Micro/nano-bubble assisted synthesis of Au/TiO₂@CNTs composite photocatalyst for photocatalytic degradation of gaseous styrene and its enhanced catalytic mechanism†

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A facile micro/nano-bubble method was firstly applied to synthesize an Au/TiO₂@CNT composite photocatalyst for photocatalytic degradation of gaseous styrene. The morphologies, structures and compositions of the photocatalysts were investigated by using a series of analytical techniques (scanning and transmission electron microscopy, FT-IR spectroscopy, Raman spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy). The micro/nano-bubbles can effectively facilitate the reaction of Au and TiO₂ NPs decorated onto CNTs, forming a stable ternary composite structure. The photocatalytic performance of Au/TiO₂@CNTs was investigated by the methodology of central composite design (CCD) in response surface methodology (RSM). The photocatalytic degradation and mineralization of styrene over Au/TiO₂@CNTs drastically increased with the rise of reaction temperature due to the formation of a compact structure. The analysis of EPR, UV-vis DRS, electrochemical properties and TPD-O₂ further revealed the enhanced photocatalytic mechanism of Au/TiO₂@CNTs. The further identification of free radicals showed that the photocatalytic degradation and mineralization of styrene were closely related to oxidative radicals such as hydroxyl radicals and superoxide radicals, which were mainly attributed to the synergistic effects of Au NPs and CNTs to enhance the photocatalytic activity. This work will provide a new insight into designing photocatalysts with high photocatalytic performance and stability for the degradation of hazardous VOCs.

1. Introduction

Photocatalytic oxidation has been extensively studied for air purification, such as the removal of volatile organic com-
efficiency TiO$_2$-based visible-light photocatalysts. For instance, doping with metals or nonmetals, as a better way to optimize the electronic structure of TiO$_2$, has been frequently used to enhance the photocatalytic performance by reducing the excitation energy and increasing the surface active sites of the photocatalyst.\textsuperscript{6–8}

Recently, the heterogeneous structures of Au nano-crystal/TiO$_2$ spheres have been attracting much attention for their visible-light photocatalytic activities due to surface plasmon resonance (SPR).\textsuperscript{9–12} As is reported, compared with single-phase TiO$_2$ photocatalysts, Au nano-crystal/TiO$_2$ spheres have a light-response range of 400–600 nm, which can significantly enhance the utilization of photons for organics degradation.\textsuperscript{13,14} However, Au nano-crystal/TiO$_2$ spheres possess low specific surface areas and also provide few adsorption active sites.\textsuperscript{15} Generally, the photocatalytic reaction takes place at the active sites of the photocatalyst defined as micro-reactors with their finite oxidizing ability and mass-transfer ability. In that case, the corresponding micro-reactors suffer a heavier burden for photocatalytic degradation of organics, resulting in the excessive accumulation of intermediates on the photocatalyst.\textsuperscript{16} As a result, the decreased contact probability between the reactants and photocatalyst can lead to a lower photocatalytic activity of Au nano-crystal/TiO$_2$. Throughout the process, the main decreased photocatalytic activity is attributed to the lower specific surface area and the mass transfer rates of Au/TiO$_2$, resulting in difficulty in desorption of intermediates and adsorption of the reactant.\textsuperscript{17–19} Thus, to obtain a high-efficiency photocatalyst with more active sites, it is necessary to conduct regulation of the surface structure and performance.

Carbon nanotubes (CNTs), as typical one-dimensional nanostructures, have been attracting much attention in fabricating novel photocatalytic materials due to their unusual mechanical, electrical, and chemical properties.\textsuperscript{20–22} Owing to their large specific surface area, CNTs have been considered to be promising co-adsorbents or supports for the adsorption and photocatalytic degradation of organic contaminants.\textsuperscript{17,18,20–22} For example, CNTs could apparently improve the photocatalytic activity of TiO$_2$ due to the CNTs being electron acceptors that promote the separation of photogenerated electron/hole pairs.\textsuperscript{23–25} Hence, it is highly desired to integrate the special characteristics of CNTs with Au/TiO$_2$ to fabricate composite photocatalysts with efficient mass transfer and high utilization of photogenerated charge carriers by an appropriate method.

Concerning the material combination of Au/TiO$_2$ with CNTs, several self-assembly strategies have been developed recently. Zeng et al.\textsuperscript{26,27} presented a self-assembly approach to fabricate Au/TiO$_2$/CNT nanocomposites by photo-assisted growth of Au nanoparticles and using premade TiO$_2$/CNTs as the support, which was considered as an appropriate method for fabricating complex 1D systems of ternary nano-composites with better control of nanoparticles with active phases (Au and TiO$_2$ nanoparticles). Nonetheless, these methods bear some negative implications, such as the utilization of an organic solvent or additive which then suppresses the photocatalytic activity due to residual organic matter.

