Electro-Fenton Process

Highly Efficient AuPd/Carbon Nanotube Nanocatalysts for the Electro-Fenton Process

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Abstract: Development of novel nanocatalysts for the highly efficient in situ synthesis of H₂O₂ from H₂ and O₂ in the electro-Fenton (EF) process has potential for the remediation of water pollution. In this work, AuPd/carbon nanotube (CNT) nanocatalysts were successfully synthesized by the facile aggregation of AuPd bimetallics on CNTs. Characterization by X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy indicated that pure AuPd bimetallic heterogeneous nanospheres (≈ 20 nm) were well dispersed outside the CNTs, which resulted in better catalytic performance than Pd/CNTs alone: 0.36 M H₂O₂ was synthe-

sized; 0.05 M Fe²⁺ optimally initiated the EF process due to the superior in situ Fe²⁺ regeneration; and the organic pollutant removal reached 100% at 37 min, with a pseudo-first-order kinetic constant $k_1 = 0.051 \text{ min}^{-1}$. Moreover, structural insights before/after catalysis revealed that Au strengthened the construction of the nanocrystals, avoided negative deactivation caused by AuPd agglomeration, and immobilized the active Pd(111). The catalytic stability of AuPd/CNTs over ten cycles implied long durability and promising applications of this material.

Introduction

Fenton oxidation, as an advanced oxidation process, has aroused great interest in water remediation over recent decades due to the formation of the highly reactive and nonselective hydroxyl radical ($\cdot\text{OH}$, oxidation potential: 2.8 V).^[1] The produced $\cdot\text{OH}$ enables superior properties of the method, that is, nonselective, strongly oxidizing, and high reactivity, which contribute to the efficient removal and mineralization of complex contaminants, such as oil wastes, dyes, bromate, chromium, arsenic, and synthetic organic wastewater.^[2] However, its application is limited by such drawbacks as the difficulty in controlling the dose of ferrous salts for catalytic oxidation, and the high cost and danger in the production, transportation, and storage of H₂O₂. Therefore, the electro-Fenton (EF) process has been under intense study owing to its continuous in situ

generation of H₂O₂ from cathodes [Eq. (1)] and Fe²⁺ from anodes [Eq. (2)].^[3] High-efficiency H₂O₂ requires electrode materials with high price and poor structural stability, such as synthetic boron-doped diamond, active carbon fiber, and gas diffusion electrodes.^[4] Furthermore, the sluggish kinetic process of oxygen reduction for H₂O₂ synthesis also depends strongly on the electrode materials, which complicates the implementation process and increases the cost.

Recently, a novel palladium-based catalyst showed great potential in direct synthesis of H₂O₂ during the EF process.^[5] The strategy can be summarized as follows. 1) Sufficient utilization of H₂ and O₂ released from electrodes [Eqs. (3) and (4)] in synthesizing H₂O₂ by electrolysis. 2) High efficiency of catalytic synthesis of H₂O₂ over the active surface of Pd atoms [Eq. (5)]. 3) Promotion of interfacial contact efficiency among catalysts, O₂, and H₂ in the three-electrode electrolysis system. The new process exhibited high performance in the degradation of many organic contaminants, including rhodamine B, trichloroethylene, phenol, and toluene in wastewater and groundwater.^[5b,d,6] Nevertheless, the weaknesses of this Pd-based EF process should not be neglected. For instance, monometallic catalysts without specific surface decoration generally have lower catalytic activity than bimetallic/intermetallic catalysts, and the Fe@Fe_xO_y substrate has less structural stability in acid media than carbonaceous substrates.^[7] Importantly, particle agglomeration of Pd supported on Fe-containing substrates in acidic solution generally results in the deactivation of the composite

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catalysts. Thus, development of efficient and active bimetallic nanocatalysts supported on robust substrates with superior structure is essential for highly efficient catalysis in the EF process.

AuPd bimetallic nanocomposite catalysts with core-shell structures,^[8] specific shapes,^[9] hierarchically porous structures,^[9] and, especially, heterogeneous growth or assembly^[10] have achieved some successes in optimizing catalytic activity for in situ synthesis of H_2O_2 from H_2 and O_2 . AuPd bimetallics exhibit outstanding ability in catalytic hydrogenation to improve the yield and selectivity of H_2O_2 formation. It has been reported that the Pd/Au(111) and Pd/Au(100) nanocrystal surfaces have superior activity and are responsible for the generation of active atomic hydrogen, which contributes to the H_2O_2 synthesis.^[11] Moreover, the promotional effects of Au on AuPd nanocomposites have drawn attention.^[12] Carbon nanotubes (CNTs), as a carbonaceous material with high surface area, good conductivity, strong mechanical properties, and chemical stability, have been identified as promising substrates in the synthesis of nanocomposites.^[13] Recent studies demonstrate that catalysts (e.g., metals, transition-metal chalcogenides and oxides) supported on CNTs can notably accelerate the electrocatalytic behavior relative to those on conventional carbon-based supports.^[14] On the one hand, the functional nanoparticles can be encapsulated and dispersed inside/outside the CNTs, thereby contributing to the elevation of the catalytic performance of the nanocomposites.^[15] On the other hand, low-load nanocrystals on CNTs not only avoid the drawback of inactivation caused by particle agglomeration, but also the CNTs themselves play distinctive roles in the electrocatalytic activity.^[16] Therefore, the novel strategy of integrating AuPd nanocrystals with CNTs is a promising way to develop a highly catalytic, durable, and low-cost catalyst for in situ production of H_2O_2 , and to achieve an efficient degradation of contaminants through the electrocatalytic EF process. However, little work has been done on directly synthesizing AuPd/CNTs for use as efficient electrocatalysts, and the role of Au nanocrystals on AuPd bimetallic nanocomposites in the catalytic generation of H_2O_2 is also poorly understood.

