

Study on the Radiation Synthesis Mechanism and the Electrochemical Property of Polyaniline

Shuo Yan^a, Zi-Fang Guo^b, Zhi-Qing Ge^a, Bao-Ying Zhang^a, Ya-Ru Zhang^a, Yi-Shao Li^a, Mo-Zhen Wang^{a*}, and Xue-Wu Ge^{a*}

^a State Key Laboratory of Precision and Intelligent Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

^b School of Nuclear Science and Technology, University of Science and Technology of China, Hefei 230026, China

Electronic Supplementary Information

Abstract As a highly promising conductive polymer material, the synthesis method, structure regulation, and performance improvement of polyaniline (PANI) are hot research topics. In this work, the radiation-induced polymerization of aniline in HNO₃ solution was successfully achieved at room temperature without the use of chemical oxidants. Through the analysis of the radiation chemical reactions of inorganic acids and nitrate salt solutions, the characterization of the intermediate free radicals in the irradiated systems, and the influence of the pH of the solutions on the polymerization activity and product morphologies, the radiation-induced polymerization mechanism of aniline is discussed in detail and proposed. Only at a condition of [HNO₃] > [aniline], i.e., pH < 2.5, PANI can be successfully obtained under γ -ray radiation. The polymerization begins with the oxidation of aniline cations to aniline cation radicals by $\cdot\text{NO}_3$ generated by radiolysis reactions, and undergoes repeated three steps of monomer free radical recombination, deprotonation, and oxidation reaction of $\cdot\text{NO}_3$, thus forming a PANI macromolecule. In addition to the polymerization reaction, the aniline units are protonated and oxidized because of the strongly acidity and oxidation of the reaction system under γ -ray irradiation, which means that the molecular chain structure of the radiation-synthesized PANI can be regulated by pH, nitrate concentration, and irradiation conditions. Radiation-synthesized PANI has a moderate protonation and oxidation state, which can be used for the preparation of PANI supercapacitors with better electrochemical properties than those prepared by chemical oxidation under the same conditions. This work presents a new radiation-synthesis method and polymerization mechanism of PANI, which not only expands the application of radiation technique in the field of polymer synthesis, but also provides a new idea for the structural regulation and electrochemical property optimization of PANI.

Keywords Aniline; Radiation-induced polymerization; Polyaniline; Electrochemical property

Citation: Yan, S.; Guo, Z. F.; Ge, Z. Q.; Zhang, B. Y.; Zhang, Y. R.; Li, Y. S.; Wang, M. Z.; Ge, X. W. Study on the radiation synthesis mechanism and the electrochemical property of polyaniline. *Chinese J. Polym. Sci.* 2025, 43, 328–340.

INTRODUCTION

Polyaniline (PANI) has emerged as a highly promising conductive polymer material in recent years, exhibiting immense potential in various fields, including supercapacitors, electrochromic devices, resistive sensors, rechargeable batteries, and biomedicine.^[1–6] PANI is mainly produced by chemical oxidative polymerization or electrochemical polymerization of aniline in acidic aqueous solutions, usually in the form of protonic-acid-doped PANI salts with different oxidation states.^[7,8] Current research shows that the conductivity of PANI is closely related to the proportion and distribution of oxidized (quinoid) and reduced (benzenoid) structural units along the molecular

chain, which are determined by the synthesis and doping conditions of PANI.^[9,10] To obtain PANI with a high conductivity ($\sigma \geq 1 \text{ S/cm}$), the chemical oxidative polymerization of aniline in the aqueous solution is typically conducted under a condition of $\text{pH} \leq 2.5$, and an oxidant to aniline monomer molar ratio greater than 1.^[7,11] PANI molecules can undergo electrochemical reversible ion doping in the electric field, which transforms the molecular chain structure between different redox states, accompanied by energy storage and release.^[12] Therefore, PANI is currently one of the potential electrode materials in the field of supercapacitors, and its specific capacitance is related to the polymerization methods and condition of aniline and protonic-acid-doped processes.^[13] Wang *et al.*^[14] investigated the electrochemical properties of H₂SO₄-doped PANI prepared by the chemical oxidative polymerization of aniline with a molar ratio of (NH₄)₂S₂O₈ to aniline in the range of 0.5–1.5, and found that PANI prepared at a molar ratio of (NH₄)₂S₂O₈ to aniline of 1.25, achieved the highest specific capacitance of 528 F/g. However,

* Corresponding authors, E-mail: pstwmz@ustc.edu.cn (M.Z.W.)