A firm chemical interface is the key factor to obtain ternary nanocomposites or more complex nanocomposites with high photocatalytic activity and an in situ self-assembly strategy proves to be an excellent method for fabricating new types of nanocomposites. However, two things need special attention when applying this strategy. First, appropriate interfacial inducers should be selected to induce the formation of chemical interfaces between CNTs and TiO$_2$ nanoparticles to avoid overusing organic matter. Recently, chemical micro/ nano-bubbles were used as a soft template through a self-assembly method to synthesize various nanomaterials due to their typical properties of interfacial charge, enduring stability, and efficient interfacial mass-transfer.\textsuperscript{28–31} Second, owing to the special interfacial characteristics of micro/nano-bubbles, they can be used as an interfacial inducer to facilitate the interfacial adsorption, mass-transfer and chemical reaction for the formation of a specialized chemical interface. That is, the micro/nano bubbles can also show potential for fabricating multi-element composite materials, such as the ternary composite material Au/TiO$_2$@CNTs.

In this work, physical micro/nano bubbles were used as a soft template to induce the synthesis of Au/TiO$_2$ NPs assembled with CNTs. Typical micro/nano-bubbles could effectively control the size and distribution of Au/TiO$_2$ nanoparticles on CNTs, resulting in the formation of a firm chemical structure between Au/TiO$_2$ and CNTs, which could significantly improve the photocatalytic performance and the stability in gas-phase styrene degradation. On the basis of the experimental results of central composite design (CCD) in response surface methodology (RSM), the intrinsic connections between the photocatalytic properties of the Au/TiO$_2$@CNT composite and various factors such as reaction temperature, the mass fraction of CNTs, the amount of HAuCl$_4$ and reaction time were systematically revealed. Furthermore, the influence of the structure and composition on the photocatalytic properties, recombination of photogenerated electron/hole pairs, electro-chemical properties and free radical generation of the Au/TiO$_2$@CNT composite was also discussed. Finally, a model photocatalyst system was carefully proposed to predict the migration and transformation mechanisms of the photogenerated electron/hole pairs according to the obtained results.

2. Experimental section

2.1 Central composite design for preparation of photocatalysts

The design approach for photocatalyst preparation was performed by using a CCD with four independent variables, including reaction temperature, the mass fraction of CNTs, reaction time and the amount of HAuCl$_4$. The determined values of the variables were referenced to our preliminary experiments as presented in Table S1.\textsuperscript{†} The experimental data were analysed by Design-Expert software and a total of 30
experimental runs were performed. The complete experimental design results are shown in Table S2.†

2.2 Synthesis

The Au/TiO$_2$@CNT composites were synthesized with a micro/nano-bubble method to induce the formation of heterostructures based on electrostatic attraction of negative charges on the surface of the micro/nano-bubbles. The functional CNTs were obtained through a modified oxidation method and the details can be seen in the ESI.† First, approximately 0.0832 g of functional CNTs, 2 mL of 2 mol L$^{-1}$ TiCl$_4$ (99%, Aladdin Reagent Co., Ltd), 2 mL of glycerol (99%, Sinopharm Chemical Reagent Co., Ltd.) and 80 mL of micro/nano-bubble water were added into a 250 mL conical flask. Second, after 30 min of ultrasonic treatment, the conical flask was placed in a water bath and 1.5 mL of ammonia (13.33 mol L$^{-1}$, Guangzhou Chemical Reagent Factory) was added into the mixture dropwise under stirring and kept for 13 h at room temperature. Third, a given amount of HAuCl$_4$ (Sinopharm Chemical Reagent Co., Ltd.) was slowly added into the conical flask and reduced with a 300 W xenon lamp (PLS-SXE300/300UV, Perfectlight Co., Ltd.) for 15 min. Then, the obtained mixture was kept at selected reaction temperature for different durations. After the reaction, the products were collected by centrifugation, washed with distilled water and ethanol (Guangzhou Chemical Reagent Factory) thoroughly, and then dried at 80 °C for 18 h. Finally, the obtained Au/TiO$_2$@CNT composite was calcined at 420 °C for 2 h with the protection of N$_2$ gas (flow rate: 30 mL min$^{-1}$). The gas used to generate the micro- and nano-bubbles was the air suctioned from the atmosphere, passing through a filter in the gas inlet. The micro/nano-bubbles were produced by a commercial micro-bubble generator (Xiazhichun Environmental Protection and Technology Co. Ltd., China) composed of a magnetic gear pump, a pressurized tank and a micro/nano-nozzle in the outlet. Deionized water was used in all experiments.