Herein, AuPd/CNT nanocomposites were directly synthesized through facile grain nucleation and heterogeneous crystal growth of AuPd on CNTs. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were employed to characterize the AuPd/CNT nanocomposites. The results indicated that heterogeneous AuPd nanocrystals were well dispersed on the CNTs and the specific heterostructure of the catalysts engendered optimized catalytic characteristics in H_2O_2 synthesis. The effects of operating parameters including solution pH, Au loading, current density, and initial contami-

nant concentration were analyzed in the EF degradation of organic contaminants. The functional and structural aspects of the promoting role of Au on nanocomposites were elucidated. Finally, proposed mechanisms for the degradation pathway of pollutants and generation of reactive oxidizing species based on AuPd/CNTs were described.

Results and Discussion

Characterization of AuPd/CNT nanocatalysts

Figure 1 a shows the powder XRD patterns of CNTs and of 1 % Pd/CNT, 1 % Au/CNT, and 0.5 % Au 0.5 % Pd/CNT nanocomposites. The as-prepared CNTs support bimetallic AuPd particles

Figure 1. a) XRD patterns of CNTs, 1 % Pd/CNTs, 1 % Au/CNTs, and 0.5 % Au 0.5 % Pd/CNTs. b) XPS spectra of 0.5 % Au 0.5 % Pd/CNT nanocomposites. The insets show the high-resolution XPS patterns of Au and Pd. c) SEM image of AuPd/CNTs. The inset shows the corresponding energy-dispersive X-ray spectrum. d) TEM image of AuPd/CNTs. The inset shows the HRTEM image of heterogeneous AuPd nanocrystals on CNTs.

(AuPd/CNTs), and monometallic Au (Au/CNTs) and Pd (Pd/CNTs). Typical diffraction peaks of CNTs can be observed at 26 and 42.9° from all the synthesized nanocomposites. Strong peaks at 40.4, 47.1, and 68° of Pd/CNTs correspond well to the (111), (200), and (220) planes of Pd. Similarly, Au/CNTs also have typical diffraction peaks of monometallic Au at 38.3 and 44.2°, which suggests the exposure of Au(111) and Au(200) planes. Notably, three diffraction peaks located at 39.4, 45.6, and 67.1° for bimetallic AuPd lie between the corresponding phase peak positions of pure Au and Pd, thus indicating the successful formation of AuPd bimetallics.^[17,18] Moreover, the AuPd/CNTs strengthen the crystal planes of alloys with strong diffraction peaks relative to Au/CNTs and Pd/CNTs under the

same load of metal (1 wt%), which suggests that the crystal planes of bimetals are strengthened and may prominently contribute to a greater potential electrocatalytic activity. The 0.5% Au 0.5% Pd/CNT nanocomposites were further characterized by XPS to confirm the elemental composition and metallic state. As can be seen from Figure 1b, only C1s, Pd3d, Pd3p, and Au4f can be found with their corresponding binding energies, without any impurity. High-resolution XPS spectra of Pd3d and Au4f peaks for the AuPd/CNT nanocomposites are shown as insets in Figure 1b. The binding energies of Pd3d at 335 and 340 eV and of Au4f at 84 and 87.7 eV are well fitted to the signals of pure metallic elements.

The SEM image illustrates the good dispersion of AuPd nanoparticles supported on CNTs (Figure 1c). The insight further reveals the purity of the nanocatalysts. The TEM image shows that the majority of spherical AuPd nanocrystals were synthesized with an approximate diameter of 20 nm stably dispersed on the surface of CNTs (see Figure 1d). A small fraction of some nanoparticles agglomerates together, with the result that some large particles with an approximate diameter of 50 nm are formed. Moreover, the heterogeneous growth of AuPd nanoparticles can be clearly observed from Figure 1d. The inset in Figure 1d shows some details of heterostructured AuPd nanoparticles with well-defined crystalline lattices: a lattice spacing of 0.192 nm corresponding to the (111) plane of Pd (0.19 nm); and a lattice at a different orientation with a spacing of 0.238 nm, similar to Au(111) (0.24 nm). Additionally, the porous network and pore size distribution of the catalyst were measured by BET analysis (Figure S1 in the Supporting Information), which illustrates that the catalyst should favor the adsorption of H₂ and O₂ during the EF process.

