. A filtration efficiency of 99.35% through the dual-scaled porous

Table 1. Comparison of COD values and removal efficiencies for RhB- and EY-containing solution before and after two-step process

Dye	COD (before)	COD (after)	COD removal (%)
RhB	276.6 mg/L	0.112 mg/L	99.96%
EY	98.1516 mg/L	0.053 mg/L	99.95%

composite ultrafiltration membrane for removal of the Au@SiO₂ photocatalyst. After the two-step strategy, the COD removal efficiency exceeded 99.9% for RhB and EY dyes. These results provide practical guidance for a highly effective and efficient two-step strategy to eliminate fluorescent dyes from wastewater in future industrial applications.

METHODS

Materials

Tetraethyl orthosilane (TEOS, ≥99%), cetyltrimethylammonium bromide (96%), HAuCl₄·3H₂O (99.9%), acetonitrile, and ethanol were purchased from Sigma-Aldrich. Rhodamine B dye, tetrabromofluorescein dye, and potassium persulfate (K₂S₂O₈) were purchased from Acros. Commercial Ti, Al, and Nb powders with the purity of 99.9% had an average particle size <75 μm, and Y₂O₃ nanoparticles with the purity of 99.9% had an average particle size <30 nm. All nanopowders were supplied by Beijing DK Nano Technology Co., Ltd.

Catalyst preparation and characterization

One-pot synthesis of the nano-Au@SiO₂ catalyst was prepared according to most procedures of the sol-gel method as reported elsewhere.⁴¹ A mixture composed of water (100 mL), ethanol (40 mL), and cetyltrimethylammonium bromide (CTAB, 0.640 g) in a three-neck round bottom flask was stirred in a water bath at 70 °C. An aqueous solution of tetrachloroaurate (HAuCl₄·3H₂O, 55 mg in 5 mL) was added into the CTAB solution and stirred for 5 min. Then, 200 μL sodium hydroxide (NaOH, 2 M) was injected to instantaneously produce nucleation of Au nanoparticles. Nanoparticle growth was completed via stirring at 600 rpm for 30 min. Afterward, 1000 μL TEOS was added dropwise to the aforementioned solution. The condensation process was conducted through a second addition of 400 μL sodium hydroxide (NaOH, 2 M). Thin SiO₂-coated Au (Au@SiO₂) nanoparticles were obtained after 2 h and filtrated using centrifugation at 10,000 rpm for 10 min. Finally, the Au@SiO₂ nanoparticles were washed in 40 mL ethanol for three times and dried at 50 °C before usage.

SEM was performed using a JEOL-6700FE instrument, and TEM images were obtained by a TecnaiG2 F20 electron microscope. N₂ adsorption-desorption isotherms were performed at 77 K on a micromeritics ASAP2020 automated sorption analyzer. The specific surface areas of Au@SiO₂ catalysts was obtained by Brunauer-Emmet-Teller model, and pore size and pore volume of the catalysts were determined based on the Barrett-Joyner-Halenda model.

EDP treatment and photocatalysis for rapid degradation of organic wastewater

Prior to degrading organic wastewater, two types of simulated organic wastewater containing RhB or EY fluorescence dyes were produced in ultrapure MilliQ water (resistance > 18 MΩ cm⁻¹) through using vigorous ultrasonic-assisted stirring. The concentrations of RhB solutions were adjusted to 50 mg/L and 3 mg/L; 50 mg/L and 1.5 mg/L EY solutions were respectively prepared.

The electrode device and power source used in this study are depicted in Fig. 1a. The electrolyzer consisted of a silica glass container with 20 × 20 × 15 cm, two parallel graphite plates connected to an anode supply, and a suspending steel wire as a cathode. K₂S₂O₈ solutions of 1 and 2 g/L were respectively used as electrolytes to form sufficient liquid-phase electrolysis plasma and generate ·SO₄⁻ with strong oxidation properties. The solvents for K₂S₂O₈ dissolution were the differently simulated organic wastewater mentioned above. To study the synergic effect, 2 mg/L Au@SiO₂ nanoparticles were added into the electrolyte solutions and stirred into stable suspensions. The electrolyte solutions with and without Au@SiO₂

nanoparticles were compared. The temperature of the electrolyte with an initial value of 75 °C was monitored over time using a k-type thermocouple. A pulsed power was adopted for liquid plasma discharge formation at a pulse frequency of 4000 Hz (on/off switch time = 3 μ s: 2 μ s) with duty cycle of 60%.

Concentrations of RhB and EY in the remaining organic solutions were determined with a spectrophotometrical method using an ultraviolet spectrophotometer (UV-5300, Japan's Hitachi) before and after EDP treatment. Recorded changes in the fluorescence intensity at wavelengths of 575 nm/540 nm were used to measure the absorbance of complexes containing various concentrations of RhB/EY to derive UV standard curves of the RhB/EY solution. The standard linear relationships of fluorescence intensity vs. RhB/EY concentrations were also obtained by using a fluorescence spectrophotometer (F-4500, Japan's Hitachi) to further confirm the concentrations of RhB and EY in the remaining solutions.

Porous composite ultrafiltration membrane preparation and filtration

To prepare the high Nb-TiAl-based porous composite ultrafiltration membrane, commercial Ti, Al, and Nb powders with an atomic ratio of 46:48:6 were first mixed with 8 wt% Nano-Y₂O₃ contents in a high-energy planetary ball mill for 10 h. The mixtures were pressed into green pellets with a 20 mm diameter under the pressure of 200 MPa. Then, a three-step heat-treatment process was used to fabricate a porous composite ultrafiltration membrane, and the entirely reactive sintering process was conducted under vacuum conditions. The pellets were heated at 120 °C for 1 h for vapor evaporation, at 600 °C for 3 h for reaction of Al and Ti, at 900 °C for 3 h for reaction of Al and Nb, and finally at 1350 °C for 3 h to form the porous composite ultrafiltration membrane.

Both RhB- and EY-containing wastewater with an initial concentration of 50 mg/L were filtrated after degradation through the porous composite membrane. After filtration, each solution became clear and transparent. The pH value of the final solution was about 4–5, and the solution temperature was about 50–60 °C, after 2 g/L K₂S₂O₈ solutions was used as electrolytes. The concentration of Au@SiO₂ nanoparticles and carbon impurities in the solutions were tested using optima 5300 ICP-OES. The COD values of RhB- and EY-containing wastewaters were also tested with a DR 9300B water quality analyzer before and after the two-step treatment.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

The idea for this paper was proposed by W.Y.G., and experiments were carried out by W.Y.G., Y.F.L., and Y.H.Q. The experimental results were analyzed and interpreted by W.Y.G., L.Q.Z., H.Z., and J.P.L. The manuscript was written and corrected by W.Y.G., H. Z., J.P.L., and X.C.L. All authors reviewed the manuscript. The manuscript was revised by W.Y.G. and H.Z.

ADDITIONAL INFORMATION

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