2.3 Characterization

The morphologies of the as-synthesized samples were observed using scanning electron microscopy (SEM, ZEISS Merlin, German) and transmission electron microscopy (TEM, Hitachi, Japan). The phases of the obtained samples were characterized on a Bruker D8 Advance X-ray diffractometer (XRD, German) with a Cu tube for generating Cu K$_\alpha$ radiation (λ = 1.5418 Å). The functional groups of the samples were analysed using a Nicolet6700 Fourier transform-infrared spectrometer (FT-IR, Thermofisher, America). The Brunauer-Emmett-Teller (BET) surface area and pore distribution were characterized using an ASAP 2020 PLUS HD88 surface area and porosity analyzer (Micromeritics, America). The chemical compositions and molecular structures of the as-synthesized samples were analysed through UV laser Raman spectroscopy (HORIBA Jobin Yvon, France). The surface electronic states were analysed by using a Phi X-tool instrument (XPS, Ulvac-Phi, Japan). Electron paramagnetic resonance (EPR) experiments were performed with a Bruker EMXPlus spectrometer operating at the X-band (9.8 GHz), equipped with a cylindrical cavity operating at 100 kHz field modulation. The presence and mobility of oxygen species on the photocatalyst were studied by using temperature-programmed desorption of oxygen (O$_2$-TPD) performed on an Autochem II 2920 chemical adsorption instrument (Micromeritics). The UV-vis diffuse reflectance spectra (DRS) were collected on an Agilent Cary 300 spectrophotometer by using BaSO$_4$ as the reflectance standard. The fluorescence spectra were collected by using an F-7000 fluorescence spectrophotometer (Hitachi, Japan) with an excitation wavelength of 321 nm at wavelengths between 330–600 nm. The electrochemical properties were analysed by using an Autolab PGSTAT302N electrochemical workstation, and the details can be seen in the ESI.†

3. Results and discussion

3.1 Morphology, structure and composition analysis

The Au/TiO$_2$@CNT ternary composite was typically synthesized using a micro/nano-bubble method and the morphologies were observed by SEM (Fig. 1a$_1$–c$_1$) and TEM (Fig. 1a$_2$–c$_2$). The ID CNTs serve as a novel support which is uniformly decorated with Au/TiO$_2$ NPs, and the Au/TiO$_2$ NPs are closely combined with the CNTs. Thus, the close neighborhood of Au/TiO$_2$ NPs and CNTs achieved by this method is believed to favor the vectorial transfer of photogenerated electrons from Au/TiO$_2$ to CNTs, resulting in the enhancement of charge separation and photocatalytic efficiency.$^{24,25}$

To investigate its interfacial structure, the resultant Au/TiO$_2$@CNT composite was also subjected to high-resolution TEM (HR-TEM) characterization. It is observed that the Au/TiO$_2$ NPs are homogeneously decorated onto the CNTs (Fig. 2a and S1†) and there is no obvious separation boundary even under ultrasonic treatment for 2 h. This further confirmed that chemical bonds could be formed among Au, TiO$_2$ and CNTs. Furthermore, a selected area electron diffraction (SAED) pattern recorded from Au/TiO$_2$@CNTs (the yellow square in Fig. 2a) shows a diffraction pattern corresponding to single-crystal anatase along the (101) zone axis (Fig. 2b). HR-TEM images (Fig. 2c and d) show that both the TiO$_2$ and Au NPs are highly crystallized, as evidenced by the well-resolved Au (111) (0.248 nm) and TiO$_2$ (101) (0.365 nm) crystalline lattices. A close contact between them can facilitate the electron transfer from the excited Au NPs or TiO$_2$ to CNTs.$^{25,26}$

The functional groups and crystal structure of the Au/TiO$_2$@CNT composite were determined by FT-IR and Raman spectroscopy to confirm the formation of chemical bonds among Au, TiO$_2$ and CNTs. As shown in Fig. 3a, the main
infrared features of oxidative CNTs are assigned to the C=O (1714 cm\(^{-1}\)) and C–OH (1215 cm\(^{-1}\)) vibrations as compared with pure CNTs.\(^3\) The abundance of functional groups such as C=O and C–OH decorated on the CNTs is more favorable for coupling with TiO\(_2\) NPs. The broad peaks at 500–900 cm\(^{-1}\) are ascribed to the Ti–O stretching vibration of TiO\(_2\) decrusted on CNTs. Typically, the decreased peak intensity of C=O and C–OH indicates that the functional CNTs are closely coupled with Au/TiO\(_2\) NPs due to possible chemical bonds between CNTs and TiO\(_2\). Fig. 3b shows the Raman spectra of TiO\(_2\), Au/TiO\(_2\) and Au/TiO\(_2@CNTs\). Au/TiO\(_2@CNTs\) shows several characteristic bands at 155, 394, 509 and 628 cm\(^{-1}\), which correspond to the \(E_g(1)\), \(B_{1g}(1)\), \(A_{1g} + B_{1g}(2)\), and \(E_g(2)\) modes of anatase TiO\(_2\), respectively.\(^{34,35}\) In particular, the observed \(E_g(1)\), \(B_{1g}(1)\), \(A_{1g} + B_{1g}(2)\), and \(E_g(2)\) bands of Au/TiO\(_2@CNTs\) are apparently shifted in comparison with the \(E_g(1)\) (146 cm\(^{-1}\)), \(B_{1g}(1)\) (398 cm\(^{-1}\)), \(A_{1g} + B_{1g}(2)\) (517 cm\(^{-1}\)), and \(E_g(2)\) (642 cm\(^{-1}\)) bands of TiO\(_2\) and Au/TiO\(_2\) NPs, which are ascribed to the bond distortion due to the possible chemical interface formed between Au/TiO\(_2\) NPs and CNTs.\(^{15}\) These results are closely consistent with the morphology and FT-IR analysis.