E-mail: xwge@ustc.edu.cn (X.W.G.)

Received September 29, 2024; Accepted October 27, 2024; Published online January 17, 2025

the substantial quantity of oxidants (such as FeCl_3 and $\text{K}_2\text{S}_2\text{O}_8$) used in the chemical oxidative polymerization makes it difficult to completely remove the impurity cations (such as Fe^{3+} and K^+), which easily remain on the PANI molecular chains and interfere with the doping degree of protons, thereby adversely affecting the electrochemical properties of PANI.^[15] The electrochemical polymerization of aniline can be initiated directly on the electrode surface to form PANI without the need for additional oxidants. However, this method is unsuitable for the deposition of PANI on poorly conductive substrates and the large-scale production of PANI nanomaterials.^[16,17] Therefore, in-depth study and development of the polymerization method of aniline have important theoretical and practical significance for the development of high-performance supercapacitor materials.

On the other hand, when aqueous solutions are exposed to high-energy radiation (such as γ -rays and electron beams), water molecules decompose to produce various active species, including oxidative $\cdot\text{OH}$ and reductive e_{aq}^- and $\cdot\text{H}$.^[18] Using these active species or the derived secondary active species, various metals, polymers, and nanocomposites have been synthesized in aqueous systems at room temperature.^[19–21] Wang *et al.*^[22] directly irradiated an air-saturated pyrrole solution containing H_2SO_4 with $\text{pH} \leq 1$ via ^{60}Co gamma rays to initiate the oxidative polymerization of pyrrole, and polypyrrole nanoparticles were obtained using the dispersant polyvinyl alcohol. The work confirmed that the reductive e_{aq}^- and $\cdot\text{H}$ in the system were converted to H_2O_2 owing to the presence of O_2 and the high concentrations of H^+ , enhancing the oxidative environment of the system to initiate the oxidative polymerization of pyrrole. However, polymerization of aniline in acidic solutions under similar irradiation conditions has not yet been successfully achieved. Karaivanov *et al.*^[23] reported that the radiation chemical yields of the radiolysis of aniline, that is, $G_{(-\text{aniline})}$ (the number of disappeared aniline molecules per 100 eV of energy absorbed) in acidic ($\text{pH}=2$) and neutral aqueous solutions saturated with argon gas were only 1.2 and 0.5, respectively. $G_{(-\text{aniline})}$ in a neutral aqueous solution saturated with N_2O (the scavenger of e_{aq}^-) increased to 3.3; however, the main radiolytic products of aniline were small molecules rather than aniline polymers. So far, there has been no comprehensive research and discussion on the effects of ionizing radiation on the polymerization of aniline in acidic aqueous solutions, or on the morphologies and properties of the radiation-synthesized PANI.

In this study, the chemical effects of γ -ray radiation of aniline in various inorganic acid aqueous solutions were investigated, and radiation-induced polymerization of aniline in HNO_3 aqueous solution was successfully achieved without the help of chemical oxidants. The radiation-induced polymerization mechanism of aniline was discussed in detail and proposed based on the analysis of the radiation chemical reactions of various inorganic acids and nitrate salt solutions, characterization of the intermediate free radicals in the irradiated systems, and influence of the pH of the aqueous solutions on the polymerization activity and product morphologies. The electrochemical properties of the PANI obtained by radiation-induced polymerization and chemical oxidative polymerization were compared. It was found that the radiation-synthesized PANI show better electrochemical proper-

ties than the chemically synthesized PANI, which opens a new route for the green synthesis of high-performance PANI.

EXPERIMENTAL

Materials

Aniline, *tert*-butanol (TBA), *N*-methylpyrrolidone (NMP), KSCN, HNO_3 (65%–68%), HCl (36%–38%), H_2SO_4 (95%–98%), H_3PO_4 (85%–95%), and NaNO_3 were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone (PVP, K88-96, $M_w=1.3 \times 10^6$), titanium sulfate, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), sulfanilamide, *N*-(1-naphthyl)ethylenediamine dihydrochloride, and tetrahydrofuran (THF) were purchased from Aladdin Chemical Co., Ltd. Nafion perfluorinated resin solution (5%) was purchased from Shanghai McLean Biochemical Technology Co., Ltd. THF was chromatographically pure, whereas the reagents were analytically pure. Aniline was purified by vacuum distillation before use. Ultrapure water with a conductivity of $0.055 \mu\text{S}/\text{cm}$ was prepared using a Smart System (SmartMiniVF) and used in all experiments.