Au-enhanced performance in the electro-Fenton process

Degradation of organic contaminants

Figure 2a illustrates the superior catalytic performance in the removal of dimethylacetamide (DMAC) based on AuPd/CNT nanocatalysts in the EF process. By comparison, in the presence of 1 g L⁻¹ 1% Pd/CNTs alone, there was only slight degradation of DMAC, which suggests inefficient adsorption of DMAC on Pd/CNTs. However, nearly 20% removal of DMAC within 60 min was attained only by electrolysis, thus implying that the removal of DMAC by a dimensionally stable anode (DSA) is also limited. In contrast, integration of 1 g L⁻¹ Pd/CNTs with electrolysis contributed to the degradation of DMAC, which can be possibly ascribed to oxidation by active radicals caused by catalytic reaction of generated H₂O₂ on the DSA or Pd/CNT cathodes. Furthermore, the addition of Fe²⁺ markedly elevated the removal efficiency of DMAC in the presence of nanocatalysts under electrolysis. For example, DMAC was totally mineralized within 50 min by Pd/CNTs, and 100% DMAC was thoroughly degraded within 37 min by the 0.5% Au 0.5% Pd/CNTs catalytic EF process under a current density of 50 mA cm⁻², 1 g L⁻¹ catalyst, initial pH 3, and 100 mg L⁻¹ DMAC. It is evident that the introduction of Au enhances the catalytic degradation of DMAC, and the performance of the AuPd/CNTs catalytic EF process is significantly superior to that reported in some similar studies.^[5a,d] The degradation of DMAC by the catalytic EF process approximately followed pseudo-first-order kinetics owing to the stable synthesis of [•]OH radicals.^[3,6] Hence, the pseudo-first-order rate constants can be calculated as 0.030 min⁻¹ (*R*²=0.995) for Pd/CNTs and 0.051 min⁻¹ (*R*²=0.986) for AuPd/CNTs. The obtained *k* value based on AuPd/CNTs

Figure 2. a) Degradation of DMAC under different conditions. b, c) Effects of Au loading on AuPd/CNTs on b) H₂O₂ generation and c) current efficiency; 1 g L⁻¹ catalyst: Au loading from 0 to 1% in AuPd/CNTs (balance Pd for 1% metal total), and 2.5% Au 2.5% Pd/CNTs. d) Cyclic voltammograms of CNTs, Pd/CNTs, and AuPd/CNTs in H₂- and O₂-saturated acidic solutions. Scan rate: 50 mV s⁻¹. e) Simultaneous changes of H₂O₂, Fe²⁺, and Fe³⁺ during the EF process in the presence of 1 g L⁻¹ 0.5% Au 0.5% Pd/CNTs. Unless otherwise specified, the reaction conditions were based on 1 g L⁻¹ catalyst (0.5% Au 0.5% Pd/CNTs and 1% Pd/CNTs), initial pH 3, 50 mA cm⁻², 100 mg L⁻¹ DMAC, and 2.5 mM Fe²⁺.

CNTs is greater than those reported by Luo et al. (0.033 min^{-1}) and Zhao et al. (0.016 min^{-1}) in similar catalytic systems.^[5a,b,19] Moreover, although the normalized concentration of AuPd on the AuPd/CNTs ($0.01 \text{ g AuPd L}^{-1}$) is one order of magnitude smaller than the concentration of Pd ($0.125 \text{ g Pd L}^{-1}$) used in the reported Pd/C catalytic EF process, the comparable k value achieved by the AuPd/CNTs catalytic EF process further highlighted its unexpectedly high catalytic capacity for such low loading of AuPd.^[5d] Therefore, it can be concluded that 0.5% Au 0.5% Pd/CNTs have superior performance in DMAC removal during the catalytic EF process compared with 1% Pd/CNTs and some similar Pd-based catalysts. Clearly, the introduction of Au on AuPd/CNTs seems to play a crucial role in the catalytic capacity for organic contaminant removal.

In situ synthesis of H_2O_2

As can be seen from Figure 2b, different loadings of AuPd on CNTs have varied efficiency in the catalytic synthesis of H_2O_2 only in electrolysis without Fe^{2+} . On comparing 1 and 5 wt% loading of alloys on AuPd/CNTs, a higher quantity of alloy resulted in a higher concentration of H_2O_2 . However, H_2O_2 synthesis did not scale linearly with the proportion of bimetallic loading, which can be ascribed to the catalytic decomposition of H_2O_2 caused by exposure of surplus active sites over the AuPd surface [Eq. (6)].^[6] The optimal in situ synthesis of H_2O_2 from 0.5% Au 0.5% Pd/CNTs was nearly 0.30 mM within 20 min. In sharp contrast, just 0.19 mM was obtained for 1% Pd/CNTs, and only 0.04 mM for 1% Au/CNTs. The results indicate an advantage in H_2O_2 synthesis by AuPd/CNTs compared with catalytic synthesis of H_2O_2 by Au/CNTs alone. However, the concentration of H_2O_2 increased with the increase of Au loading from 0.25 to 0.50% on AuPd/CNTs, further suggesting the promoting role of Au for H_2O_2 synthesis. Moreover, with the further increase of Au loading to 0.75%, a slight decrease was observed after 20 min. Therefore, an appropriate Au loading on AuPd/CNTs is beneficial for optimizing synthesis of H_2O_2 .