To investigate the crystal structure of the as-synthesized photocatalysts, the X-ray diffraction spectra of TiO\(_2\) and Au/TiO\(_2@CNTs\) were carefully analysed (Fig. S2†). The anatase phase of TiO\(_2\) (PDF# 21-1272) is observed as the main crystal structure in the Au/TiO\(_2@CNT\) composite. The characteristic peaks observed at 2\(\theta\) = 38.2 and 44.3° are assigned to the crystal faces (111) and (200) of Au NPs (PDF# 65-2870), respectively, which are consistent with the HR-TEM results. However, no obvious peaks of CNTs are observed from the spectra, which is possibly ascribed to the characteristic peak at 2\(\theta\) = 26.0° of CNTs being covered by the main peak of anatase TiO\(_2\) at 2\(\theta\) = 25.3°, although the highly crystallized structure is beneficial for developing photocatalysts with high photocatalytic activity.\(^{18}\)

Furthermore, XPS was performed to confirm the composition of the Au/TiO\(_2@CNT\) composite. Fig. S3† shows the characteristic peaks of Au4f, Ti2p, O1s and C1s from the full XPS spectra of Au/TiO\(_2@CNTs\), further providing evidence for the formation of the Au/TiO\(_2@CNT\) ternary composite. It can be seen from Fig. S4a† that the main sharp peaks of Ti 2p1/2 located at 465.2 eV and Ti 2p3/2 located at 459.4 eV were assigned to Ti\(^{4+}\) in TiO\(_2\). The small peaks at 463.4 eV for Ti 2p1/2 and 460.7 eV for Ti 2p3/2 clearly indicate the presence of Ti\(^{3+}\).\(^{36,37}\) From the deconvolution plots (Fig. S4b†), the O element is mainly in the form of lattice oxygen in anatase TiO\(_2\) (530.7 eV), Ti–OH or O=C–O (532.2 eV), C–O species of CNTs (533.1 eV) and O–H of adsorbed H\(_2\)O (534.5 eV), respectively.\(^{38,39}\) The peak of C1s is divided into four peaks, 284.6, 285.9, 287.6 and 289.0 eV (Fig. S4c†), which are ascribed to
the sp²-hybridized carbon of CNTs, defect-containing sp²-hybridized carbon, C–O species and O=–C–O of CNTs, respectively.27,38,40 As shown in Fig. 5d, the characteristic peaks of Au are observed at 84.3 eV (Au 4f7/2) and 87.8 eV (Au 4f5/2). The lower peak intensity of Au 4f is mainly ascribed to the excessively low concentration.

3.2 CCD-RSM model establishment and analysis

To obtain a stable structure and high photocatalytic activity, the RSM was applied to optimize the experimental factors and regulate the structure influencing the degradation and mineralization performance of the Au/TiO2@CNT composite. All experimental data in CCD for the degradation and mineralization of gaseous styrene are listed in Table S2.† Based on the experimental data, a semi-empirical expression with a quadratic polynomial model is obtained using the Design-Expert software and expressed as follows (equations in terms of coded factors):

\[
Y_{\text{Deg}} = 23.28 + 9.83A + 0.51B + 0.47C - 4.00D - 4.56AB + 3.62AC - 2.76AD + 3.96BC + 0.12BD + 2.64CD + 1.02A^2 - 0.69B^2 - 0.12C^2 + 2.99D^2
\]  \tag{1}

\[
Y_{\text{Miner}} = 17.56 + 5.60A - 4.41B - 1.55C - 5.75D - 5.36AB + 1.33AC - 4.66AD + 6.16BC + 2.38BD + 1.19CD + 2.19A^2 + 4.08B^2 - 5.34C^2 + 1.82D^2
\]  \tag{2}

where \(Y_{\text{Deg}}\) and \(Y_{\text{Miner}}\) are the response variable of degradation and mineralization efficiency of styrene, respectively.

The given eqn (1) is used to predict the photocatalytic degradation efficiency of gaseous styrene catalyzed by Au/TiO2@CNTs. From Table S2,† it is found that the predicted degradation efficiencies of gaseous styrene matched with the experimental values very well. This is also observed from the plot of the predicted values against the experimental values (Fig. S5a†), with a high correlation coefficient (\(R^2 = 0.9584\)). From the variance (ANOVA) analysis (Table S3†), the adjusted \(R^2 = 0.9196\) is very close to the corresponding \(R^2\) value, suggesting good consistency between the experimental and predicted values of the degradation efficiencies of gaseous styrene catalyzed by Au/TiO2@CNTs.