Radiation-induced Polymerization of Aniline

A certain amount of aniline and PVP were dissolved in 10 mL of an aqueous solution of inorganic acids (HCl, H_2SO_4 , HNO_3 , and H_3PO_4) under magnetic stirring. After deoxygenation by bubbling with N_2 for 10 min, the system was sealed and exposed to ^{60}Co γ -ray radiation field (activity of 7.4×10^{14} Bq, located at the University of Science and Technology of China) for a certain period. The dose rate was 29 Gy/min, calibrated using alanine-EPR dosimetry. After γ -ray irradiation, the precipitates in the solution were centrifuged, and washed sequentially with water and ethanol. The products were dried to a constant weight in a drying oven at 50°C . The PANI sample obtained by radiation synthesis was labelled as PANI-R.

Chemical Oxidative Polymerization of Aniline

For comparison, a PANI sample was also prepared using the conventional chemical oxidative polymerization method. The synthesis process was as follows: 100 mg of aniline (1.1 mmol) and 10 mg of PVP were dissolved in 5 mL of HNO_3 or HCl aqueous solution under magnetic stirring in an ice-water bath. Then, 5 mL of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution (0.2 mol/L) was added dropwise to the aniline solution, and allowed to react in an ice water bath for 24 h. The precipitate in the solution was centrifuged, and washed sequentially with water and ethanol. The product, labelled as PANI-C, was dried to a constant weight in a drying oven at 50°C .

Characterization

The pH of the reaction system was determined by using a pH meter (PHS-3C). The morphologies of the samples were observed using cold-field emission scanning electron microscopy (SEM, HITACHI SU8220, 3 kV). The samples were first dispersed in water, dropped onto a silicon wafer to dry naturally, and finally sprayed with Pt. Fourier transform infrared (FTIR) spectra were recorded in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$ on a Thermo Fisher Nicolet 6700 spectrometer with a resolution of 0.1 cm^{-1} using KBr pellets. X-ray diffraction (XRD) spectra were obtained using a Rigaku SmartLab X-ray diffraction instrument ($\text{Cu K}\alpha$, $\lambda=1.5418 \text{ \AA}$) with a scanning speed of $8 (^\circ)/\text{min}$ and a scanning range of $10^\circ\text{--}70^\circ$. To detect the active free radicals

generated during irradiation, a free radical scavenger (DMPO) was added to the solutions before irradiation. Electron paramagnetic resonance (EPR) spectra of the irradiated solutions were immediately measured using an electron paramagnetic resonance spectrometer (JEOL JES-FA200) at a working frequency of 9.081 GHz. The concentrations of H_2O_2 and NO_2^- in the irradiated solutions were determined using the colorimetric method with titanium sulfate and *N*-(1-naphthyl)ethylenediamine dihydrochloride/sulfanilamide, respectively.^[24,25] The UV-vis absorption spectra of the solutions were recorded using an ultraviolet-visible spectrophotometer (UV-Vis, UV 3600 plus). The MS spectra of the samples dissolved in methanol were analyzed using matrix-assisted laser desorption tandem time-of-flight mass spectrometry (MALDI-TOF MS, Autoflex Speed TOF/TOF). The molecular weight was measured by gel permeation chromatography (GPC, 1260 Infinity II) at 25 °C. The sample was dissolved in THF and filtered through a 0.22 μm organic (nylon) filter. THF was used as the mobile phase at a flow rate of 1.0 mL/min. Monodisperse polystyrene was used for molecular weight calibration.