In addition, the current efficiency (CE) for different loadings of Au on AuPd/CNTs was investigated. A gradual decay of CE with time was observed as shown in Figure 2c. In particular, the highest CE of nearly 35% was obtained by 2.5% Au 2.5% Pd/CNTs at the beginning of the electrolysis with 50 mA cm^{-2} , which is close to the previously reported value.^[5d] As expected, the CE gradually decreased with the process of electrolysis. The 0.5% Au 0.5% Pd/CNTs still had the highest CE of 6.1% at 60 min compared with the same loading of 1% AuPd bimetals. Thus, the functional role of the appropriate Au loading in accelerating the transport of electrons over the surface of nanocatalysts is further confirmed, thereby demonstrating its effectiveness in the direct synthesis of H_2O_2 from H_2 and O_2 released by water electrolysis.^[20]

To investigate the synthesis of H_2O_2 over different nanocatalysts in more depth, the cyclic voltammograms of CNTs, 1%

Pd/CNTs, and 0.5% Au 0.5% Pd/CNTs in H_2 - and O_2 -saturated acidic solution were evaluated. As shown in Figure 2d, a broad flat curve of CNTs was observed in the potential range from 0 to 1.2 V, and the peak of H_2 evolution appeared at 0 to -0.2 V . As for Pd/CNTs and AuPd/CNTs, the response current increased significantly, and the peak at 0.4 V corresponding to the oxygen reduction reaction (ORR) could be found for both nanocatalysts in O_2 -enriched solution,^[21] which verified their electrocatalytic activity for H_2O_2 synthesis. In contrast, the limiting current density of AuPd/CNTs for ORR electrocatalysis was 0.78 mA cm^{-2} , whereas that for Pd/CNTs was just 0.60 mA cm^{-2} , which demonstrated that AuPd/CNTs have enhanced catalytic performance for H_2O_2 synthesis compared with Pd/CNTs and bare CNTs. The promoting function of Au loading on AuPd/CNTs was again confirmed. As reported,^[22] a two-step reaction mechanism of H_2O_2 synthesis is widely accepted, starting from the dissociation of O_2 [Eq. (7)] on the Pd surface and a subsequent two hydrogen atom [Eqs. (8) and (9)] combination. However, an undesirable pathway of dioxygen dissociation always leads to the nonselective formation of H_2O [Eq. (10)], which is detrimental for H_2O_2 generation. The presence of surface Au atoms blocks this dissociation and increases the selectivity toward H_2O_2 [Eq. (11)]. Therefore, appropriate loading of Au on AuPd/CNTs notably increases the H_2O_2 formation rate, and the optimized ratio of Au and Pd significantly improves the catalytic selectivity and reduces the activation energy of the H_2O_2 synthesis reaction.

In situ regeneration of Fe^{2+}

A certain amount of added Fe^{2+} (140 mg L^{-1}) at initial pH 3 could homogeneously catalyze the decomposition of H_2O_2 into $\cdot\text{OH}$ radicals. To further reveal the contribution of iron species and accumulation of H_2O_2 during the catalytic electrolysis, dissolved concentrations of Fe^{2+} , Fe^{3+} , and H_2O_2 were monitored during electrolysis (Figure 2e). The total dissolved Fe species gradually decreased from 140 to 104 mg L^{-1} , which indicated that sedimentation of Fe was inevitable. Dissolved Fe^{2+} was distinctly dominant among the dissolved species (Figure S2 in the Supporting Information). The proportion of Fe^{2+} in the total dissolved Fe species increased from 88.6 to 98.1%, which demonstrates a continuous accumulation of dissolved Fe^{2+} through the pathway of Fe^{3+} reduction. The slight change in Fe^{2+} concentration suggests that homogeneous catalysis by dissolved Fe^{2+} is significant and in situ regeneration of Fe^{2+} in the AuPd/CNTs catalytic EF process is also effective. Notably, acidic Fenton chain reactions generally result in a final accumulation of Fe^{3+} due to the relatively high reaction rate con-

stants indicated in Equations (12) and (13).^[4] However, in this AuPd/CNTs catalytic EF system, the in situ transformation of Fe^{3+} to Fe^{2+} promoted by H atoms released from the surface of nanocatalysts is of great importance. Actually, the reducing action of the H atom is enhanced by the AuPd/CNTs catalytic system, which finally leads to a distinct reaction environment compared with the initial conditions: only 2.12 mg L^{-1} Fe^{3+} was left within 60 min. Meanwhile, under the intensive regeneration of Fe^{2+} , the strong generation of H_2O_2 resulted in approximately linear growth of H_2O_2 , which followed zeroth-order kinetics (see straight line in Figure 2e, $k=0.007$).^[6] As seen from Figure 2e, although the mole ratio of Fe^{2+} to H_2O_2 declined from 24.01 to 4.13 in 60 min, this is still much higher than the optimal value (1.0 to 0.2) accepted for the EF process.^[23] In other words, the initial Fe^{2+} dosage of 2.5 mM used here, which was also widely adopted in similar studies,^[5a,d] was superfluous. As a result, the advantageous regeneration of Fe^{2+} in the AuPd/CNTs catalytic EF process is critical to decrease the initial dosage requirement for Fe^{2+} .

Effects of initial pH, current density, Fe^{2+} dosage, and DMAC concentration on DMAC degradation