The mineralization performance of Au/TiO2@CNTs was also considered (eqn (2) and Table S2†), and a good correlation between experimental and predicted values was also observed with a high correlation coefficient (\(R^2 = 0.9513\)) (Fig. S5b†), suggesting that the statistical model is appropriate to explain the relationship of mineralization efficiencies and structural performance. From Table S4,† the adjusted \(R^2 = 0.9092\) based on the experimental results further confirms the adaptability of this model. Besides, the data residuals according to the analysis of the experimental and predicted values are given to evaluate the adequacy of the model (Fig. S6†). All data residuals showed obvious linearity with the degradation or mineralization efficiency, and there was no severe non-normality. Meanwhile, the scatter diagram of data residuals against predicted values also demonstrates that the residuals appear to be a random scatter, suggesting that the model is adequate to describe the correlation of the responses and the four factors for the synthesis of the Au/TiO2@CNT composite.

The significance and adequacy can be tested based on variance analysis of the quadratic model. From the ANOVA results (Tables S3 and S4†), the total variation is subdivided into two components: variation related to the model and the experimental error, to decide whether the variation from the model is significant or not when compared with the residual error.31–43 This comparison is performed using the \(F\)-value, which is the ratio of the mean square of the model to the residual error. If the model is adequate, the \(F\)-value should be greater than the tabulated value of the \(F\)-distribution for a certain number of degrees of freedom in the model at a level of significance. In this study, the \(F\)-values are obtained as 24.69 and 21.75 for the degradation and mineralization efficiencies, respectively. These are clearly greater than the tabulated \(F\)-values (2.43 at 95% significance), indicating the adequacy of the model.

The Pareto analysis gives more significant information to interpret the results, and the percentage effect of each variable on the response can be calculated according to the following equation (eqn (3))17,43

\[
P_i = \frac{a_i^2 \times 100}{\sum a_i^2}\quad \tag{3}
\]

where \(P_i\) represents the percentage of each variable and \(a_i\) represents statistically significant coefficients in eqn (1) and 2, respectively.

As shown in Fig. 4a, the reaction temperature (A, 51.46%) and amount of HAuCl₄ (D, 8.52%) for Au/TiO₂@CNT synthesis are the main contributors to its photocatalytic degradation of gaseous styrene. As such, the reaction temperature (A, 13.24%), mass fraction of CNTs (B, 8.21%) and HAuCl₄ amount (D, 13.96%) play important roles in the mineralization of gaseous styrene (Fig. 4b). Because the formation of a contact structure between Au/TiO₂ and CNTs is closely related to the reaction temperature, it determines the interfacial charge transfer and formation rate of radicals.24,25 Meanwhile, the amount of HAuCl₄ determines the amount of Au

![Fig. 4 Pareto graphic analyses for the degradation (a) and mineralization (b) efficiencies of gaseous styrene catalyzed by the Au/TiO₂@CNT composite.](image-url)
NPs supported on TiO₂, which is associated with the utilization of photons. Hence, the parameters of reaction temperature and the amount of HAuCl₄ are very beneficial for enhancing the photocatalytic degradation of gaseous styrene. Note that the mineralization efficiency is also associated with the mass fraction of CNTs aside from the above two important parameters because the CNT amount can also enhance the specific surface area of the composites and promote the adsorption of styrene.

To reveal the interaction effects of the synthesized variates of the Au/TiO₂@CNT composite on the degradation and mineralization efficiencies, three-dimensional response surface plots were constructed with the statistical software and are shown in Fig. 5. Fig. 5a₁ shows the effect of the reaction temperature and mass fraction of CNTs on the degradation efficiency of styrene (amount of HAuCl₄, 0.018 mmol; reaction time, 12 h). Note that when the reaction temperature increases from 25 °C to 85 °C (mass fraction of CNTs, 26%), the degradation efficiency rapidly increases from 7.8% to 47.0%, suggesting the important role of reaction temperature in enhancing the degradation efficiency. Possible reasons can be found from the characteristic results in Fig. 1. In the case of the mass fraction of CNTs, the degradation efficiency slightly increases from 19.6% to 23.1% with the increase of mass fraction of CNTs from 4% to 37%. Meanwhile, the mineralization efficiency of styrene firstly decreased from 42.6% to 16.2%, and then gradually increased to 17.2%. These results showed that a higher reaction temperature was not only conducive to styrene degradation but also its deep oxidation process.

In the case of the mass fraction of CNTs, the degradation efficiency slightly increases from 19.6% to 23.1% with the increase of mass fraction of CNTs from 4% to 37%. Meanwhile, the mineralization efficiency of styrene firstly decreased from 42.6% to 16.2%, and then gradually increased to 17.2%. These results indicate that the high mass fraction of CNTs in Au/TiO₂@CNTs can restrain the deep oxidation of gaseous styrene. This is mainly due to the increase of the amount of CNTs improving the adsorption capacity of styrene in a continuous reaction system, which surely can facilitate the degradation of styrene.¹⁷,¹⁸ The fluorescence analysis also demonstrates that the increasing mass fraction of CNTs effectively promotes the separation of photogenerated electron/hole pairs and increases the formation rate of radicals (Fig. 6c). However, with the accumulation of large amounts of intermediates on the surface of the photocatalyst, the deep-oxidation process is possibly hindered due to ineffective mass transfer and formation of interfacial radicals.¹⁴–⁴₆