Electrochemical Measurements

All electrochemical measurements were performed in 1 mol/L H_2SO_4 aqueous solution on a CHI660D electrochemical workstation (Shanghai Chenhua) using a standard three-electrode electrolytic cell. The working electrode was prepared as follows: 4 mg of the PANI sample was dispersed ultrasonically in a mixture of 980 μL of NMP and 20 μL of Nafion solution to form a uniform slurry. The working electrode was obtained by dropping 5 μL of the slurry onto a glassy carbon electrode and drying in air. A platinum sheet and Ag/AgCl electrode with saturated KCl solution were used as the counter and reference electrodes, respectively. Cyclic voltammetry (CV) curves were obtained in a voltage window ranging from -0.2 V to 0.8 V at scan rate of 10, 20, 50 and 100 mV/s. Galvanostatic charge-discharge (GCD) tests were conducted at current densities of 0.2, 0.5, 1 and 2 A/g. The specific capacitance (C_m) of the test system can be calculated from the discharge curve:^[26]

$$C_m = \frac{2i \int V(t) dt}{m\Delta V^2} \quad (1)$$

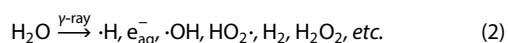
where i is the discharge current (A), $V(t)$ is the instantaneous voltage (V), ΔV is the voltage window, and m is the mass of the electroactive electrode material (g). Thus, the unit of C_m is F/g.

Electrochemical impedance spectra (EIS) were obtained at an open circuit voltage of 0.4 V and a frequency ranges from 10^5 Hz to 10^{-2} Hz.

RESULTS AND DISCUSSION

Radiation-induced Polymerization of Aniline

It is well known that, liquid neutral pure water can be decomposed by high-energy rays, inducing a series of rapid reactions and producing various types of active species, mainly e_{aq}^- , $\cdot\text{OH}$, and $\cdot\text{H}^{\cdot}$ ^[18,27]



However, when the inorganic acid aqueous solution is exposed to the γ -ray radiation, e_{aq}^- produced by water radiolysis reacts quickly with H^+ , and can be removed because of the

high concentration of H^+ . At the same time, the radiolysis of acid group anions can also produce other oxidizing active free radicals ($E^\theta(\cdot\text{NO}_3/\text{NO}_3^-)=+2.67$ V_{NHE} , $E^\theta(\cdot\text{SO}_4/\text{SO}_4^{2-})=+2.44$ V_{NHE} , $E^\theta(\text{H}_2\text{PO}_4^{\cdot}/\text{H}_2\text{PO}_4^-)=+2.52$ V_{NHE} , $E^\theta(\cdot\text{Cl}/\text{Cl}^-)=+2.43$ V_{NHE} , $E^\theta(\text{Cl}_2^{\cdot-}/\text{Cl}^-)=+2.13$ V_{NHE} , etc.), making the system highly oxidizing.^[28–32] In this work, aniline was first dissolved respectively in N_2 saturated H_2O and 0.2 mol/L H_2SO_4 , HCl , H_3PO_4 , and HNO_3 aqueous solutions, and then the mixed solutions were irradiated with ^{60}Co γ -rays for 24 h (dose rate of 29 Gy/min, total absorbed dose of 41.8 kGy). The reaction solutions before and after irradiation are shown in Fig. 1(a). Except for the HNO_3 aqueous solution, all aqueous solutions were pale yellow after irradiation, and no polymeric products appeared, which is in agreement with the results of similar irradiated systems reported in the literature.^[23,33] MS spectra of the products from the H_2O , H_2SO_4 , HCl , and H_3PO_4 systems in Fig. 1(b) also confirm that they are small molecular substances with molecular weights below 500. However, the HNO_3 aqueous solution containing aniline is dark green after irradiation, which is close to the color of the product (PANI-C) obtained by the chemical oxidative polymerization of aniline initiated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Fig. 1a). The yield of the radiation-synthesized product (PANI-R) obtained in an HNO_3 aqueous solution was approximately 20%, which is comparable to that of H_2O_2 as an oxidant. PANI-R was only partially dissolved in THF. The GPC chromatogram of the THF-soluble component showed that the M_w of the component was as high as 15600 (Fig. 1c), indicating that γ -ray irradiation of aniline in HNO_3 aqueous solution can yield polymerization products.