As mentioned above, it was found that the AuPd/CNTs catalytic EF process had excellent advantages compared with some previous studies focused on the Pd-based catalytic EF process,^[5a,b] such as superior effectiveness in the synthesis of H_2O_2 , regeneration of Fe^{2+} , and removal of organic pollutants. On this basis, the effects of pH, current density, initial Fe^{2+} dosage, and initial DMAC concentration on the degradation of DMAC were further investigated to optimize the AuPd/CNTs catalytic EF process. Initial solution pH plays a vital role in the EF process.^[24] Figure 3a illustrates the effects of initial solution pH on DMAC degradation. With an initial pH higher than 6 there is scarcely any removal of DMAC within 60 min of treatment, which indicates that near-neutral pH conditions are undesirable for the formation of H_2O_2 . On decreasing the pH from 5 to 3, the highest pseudo-first-order kinetic constant of DMAC removal was attained at pH 3 ($k_1=0.24$), further suggesting that the optimal pH 3 not only contributes to the optimization of the EF reaction, but also benefits the generation and stabilization of H_2O_2 . However, when the pH drops to 2, the removal of DMAC only reaches 79% at 60 min. It is reasonable that an overly acidic condition ($\text{pH} \leq 2$) leads to excessive dissolution of Fe^{2+} from the cathode, which can accelerate the competitive combination with $\text{OH}^\bullet$ radicals [Eq. (2)]^[25] and reduces the utilization of $\text{OH}^\bullet$ in DMAC removal. Additionally, strong acidity might destroy the heterostructure of the AuPd nanocrystals. Therefore, the optimal initial solution pH is 3. Applied current density is employed as the main driving force for the release of H_2 and O_2 from the electrodes under electrolysis. As a result, the degradation of DMAC increases with increasing current density (Figure 3b). Current densities of 12.5, 25, and

Figure 3. Effects of a) initial pH, b) current density, c) initial Fe^{2+} dosage, and d) initial DMAC concentration on DMAC degradation. C_0 represents initial DMAC concentration; C is the concentration of DMAC with time. Unless otherwise specified, the reaction conditions were based on 1 g L^{-1} AuPd/CNTs (0.5 wt % Au, 0.5 wt % Pd), initial pH 3, 50 mA cm^{-2} , and 100 mg L^{-1} initial DMAC concentration.

50 mA cm^{-2} exhibited considerably different performance in the degradation of DMAC, with corresponding kinetic constants of 0.0014, 0.017, and 0.049 min^{-1} , respectively, whereas with a current density of 100 mA cm^{-2} , superior removal efficiency was observed. A 100 mg L^{-1} concentration of DMAC was absolutely destroyed within 30 min, which is mainly ascribed to the anodic oxidation of DMAC. Actually, as current density increases, some negative factors, including concentration polarization and anodic cleanout of H_2O_2 , cannot be ignored.^[26] Thus, the best current density is 50 mA cm^{-2} . The initial dosage of Fe^{2+} determines the catalytic efficiency of the EF process and the decay of DMAC. As shown in Figure 3c, more than 85% DMAC still remained after 60 min without addition of Fe^{2+} . As the Fe^{2+} dosage increases from 2.5 to 10 mM, a distinct decline of DMAC can be observed (k_1 reduces from 0.066 to 0.0003 min^{-1}). As mentioned before, large amounts of Fe^{2+} damage the startup of the EF process and cause a poor ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. Furthermore, the in situ regeneration of Fe^{2+} by active H atoms released from the AuPd/CNTs catalytic process is potent.^[27] On this basis, a 0.05 mM initial dosage of Fe^{2+} (the tested concentration is much lower than those reported before^[5a,d]) was evaluated, and the results demonstrated that 0.05 mM of Fe^{2+} can also adequately initiate the AuPd/CNTs catalytic EF process and perform as well as 2.5 mM Fe^{2+} . The remarkable removal efficiency of DMAC under 0.05 mM of Fe^{2+} within 60 min was 95.16%, further revealing the intensive in situ regeneration of Fe^{2+} based on AuPd/CNT nanocatalysts. Because of the requirement of a low level of Fe^{2+} in the AuPd/CNTs catalytic EF process, 0.05 mM Fe^{2+} for initiating the EF process is sufficient, which suggests great potential cost savings at the engineering scale. Various initial concentrations of DMAC (20 to 500 mg L^{-1}) were used to evaluate the degrada-

tion capacity of the AuPd/CNTs catalytic EF process. Figure 3d illustrates that the decay of different initial concentrations of DMAC was well fitted by pseudo-first-order kinetics. The obtained kinetic constants decreased with increasing initial DMAC concentration, which was mainly due to the limited production of $\cdot\text{OH}$ radicals released from the AuPd/CNTs catalytic EF process. The optimal concentration of DMAC chosen at 100 mg L^{-1} is reasonable for full catalytic degradation under the conditions of 0.5% Au 0.5% Pd/CNT nanocatalysts, 50 mA cm^{-2} , and initial pH 3.

The catalytic characteristics of AuPd/CNT nanocatalysts

The Au loaded on AuPd/CNT nanocatalysts enhanced their performance relative to that of Pd/CNT nanocatalysts in many aspects, giving a much higher level of H_2O_2 synthesis, higher-efficiency regeneration of Fe^{2+} , and more complete degradation of organic pollutants. The characteristics of AuPd/CNTs were further investigated by XRD and XPS analysis. Figure 4 shows the XRD patterns of 1% Pd/CNTs and 0.5% Au 0.5% Pd/CNTs before and after catalysis under different exposure levels of Fe^{2+} . As can be seen from Figure 4a, the characteristic peaks of 1% Pd/CNTs at $2\theta=40.4$ and 47.1° were observed before catalysis. However, clear decay of Pd peaks was found after catalysis in the presence of 0.05 and 2.5 mM Fe^{2+} . To verify the promoting role of Au in structural stabilization of AuPd/CNT nanocrystals during the catalytic EF process, the harsh Fe^{2+} condition of 2.5 mM was evaluated. In sharp contrast with Pd/CNTs, strong diffraction peaks at 38, 44, and 66° were precisely matched with standards of pure AuPd before and after the catalysis (Figure 4b). It was further revealed that the Au on AuPd/CNTs changes the nanostructure of heterogeneous AuPd nanocrystals. Specifically, Au rearranges the AuPd alloy to expose the active Pd(111) crystal plane,^[11] which was also confirmed from the high-resolution transmission electron microscopy (HRTEM) images. Moreover, the slight modification of crystal-line structure originating from the introduction of Au might contribute greatly to the electrocatalytic activity of AuPd/CNTs.