Fig. 5a₂ shows the effect of the reaction temperature and amount of HAuCl₄ (mass fraction of CNTs, 26%; reaction time, 12 h) on the degradation efficiency. The degradation efficiency is found to slowly decrease with increasing amount of HAuCl₄ from 0.004 to 0.032 mmol. Similar to the degradation efficiency, the mineralization efficiency also slightly decreases with the increase of the amount of HAuCl₄. This is because the excessive load capacity of Au NPs can increase the recombination of photogenerated electron/hole pairs as described in Fig. 6b, inhibiting the degradation of styrene and the subsequent deep-oxidation process.⁴³,⁴⁷,⁴₈

As for the effect of reaction temperature and reaction time (mass fraction of CNTs, 26%; amount of HAuCl₄, 0.018 mmol) (Fig. 5a₃), the degradation efficiency of styrene increases rapidly with the increase of the reaction temperature, but an increase of only 1.9% in degradation efficiency is observed when the reaction time was increased from 4 to 20 h. Obviously, the reaction time has a lower contribution to the degradation efficiency. However, the relationship of the reaction time and mass fraction of CNTs has a significant effect on the mineralization efficiency as shown in Fig. 5b₃ (reaction temperature, 55 °C; amount of HAuCl₄, 0.018 mmol). A
notable decrease in mineralization efficiency is obtained from 42% to 17.3% with the increase of the mass fraction from 4.0% to 37.0%, indicating the adverse impact on the mineralization efficiency. The effects of reaction time show that the mineralization efficiency gradually increased to 17.7% when the reaction time increased from 4 to 11 h. However, further increasing the reaction time would reduce the mineralization efficiency. These results may be attributed to an increase in particle size of TiO2 over CNTs with the increase of reaction time, which can contribute to the recombination of photogenerated electron/hole pairs (Fig. 6d).

To sum up, the reaction temperature was found to be the key parameter in adjusting the photocatalytic degradation and mineralization efficiencies of gaseous styrene on the Au/TiO2@CNT composite photocatalyst, based on the experimental results. Although the CNTs are conducive to the enhancement of the photocatalytic degradation efficiency, excessively high proportions of CNTs in the composites lead to the accumulation of intermediates due to the excessive adsorption of styrene and will restrain the deep-oxidation process of styrene. The addition of Au NPs can effectively improve the photocatalytic activity of Au/TiO2@CNTs, but the excessive load capacity of Au NPs can increase the recombination of photogenerated electron/hole pairs. Herein, a verification experiment was carried out under the optimized conditions based on the numerical optimization results in the Design Expert software. The highest photocatalytic degradation efficiency of 69.2% and mineralization efficiency of 52.5% for gaseous styrene are obtained with the optimum values of the variables of 85 °C, 4.04%, 6.58 h and 0.004 mmol for the reaction temperature, mass fraction of CNTs, reaction time and amount of HAuCl4, respectively. For comparison, the photocatalytic performance of this optimum sample was also measured under visible-light (VL) irradiation. The results indicate that the VL sample shows lower photocatalytic degradation (31.2%) and mineralization efficiencies (12.8%) compared with the sample under simulated solar light, suggesting that the excitation of TiO2 by UV light was also important to enhance the photocatalytic performance of this composite photocatalyst.

3.3 Enhanced photocatalytic mechanism of Au/TiO2@CNTs

According to the results of CCD-RSM analysis, Au/TiO2@CNTs possesses higher photocatalytic activity under simulated solar light. For comparison, the photocatalytic performance curves of pure TiO2, TiO2/CNT and Au/TiO2 photocatalysts are also given in Fig. S7. As seen from Fig. S7 and Table S5, the photocatalytic activity and stability of the Au/TiO2@CNT photocatalyst were much higher than those of TiO2, TiO2/CNT and Au/TiO2 photocatalysts. The additional XRD spectra shown in Fig. S8† reveal that there are no changes in the crystal structure of Au/TiO2@CNTs after the photocatalysis test, confirming the stability of the photocatalyst. However, the essential reasons for the enhanced photocatalytic mechanism of the Au/TiO2@CNT composite are still not clear. To give a reasonable explanation for the enhanced photocatalytic activity of Au/TiO2@CNTs, further evidence is given to further reveal the synergistic mechanism of CNTs coupled with Au NPs for enhancing the photocatalytic performance of TiO2 NPs.