The FTIR spectra of aniline, PANI-R, and PANI-C are shown in Fig. 1(d). Due to the covalent linkage between the benzene ring and N atom, two pairs of characteristic bands corresponding to the benzene ring skeleton vibration (1622 , 1600 cm^{-1} , and 1500 , 1460 cm^{-1}), as well as the bands for the C—H out-of-plane bending vibration of the mono-substituted benzene ring (748 and 694 cm^{-1}) appeared in the FTIR spectrum of aniline.^[34,35] However, the bands at 1622 and 1600 cm^{-1} disappeared in the FTIR spectra of both PANI-R and PANI-C, while a band at 826 cm^{-1} corresponding to the C—H out-of-plane deformation vibration of the 1,4-disubstituted benzene ring emerged, providing further evidence for the PANI structures.^[36–38] The XRD patterns of PANI-R and PANI-C shown in Fig. 1(e) are almost identical, exhibiting two diffraction peaks at $2\theta=19.6^\circ$ and 26.3° , consistent with the results of PANI salts in the literature.^[39,40] The peak at 19.6° corresponds to the spacing between the ring planes of benzene rings in adjacent chains, whereas the peak at 26.3° correlates with the spacing for the face-to-face interaction of the phenyl rings of PANI chains. These results indicate that high-energy γ -rays can directly initiate the polymerization of aniline in 0.20 mol/L HNO_3 solution at room temperature without the need for additional chemical oxidants.

The radiation-induced polymerization mechanism of aniline can be studied by analyzing the main radiation chemical reactions in water and inorganic acid solutions, as shown in Table 1. The pH values of H_2O , HNO_3 , H_2SO_4 , HCl , and H_3PO_4 solutions were 6.73, 0.81, 0.73, 0.80, and 1.41, respectively. The types of active species generated by the radiolysis of liquid water and the corresponding radiation chemical yield,