CNT substrates also make a significant contribution to the stabilization of the crystalline structure of AuPd/CNTs. On the one hand, the compact three-dimensional spatial structures built by the stacked nanotubes enhance the stability of the total spatial structure of AuPd/CNT nanocomposites. On the other hand, this framework network structure is beneficial to ensure homogenization and transport between the reactants and AuPd nanocrystals. In particular, as can be observed from Figure S3 in the Supporting Information, AuPd nanocrystals are stably embedded in the spatial structure built by CNTs after high catalytic EF performance, which further demonstrates that the well-structured AuPd nanocrystals are protected by the spatial network, and the deactivation observed for synthesized nanocatalysts caused by the agglomeration of nanoparticles is avoided with AuPd nanocrystals. As such, the leaching of AuPd was largely prevented. Additionally, Figure 4c and 4d illustrate the different elemental composition and metallic state of Pd/CNTs and AuPd/CNTs before and after catalysis, respectively. Notably, peaks of Fe 2p and Fe 3p can be seen with their corre-

Figure 4. a) XRD patterns of 1% Pd/CNTs before and after 0.05 mM Fe^{2+} catalysis, and after 2.5 mM Fe^{2+} catalysis. b) XRD patterns of 0.5% Au 0.5% Pd/CNTs before and after 2.5 mM Fe^{2+} catalysis. c) XPS spectra of 1% Pd/CNTs before and after 2.5 mM Fe^{2+} catalysis. d) XPS spectra of 0.5% Au 0.5% Pd/CNTs before and after 2.5 mM Fe^{2+} catalysis. Unless otherwise specified, the reaction conditions were based on 1 g L^{-1} catalysts, initial pH 3, and 50 mA cm^{-2} .

sponding binding energies after the Fe^{2+} catalysis, thus revealing the deposition of Fe species on AuPd/CNTs. Specifically, characteristic peaks at 711, 719, and 724 eV represent the binding energies of $\text{Fe}2p_{3/2}$, shake-up satellite of $\text{Fe}2p_{3/2}$, and $\text{Fe}2p_{1/2}$ (Figure S5 in the Supporting Information), which sug-

gest the possible composition of Fe-containing substances supported on CNTs. It can be concluded that the introduction of Au on AuPd/CNTs leads to distinctive catalytic characteristics in several aspects, such as excellent structural stability of AuPd nanocrystals, protection of the crystalline structure by CNTs, and synergetic combination with Fe-containing substances on CNTs.

Catalytic stability of AuPd/CNTs for repeated degradation

As mentioned above, Au introduces superior catalytic characteristics to AuPd/CNTs, and the catalytic capacity of AuPd/CNTs over ten cycles of degradation of different organic pollutants (using DMAC and phenol as probes) was evaluated. The used AuPd/CNTs were separated from the solution by filtration, and then the washed and dried nanocatalysts were dropped into the reloaded contaminated solution again. Figure 5 illustrates

Figure 5. Changes of removal efficiency of DMAC and phenol as a function of treatment cycle. Each treatment was carried out with 2.5 mM Fe^{2+} , 1 g L $^{-1}$ catalyst (0.5% Au 0.5% Pd/CNTs), initial pH 3, 50 mA cm $^{-2}$, and 100 mg L $^{-1}$ DMAC or phenol with 40 min of electrolysis.

that the removal efficiency of DMAC and phenol can be steadily maintained at nearly 80% and more than 90%, respectively, thus demonstrating a desirable level of catalytic stability for AuPd/CNTs. Moreover, SEM images of AuPd/CNTs after ten utilization cycles show that there is no obvious aggregation of AuPd/CNT nanocomposites (Figure S6 in the Supporting Information). Therefore, AuPd/CNTs have good potential for sustainable recycling in the EF process.

Proposed mechanisms of organic pollutant degradation based on AuPd/CNTs

The proposed mechanism of the degradation of organic pollutants based on the AuPd/CNTs catalytic EF process was inferred according to the scavenging of $\cdot\text{OH}$ radicals by *tert*-butyl alcohol (TBA) and ESR assay. Degradation of phenol was clearly inhibited by the addition of TBA, with the kinetic constant dropping from 0.022 to 0.005 min $^{-1}$ (Figure S7 in the Supporting Information). As seen from Figure 6a, characteristic ESR signals of $\cdot\text{OH}$ were observed on the addition of AuPd/CNTs and Fe^{2+} under 30 min of electrolysis, thus validating the great contribution of $\cdot\text{OH}$ to the removal of organic pollutants. Furthermore,

the signals intensified with the increasing loading of AuPd on CNTs (from 1 to 5 wt%). However, AuPd/CNTs without Fe^{2+} in the electrolytic system resulted in no signal in response to $\cdot\text{OH}$. The proposed mechanism in the AuPd/CNTs catalytic EF process is shown in Scheme 1. The main contribution to the degradation of organic pollutants seems to be ascribable to the formation of $\cdot\text{OH}$ radicals released from the AuPd/CNTs catalytic system.