To obtain information about the oxygen vacancies, EPR spectra were measured (Fig. S9†). For Au/TiO2, the sharp peak with the corresponding gzz = 2.004 is assigned to oxygen vacancies,56 and the highest intensity means that Au/TiO2 has the highest level of oxygen vacancies compared with the other samples. The EPR signals at gxx = 2.104 and gzz = 1.938 can be attributed to O2− and Ti3+56. From the EPR spectra, the characteristic peaks of CNTs in Au/TiO2@CNTs and TiO2/CNTs are observed and exhibit three components including a wide component, narrow component and broad component compared with TiO2 and Au/TiO2. Among them, the wide component was related to both the external magnetic field and the molecular field; the narrow peak is assigned to either amorphous localized defects, such as vacancies, or dangling bonds; the broad peak is assigned to the delocalized electrons over the conducting domains of carbon nanotubes.51 From the spectral analysis and the photocatalytic experimental results, the obtained numbers of oxygen vacancies of TiO2 and Au/TiO2 are higher than that of Au/TiO2@CNTs, but their photocatalytic performances are lower than that of Au/TiO2@CNTs. That is, the enhanced photocatalytic performance of Au/TiO2@CNTs is related to not only the properties of Au/TiO2 but also the electric conductivity and oxygen active sites of CNTs.20,21

It is known that the adsorption and mass transfer of VOCs onto the photocatalyst are not only closely related to the essential attributes of the specific surface area (S BET) but also the pore size of the photocatalyst. As shown in Fig. 7, the specific surface area of Au/TiO2@CNTs was determined to be 104.4 m2 g−1, which is higher than that of TiO2 (61.4 m2 g−1), TiO2/CNTs (78.7 m2 g−1) and Au/TiO2 (90.0 m2 g−1). The higher S BET of the Au/TiO2@CNT composite would allow it to have more adsorption sites and active sites, which can obviously promote the adsorption and degradation of gaseous styrene.52 Besides, Au/TiO2@CNTs possessed a larger pore size of 34.7 Å, which made it exhibit lower resistance of mass transfer during the degradation of gaseous styrene, resulting in a rapid mineralization of the intermediates from gaseous styrene into CO2 and H2O.

**Fig. 7** Nitrogen adsorption−desorption isotherms (a) and pore size distribution (b) of TiO2, TiO2/CNT, Au/TiO2 and Au/TiO2@CNT composite. The adsorption and desorption portions of the isotherms in (a) are marked with closed and open markers, respectively.
Optical characterization techniques such as UV-vis and fluorescence spectroscopy also provide information on optical adsorption and electron transfer, which can indirectly reflect the photocatalytic performance of photocatalysts. As shown in Fig. 8a, it is noted that the absorption intensity of Au/TiO$_2$@CNTs is higher than that of TiO$_2$ and Au/TiO$_2$ due to the excellent electrical conductivity of CNTs. For the Au/TiO$_2$ photocatalyst, there is a large broad peak ranging from 500 to 700 nm, suggesting the excellent visible-light response of TiO$_2$ decorated with Au NPs. In addition, the fluorescence spectrum also shows that the PL intensity of the Au/TiO$_2$@CNT composite is much lower than that of TiO$_2$ and Au/TiO$_2$ (Fig. 8b), indicating that the Au/TiO$_2$@CNT composite possessed a higher separation efficiency of photocatalytic electron/hole pairs. According to these results, the co-modification of CNTs and Au NPs will surely increase the utilization of photons and depress the recombination of photogenerated electron/hole pairs of the TiO$_2$ photocatalyst.

To deeply understand the migration and recombination of photoinduced electron/hole pairs, the photoelectrochemical properties of the photocatalysts were also carefully discussed. From Fig. 8c, the Au/TiO$_2$@CNT photocatalyst shows a higher photocurrent intensity and still possesses high photocurrent response after five cycles compared with pure TiO$_2$ and Au/TiO$_2$, indicating higher visible-light response and efficient electron transfer. In addition, the EIS analysis gives the appropriate evidence to further explain the separation efficiency of photogenerated electron/hole pairs. From the Nyquist curve (Fig. 8d), the Au/TiO$_2$@CNT composite shows a smaller semicircular diameter compared with TiO$_2$ and Au/TiO$_2$, where a smaller arc radius indicates a higher separation efficiency in charge transfer, suggesting that the Au/TiO$_2$@CNT composite possessed higher separation and transfer efficiency of photogenerated electron/hole pairs. Through the analysis of the experimental results, it is speculated that the synergetic effect of Au NPs and CNTs can greatly promote the separation and facilitate the transfer of photogenerated electron/hole pairs, which is very beneficial for the formation rate of interfacial radicals which then influences the photocatalytic performance of the Au/TiO$_2$@CNT composite.

It is well known that enhanced mobility is another crucial parameter for enhancing the catalytic activity due to the promotion of O$_2$ adsorption and activation. Herein, temperature programmed desorption of oxygen (O$_2$-TPD) was also conducted to confirm the ability of oxygen activation over different photocatalysts (Fig. S10†). Two O$_2$ desorption peaks are observed over the Au/TiO$_2$@CNT composite. The peak at 75 °C is attributed to the chemisorption of O$_2$ onto the surface, and another peak at 160 °C could be attributed to the desorption of surface capping oxygen. As compared with pure TiO$_2$ and Au/TiO$_2$, enhanced desorption of O$_2$ is observed for Au/TiO$_2$@CNTs, indicating that more O$_2$ can adsorb onto this ternary photocatalyst at 40 °C. Typically, this effect is obvious for Au/TiO$_2$@CNTs, which is consistent with the fact that Au/TiO$_2$@CNTs shows the highest photocatalytic performance under the same conditions.