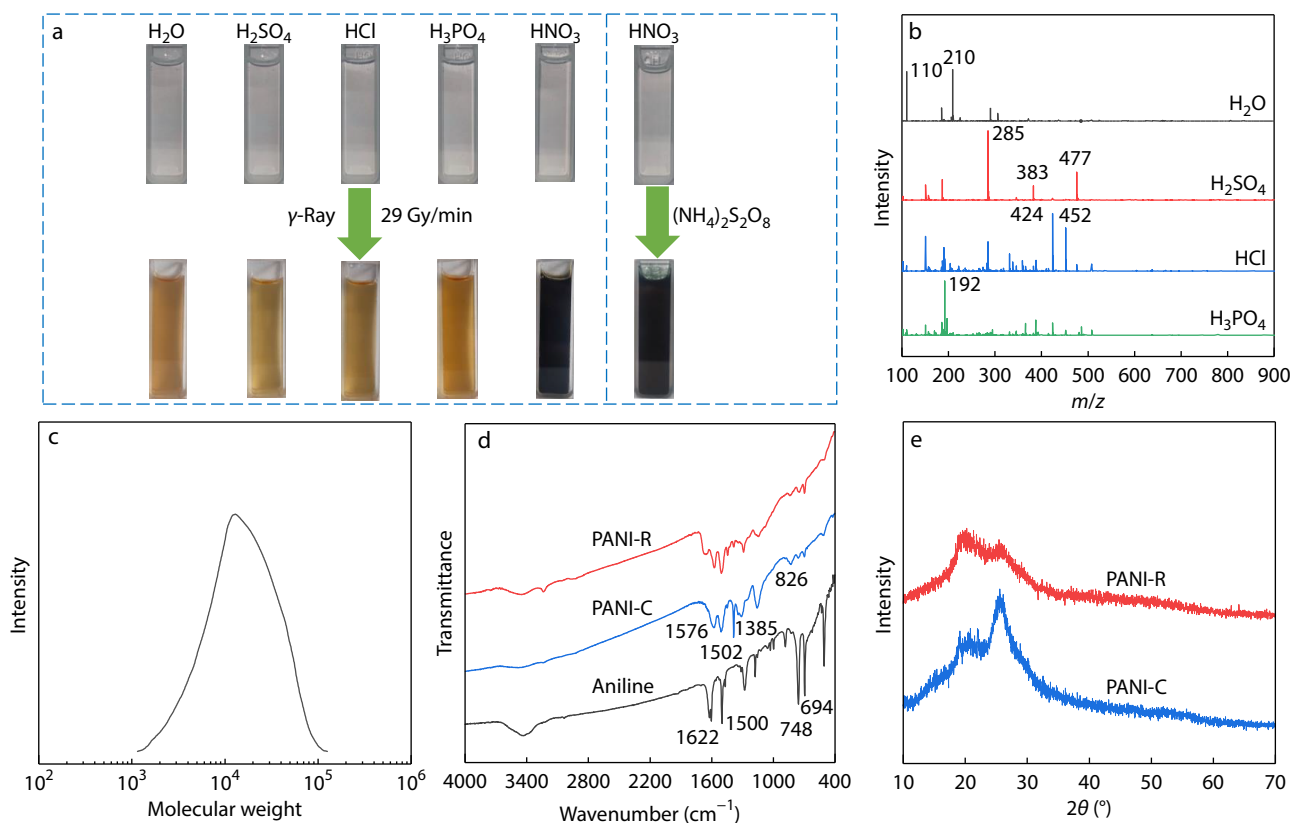


Fig. 1 (a) Digital photos of H_2O and inorganic acid (0.2 mol/L) solutions containing aniline before and after γ -ray irradiation ([aniline]=0.11 mol/L, dose rate: 29 Gy/min, absorbed dose: 41.8 kGy), as well as the photos of the same HNO_3 /aniline system before and after the addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$; (b) MS spectra of the products obtained from the H_2O /aniline, H_2SO_4 /aniline, HCl /aniline, and H_3PO_4 /aniline systems; (c) GPC chromatogram of the THF-soluble component of the product from the irradiated HNO_3 /aniline system; (d, e) FTIR spectra and XRD patterns of the products (PANI-R and PANI-C) obtained by radiation-induced polymerization and chemical oxidation polymerization of aniline in HNO_3 solution.

Table 1 Main radiation chemical reactions and the corresponding rate constants in H_2O and inorganic acid solution systems in an inert atmosphere ([acid]=0.2 mol/L).

System	pH	Reaction	$k_p (\text{M}^{-1}\cdot\text{s}^{-1})$	Ref.
H_2O	6.76	$\text{H}_2\text{O} \rightarrow e_{\text{aq}}^-, \cdot\text{H}, \cdot\text{OH}, \text{HO}_2^-, \text{H}_2, \text{H}_2\text{O}_2$	—	[41]
$\text{HNO}_3/\text{H}_2\text{O}$	0.81	$e_{\text{aq}}^- + \text{H}^+ \rightarrow \cdot\text{H}$	2.3×10^{10}	[32]
		$\text{NO}_3^- \rightarrow \cdot\text{NO}_3 + e^-$	—	[32]
		$\text{HNO}_3 + \cdot\text{OH} \rightarrow \cdot\text{NO}_3 + \text{H}_2\text{O}$	5.3×10^7	[32]
		$\text{NO}_3^- + \cdot\text{H} \rightarrow \cdot\text{NO}_2 + \text{OH}^-$	1.0×10^7	[32]
		$\cdot\text{NO}_2 + \cdot\text{H} \rightarrow \text{HNO}_2$	1.0×10^{10}	[32]
		$\text{HNO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{ONOOH} + \text{H}_2\text{O}$	7.2×10^5	[32]
$\text{H}_2\text{SO}_4/\text{H}_2\text{O}$	0.73	$e_{\text{aq}}^- + \text{H}^+ \rightarrow \cdot\text{H}$	2.3×10^{10}	[42]
		$\text{SO}_4^{2-} \rightarrow \cdot\text{SO}_4^- + e^-$	—	[42]
		$\cdot\text{SO}_4^- + \cdot\text{H} \rightarrow \text{HSO}_4^-$	1.0×10^{10}	[42]
		$\cdot\text{SO}_4^- + \cdot\text{OH} \rightarrow \text{HSO}_4^-$	1.0×10^9	[42]
		$\cdot\text{SO}_4^- + \text{HO}_2 \rightarrow \text{HSO}_4^- + \text{O}_2$	3.5×10^{10}	[42]
$\text{HCl}/\text{H}_2\text{O}$	0.80	$e_{\text{aq}}^- + \text{H}^+ \rightarrow \cdot\text{H}$	2.3×10^{10}	[43]
		$\text{Cl}^- \rightarrow \cdot\text{Cl} + e^-$	—	[43]
		$\text{Cl}^- + \cdot\text{OH} \rightarrow \text{ClOH}^-$	4.3×10^9	[43]
		$\text{ClOH}^- + \text{H}^+ \rightarrow \cdot\text{Cl} + \text{H}_2\text{O}$	2.1×10^{10}	[43]
		$\cdot\text{Cl} + \text{Cl}^- \rightarrow \text{Cl}_2^-$	2.1×10^{10}	[43]
		$\text{Cl}_2^- + \cdot\text{H} \rightarrow 2\text{Cl}^- + \text{H}^+$	8.0×10^9	[43]
		$\text{Cl}^- + \cdot\text{H} \rightarrow \text{Cl}^- + \text{H}^+$	1.0×10^{10}	[43]
$\text{H}_3\text{PO}_4/\text{H}_2\text{O}$	1.41	$e_{\text{aq}}^- + \text{H}^+ \rightarrow \cdot\text{H}$	2.3×10^{10}	[31]
		$\text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{PO}_4^- + \text{H}^+ + e^-$	—	[31]
		$\text{H}_2\text{PO}_4^- + \cdot\text{H} \rightarrow \text{H}_3\text{PO}_4$	1.3×10^{10}	[31]
		$\text{H}_2\text{PO}_4^- + \cdot\text{OH} \rightarrow \text{H}_3\text{PO}_5$	4.0×10^9	[31]
		$\text{H}_2\text{PO}_4^- + \text{HO}_2 \rightarrow \text{H}_3\text{PO}_4 + \text{O}_2$	3.0×10^9	[31]