Scheme 1. Proposed mechanism in the AuPd/CNTs catalytic EF process.

Figure 6b demonstrates the catalytic capacity of AuPd/CNTs for DMAC and phenol degradation. The degradation of phenol was also well fitted by pseudo-first-order kinetics. As a result, the removal of phenol was more effective ($k_1=0.026$) than that of DMAC ($k_1=0.022$), and phenol totally disappeared within 40 min. However, the inset of Figure 6b shows that at least 20% of the residual total organic carbon (TOC) remained after 60 min of phenol degradation and nearly 45% was left in DMAC degradation, which suggests incomplete mineralization of the organic pollutants. To understand the degradation pathway of organic pollutants based on the AuPd/CNTs catalytic EF process, HPLC was employed to separate the components of the treated bulk solution. Chemical standards corresponding to conceivable products, such as pyrocatechin and *p*-benzoquinone, were characterized prior to the analysis of intermediates. As shown in Figure 6c, the peaks appearing at 5.6 and 4.8 min represent DMAC and its main intermediate acetamide, respectively. The peaks of acetamide increased rapidly from 10 to 20 min and decreased as the reaction proceeded from 20 to 40 min. No high molecular weight substance was left at 50 min. Similarly, the main intermediates in phenol degradation are pyrocatechin and *p*-benzoquinone with corresponding peaks at 3.5 and 3.1 min (Figure 6d). The peak intensity of phenol declined quickly within 20 min, and meanwhile the peaks of the two intermediates remained unchanged. Interestingly, the peaks of pyrocatechin and *p*-benzoquinone both decreased until 30 min, which indicated that the accumulation and degradation rates of the intermediates were the same. In summary, it can be concluded from the above results that the components with high molecular weight are decomposed into

Figure 6. a) Production of $\cdot\text{OH}$ from different nanocatalysts measured by ESR. The samples for ESR measurement were obtained under reaction conditions: 1 g L^{-1} catalyst, initial pH 3, 50 mA cm^{-2} , and 30 min electrolysis. b) Changes of DMAC and phenol concentration during the catalytic EF process. 1 g L^{-1} 0.5% Au 0.5% Pd/CNT catalysts, initial pH 3, 50 mA cm^{-2} , and 100 mg L^{-1} initial DMAC and phenol. The inset shows the corresponding change of TOC. C_0 represents initial TOC; C is the TOC with time. c, d) HPLC analysis of DMAC (c) and phenol (d) during the catalytic EF process as a function of time. Main intermediates were analyzed by addition of conceivable products as standard chemical reagents.

low molecular weight compounds through the AuPd/CNTs catalytic EF process. In addition, the residual TOC after 40 min of organic pollutant degradation can be attributed to the prod-

ucts resulting from the further decomposition of intermediates, such as formic acid, acetic acid, and methanol. Fortunately, although these substances cannot be perfectly separated through HPLC, they are biodegradable.

Conclusion

In this work, AuPd/CNT heterogeneous nanocomposites used as three-dimensional electrodes during the EF process were successfully synthesized, which exhibited superior catalytic activity in the in situ production of H_2O_2 from H_2 and O_2 , in situ regeneration of Fe^{2+} , and excellent removal efficiency of organic pollutants. In sharp contrast with the performance of Pd/CNT nanocatalysts, appropriate loading of Au on AuPd/CNTs significantly elevated the catalytic activity under the same loading of noble metal. The main conclusions that can be drawn are given below.

A better pseudo-first-order rate constant for degradation of the probe organic pollutants was calculated (0.050 min^{-1} , $R^2 = 0.986$) based on 0.5% Au 0.5% Pd/CNTs, compared with only 0.030 min^{-1} ($R^2 = 0.995$) for 1% Pd/CNTs; the optimal in situ production of H_2O_2 from 0.5% Au 0.5% Pd/CNTs was nearly 0.30 mM within 20 min, but only 0.19 mM for 1% Pd/CNTs; and the favorable in situ Fe^{2+} regeneration of 0.5% Au 0.5% Pd/CNTs implied the required initial Fe^{2+} dosage was only 0.05 mM . The ideal catalytic efficiency peaked at initial pH 3 and increased with increasing current density, whereas it decreased with increasing initial concentrations of DMAC and Fe^{2+} . It was found that the introduction of Au on AuPd/CNT nanocomposites enhanced the in situ synthesis of H_2O_2 and the catalytic efficiency of pollutant degradation. Au strengthens and stabilizes the nanostructure of AuPd nanocrystals and, theoretically, Au changes the structure of heterogeneous AuPd nanocrystals to give more exposure of atomic H chemisorbed on the active Pd(111) surface. The long durability of AuPd/CNTs over ten cycles in the catalytic EF process implied that AuPd/CNTs had good catalytic stability and promise for engineering applications. A catalytic mechanism was proposed describing how AuPd/CNTs exhibited outstanding performance in the release of $\cdot\text{OH}$ radicals during the catalytic EF process. Meanwhile, high molecular weight pollutants were decomposed into low molecular weight compounds through the AuPd/CNTs catalytic EF process.