The reactive oxidizing species (ROS) associated with the separation of photogenerated electron/hole pairs are the key factors for the decomposition of gaseous styrene. Here, the EPR spectra were recorded by using DMPO as the trapping agent (see the ESI†). As shown in Fig. 9, strong EPR signals of DMPO–OH adducts with a 1 : 2 : 2 : 1 intensity and DMPO–O$_2$– adducts with six characteristic peaks are observed in the Au/TiO$_2$@CNT photocatalyst system under stimulated solar light irradiation, indicating that ‘OH and O$_2$– are the important ROS in this system. Moreover, the EPR intensity for DMPO–OH and DMPO–O$_2$– of Au/TiO$_2$@CNTs is much higher than that of TiO$_2$ and Au/TiO$_2$, demonstrating the synergistic effects of Au NPs and CNTs on enhancing the photocatalytic activity of TiO$_2$.

Based on the above analytical results, a possible enhanced photocatalytic mechanism of the Au/TiO$_2$@CNT photocatalyst under solar light irradiation is proposed in Fig. 10. Generally, electrons and holes are produced by the excitation of TiO$_2$ by a small amount of UV from solar light, and rapidly accumulate on the conduction band (CB) and valence band (VB) of TiO$_2$, respectively. Owing to the oxidability of holes, they can oxidize H$_2$O into 'OH in the photocatalytic reaction. In particular, the CB potential of TiO$_2$ is higher than those of CNTs and Au NPs. Hence, there are two migration and transformation patterns for the photogenerated electrons: (1) the photogenerated electrons transfer from TiO$_2$ to the carbon chains of CNTs, and subsequently react with the adsorbed O$_2$...
to form $\text{O}_2^{-}$ due to local surface plasmon resonance (LSPR); the produced electrons on the surface of Au NPs can also transfer to the carbon chains of CNTs or react with the adsorbed $\text{O}_2$ to form $\text{O}_2^{2-}$\cite{5,6}. It is well known that $\text{O}_2^{-}$ is an important ROS\cite{64} which also participate in the photocatalytic degradation of styrene. Meanwhile, $\text{O}_2^{-}$ can be transformed into ‘OH through a series of reactions, promoting styrene degradation. Due to the combined effect of $\text{h}^+$, ‘OH and $\text{O}_2^{-}$, the gaseous styrene could be subsequently mineralized into $\text{CO}_2$ and $\text{H}_2\text{O}$\cite{64}. This is because for a single TiO$_2$ photocatalysis system, only ‘OH is the main ROS.\cite{61,65} Unlike the TiO$_2$ photocatalysis system in this work, more charge carriers were transformed into oxidative radicals on Au/TiO$_2$@CNTs which participate in the photocatalytic degradation of gaseous styrene. As described in the visible-light photocatalytic tests, the Au/TiO$_2$@CNT photocatalyst still has photocatalytic activity under visible-light irradiation, which is mainly attributed to the contribution of LSPR of Au NPs and electron transfer of CNTs for the formation of $\text{O}_2^{-}$ to degrade styrene. The Au/TiO$_2$@CNT system with high $S_{\text{BET}}$ provides not only more $\text{O}_2$ adsorption sites for efficiently enhancing the formation rate of oxidative radicals, but also more adsorption and active sites due to the addition of CNTs. In a word, the high decomposition of gaseous styrene is attributed to the intrinsically strong photo-oxidation ability of Au/TiO$_2$ and high adsorption capacity and electron transfer of CNTs, resulting in efficient photocatalytic degradation and mineralization of gaseous styrene. But the formation of firm chemical interfaces between Au/TiO$_2$ and CNTs is confirmed to be very necessary during the synthesis of the Au/TiO$_2$@CNT composite, facilitating the formation of this ternary photocatalyst with high performance and stability.

Conclusions

An Au/TiO$_2$@CNT ternary composite was firstly synthesized by a self-assembly method with micro/nano-bubbles as a soft template. Based on the CCD-RSM results, the reaction temperature was found to be the key factor for the enhancement of the degradation and mineralization efficiencies of gaseous styrene. In particular, the enhanced mechanism of the photocatalytic performance of the Au/TiO$_2$@CNT composite was carefully discussed. It was noted that the photocatalytic performance and durability of the Au/TiO$_2$@CNT composite are by far higher than those of TiO$_2$, TiO$_2$/CNT and Au/TiO$_2$ photocatalysts. This was mainly because the synergetic effects of Au NPs and CNTs could not only increase the migration and transformation rates of photogenerated electron/hole pairs, but also provide more adsorption and active sites for gaseous styrene. This work may provide deep insight into designing multiple-element photocatalysts with high efficiency and stability for removal of typical VOCs, and typically reveals the significant influence of the structure and composition on the photocatalytic performance and durability of the as-synthesized photocatalysts.

Conflicts of interest

There are no conflicts to declare.

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Notes and references