that is, $G(X)$ (defined as the number of X species that have changed per 100 eV energy absorbed), are closely related to the pH of the solution.^[41] In an inert atmosphere, when neutral or weakly alkaline aqueous solutions are exposed to γ -ray radiation, the oxidative $\cdot\text{OH}$ and reductive e_{aq}^- have similarly high G values of approximately 2.7. Even though the oxidation-reduction potential of $\cdot\text{OH}$ is as high as 2.31 V, it is difficult to carry out oxidative polymerization in a neutral or near-neutral solutions because there also exists a large amount of e_{aq}^- .^[22] In contrast, e_{aq}^- can be quickly removed by the reaction with H^+ in a strongly acidic aqueous solution, to be converted to $\cdot\text{H}$. The inorganic acid group anions can react with some active free radicals generated by water radiolysis, but can also be ionized by γ -rays to generate the corresponding free radicals and further undergo various reactions. According to the radiation chemical reactions in HNO_3 aqueous solution listed in Table 1, NO_3^- can be ionized directly to form strongly oxidative $\cdot\text{NO}_3$, but it can also react with $\cdot\text{OH}$ and $\cdot\text{H}$ to generate $\cdot\text{NO}_3$ and $\cdot\text{NO}_2$, respectively. The newly generated $\cdot\text{NO}_2$ can continue to consume $\cdot\text{H}$ and convert it into weakly oxidative NO_2^- .^[32] This means that the HNO_3 aqueous solution was fully oxidized under γ -ray irradiation. For H_2SO_4 aqueous solution, the ionization of SO_4^{2-} can generate oxidative $\cdot\text{SO}_4^-$, which can consume $\cdot\text{H}$ and $\cdot\text{OH}$ and convert it to non-oxidizing HSO_4^- and HSO_5^- .^[42] In HCl aqueous solution, Cl^- is ionized and reacts with $\cdot\text{OH}$ to form oxidative $\text{Cl}\cdot$ and $\text{Cl}_2^{\cdot-}$, which then reacts with $\cdot\text{H}$ and returns to Cl^- .^[43] Similarly, the ionization of H_3PO_4 yields oxidative $\text{H}_2\text{PO}_4^{\cdot-}$, which rapidly combines with $\cdot\text{H}$ and $\cdot\text{OH}$ to form H_3PO_4 and H_3PO_5 .^[31] After the addition of aniline to these inorganic acid aqueous solutions ($[\text{aniline}] = 0.11 \text{ mol/L}$), the pH of the solutions slightly increases to 1.23 (HNO_3), 1.13 (H_2SO_4), 1.25 (HCl), and 2.18 (H_3PO_4), and the main radiation chemical reactions in the solutions are listed in Table 1. The free radicals produced by the ionization of SO_4^{2-} , Cl^- , and H_3PO_4 undergo a series of reactions with oxidative and reductive species produced by water radiolysis, resulting in the generation of non-oxidizing species. Only in HNO_3 aqueous solution, the oxidizing atmosphere can only be maintained during the irradiation process. Radiation-induced polymerization of aniline is closely related to the oxidation reaction.