Experimental Section

Chemicals

Dimethylacetamide (DMAC, 95 wt%) and phenol (99.5 wt%), as the main probe organic contaminants, were purchased from Sino-pharm Chemical Reagent Co., Ltd. (Shanghai, China). 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was provided by Aldrich. CNTs were obtained from Tsinghua University (Beijing, China). Palladium dichloride and chloroauric acid hydrate were supplied by Guoyao Group Chemical Reagent Co. Ltd., China. Ultrapure water was produced by a Millipore water purification system (Advantage A10, Millipore), with a resistivity of $\geq 18.2 \text{ M}\Omega \text{ cm}^{-1}$. Other chemical reagents were of at least analytical grade and used as received.

Catalyst synthesis

The AuPd/CNT nanocomposites were synthesized by a one-step chemical solution deposition method.^[28] First, ultrapure water (200 mL) was placed in an Erlenmeyer flask at 80 °C in a water bath with vigorous stirring at 800 rpm. Then, the prepared palladium dichloride solution, chloroauric acid hydrate solution (the weights of Pd and Au were varied proportionally), and activated CNTs were added rapidly to the flask. The mixture was held in the vessel for 6 h at 80 °C followed by 30 min of ultrasonic treatment. The resulting homogeneous, dark black suspension was further treated by dropwise addition of sodium borohydride (10 mL, 1 M). Finally, the mixture was held for 3 h at 80 °C, then the sediments removed by filtration. The precipitates were washed by ultrapure water and dried at room temperature. The integrated AuPd/CNTs with specific AuPd loading were thus obtained.

Catalytic activity tests

The electrolytic trial was conducted in a conventional undivided cylindrical cell of 150 mL capacity at (25 ± 1) °C. A dimensionally stable anode (DSA) and a stainless steel cathode (2.5 × 5.0 cm) were used with a spacing of 3 cm. The probe solution was stirred with a Teflon-coated magnetic bar at 400 rpm to ensure homogenization and transport of reactants and catalysts towards/from the electrodes. A constant electric current from 10 to 1000 mA was applied with a cell potential from 3 to 8 V. All the electrodes had been previously polarized in 0.1 M Na₂SO₄ at 200 mA within 30 min to remove impurities. For each test, the probe solution (100 mL) was transferred into the electrolytic cell, and then Na₂SO₄ powder (2.13 g) and AuPd/CNTs (0.1) were dropped simultaneously into the vessel. The solution was constantly stirred at 400 rpm after ultrasonic treatment for 10 min. Subsequently, 1 M H₂SO₄ was injected to adjust the initial pH to 3. Samples of about 1 mL were collected periodically at intervals and filtered by filter paper (0.45 μm) for chemical analysis. All experiments were carried out in duplicate. The performance of the EF process using the AuPd/CNTs was further evaluated by degrading DMAC (20, 100, 250, and 500 mg L⁻¹) under various conditions: different current densities (12.5, 25, 50, and 100 mA m⁻²), loading of Au on AuPd/CNTs (0, 0.25, 0.5, 0.75, and 1.0 wt% Au), initial pH (2, 3, 4, 5, 6, and 7), and ferrous dosages (0, 0.05, 2.5, 5, and 10 mM). The efficiency of AuPd/CNTs after repeated use was finally tested by degradation of DMAC and phenol independently for ten cycles under optimized conditions. The tested AuPd/CNTs were recycled by filtration and washing with ultrapure water.

Analytical methods

Powder X-ray diffraction (XRD) of the AuPd/CNTs was recorded on a D8 Advance (Bruker) X-ray diffractometer with Cu K_α radiation (λ = 1.54059 Å). The step size and scan rate were set at 0.05° and 0.025° s⁻¹, respectively. N₂ adsorption-desorption was conducted at 77 K using a Brunauer-Emmett-Teller (BET) surface area apparatus (Micromeritics ASAP2020). Scanning electron microscopy (SEM) was performed on an FEI Sirion 200 scanning electron microscope. Transmission electron microscopy coupled with energy-dispersive X-ray spectrometry (TEM/EDX) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a TEM H-800 instrument (Hitachi, Japan) at an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS-Ultra instrument (Kratos Analytical, UK) using monochromatic Al K_α radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. Cyclic voltam-

metry of CNTs, Pd/CNTs, and AuPd/CNTs was performed at a scan rate of 50 mV s⁻¹ between 1.2 and -0.2 V in H₂- and O₂-saturated acidic solution by using a CHI 830 electrochemical analyzer (CHI, Inc., USA). DMAC, phenol, and their degradation products were analyzed by reversed-phase high-performance liquid chromatography (HPLC) with a Hitachi HPLC apparatus (diode-array detector L-2450, column oven L-2300, and pump L-2130). The mobile phase for DMAC was a mixture of methanol and water (30:70, v/v). The flow rate was 0.6 mL min⁻¹ and the detection wavelength was set at 220 nm. As for phenol, the mobile phase consisted of acetonitrile and water (50:50, v/v) at 1 mL min⁻¹. The detection wavelength was 210 nm. The 1,10-o-phenanthroline colorimetric method was employed to determine ferrous ion content at 510 nm. The concentration of total organic carbon (TOC) was measured using a multi N/C 3000 TOC analyzer (Analytik Jena AG, Germany). Electron spin resonance (ESR) spectra were utilized to indirectly determine the concentration of generated ·OH using DMPO as the scavenger. The operating parameters of the electron paramagnetic resonance spectrometer (ESP 300E, Bruker) were: center field, 3480.00 × G; microwave frequency, 9.79 GHz; power, 5.05 mW.^[29,30]

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