To further verify the effect of the active species generated by the radiolysis of NO_3^- , a 0.2 mol/L NaNO_3 solution was used instead of HNO_3 solution as the reaction medium, as shown in Fig. 2(a). The pH of the system is 7.37. At the same absorbed dose, the system changed from colorless to dark brown with traces of visible precipitates. However, the precipitates can be completely dissolved in THF, and the MS spectrum (Fig. 2b) reveals that the peak with the highest abundance corresponds to $m/z = 290$ ($\text{C}_{18}\text{H}_{15}\text{N}_3\text{O} + \text{H}^+$). There are almost no peaks with m/z exceeding 800, although a few peaks that are particularly small in abundance exist between $m/z = 500$ to $m/z = 800$. Compared with the irradiation products of H_2SO_4 , HCl , and H_3PO_4 aqueous solutions (Fig. 1b), the product from the NaNO_3 /aniline system contained molecules with higher molecular weights, which is consistent with the darker color of the product. The main radiation chemical reactions in the NaNO_3 aqueous solution are listed in Table 2. In contrast to the HNO_3 aqueous solution, the NaNO_3 aqueous

solution (pH=6.8) is near-neutral and has a high G value of e_{aq}^- . The reaction rates of NO_3^- and e_{aq}^- are two orders of magnitude faster than those of NO_3^- and $\cdot\text{H}$.^[44] The consumption of NO_3^- by a large amount of e_{aq}^- leads to a decrease in the content of highly oxidative $\cdot\text{NO}_3$. Fig. 2(c) shows the simulated concentrations of four radiolytic species ($\cdot\text{OH}$, $\cdot\text{NO}_3$, $\cdot\text{H}$ and e_{aq}^-) in pure water, HNO_3 and NaNO_3 solutions using chemical kinetic simulation software (MCAP-FACSIMILE). The concentrations of $\cdot\text{OH}$ and $\cdot\text{H}$ produced in pure water were the highest, followed by those of e_{aq}^- . However, in both HNO_3 and NaNO_3 aqueous solutions, the concentration of $\cdot\text{NO}_3$ is the highest, followed by that of $\cdot\text{OH}$. The concentrations of $\cdot\text{H}$ and e_{aq}^- exhibited a sharp decrease, with the latter having the lowest level. The concentrations of $\cdot\text{NO}_3$ and $\cdot\text{H}$ in the NaNO_3 aqueous solution were slightly lower than those in the HNO_3 aqueous solution, whereas the concentration of e_{aq}^- was higher than that in the HNO_3 aqueous solution. These results indicate that the radiation-induced polymerization of aniline is related to oxidative $\cdot\text{NO}_3$, which is an oxidative polymerization mechanism. However, the presence of e_{aq}^- inhibited the polymerization of aniline. Thus, it is necessary to remove e_{aq}^- and maintain strongly oxidative conditions.

To analyze the possible types and reactions of free radicals in the polymerization system via EPR, the free radical scavenger DMPO was added to the reaction system before γ -ray irradiation. As shown in Fig. 3(a), four characteristic peaks of DMPO- $\cdot\text{OH}$ (1:2:2:1) and nine characteristic peaks of DMPO- $\cdot\text{H}$ (1:1:2:1:2:1:2:1:1) can be detected in the EPR spectrum of pure water after γ -ray irradiation,^[45] which is consistent with the theoretical simulation results shown in Fig. 2(c), because the concentrations of $\cdot\text{OH}$ and $\cdot\text{H}$ in the system are both high. However, the irradiated water dissolved with aniline only produces the characteristic signal of DMPO- $\cdot\text{H}$, indicating that $\cdot\text{H}$ does not participate in the reaction or reacts very slowly (captured by DMPO), whereas $\cdot\text{OH}$ can react quickly with aniline, leading to the disappearance of the DMPO- $\cdot\text{OH}$ signal. However, no other intermediate radicals were captured by DMPO. After γ -ray irradiation of 0.2 mol/L HNO_3 and NaNO_3 aqueous solutions, there was no characteristic signal of DMPO- $\cdot\text{H}$, and only the signal of $\cdot\text{OH}$ appeared in the EPR spectra, because DMPO- NO_3 is easily decomposed into DMPO- $\cdot\text{OH}$ in aqueous solutions according to the results in the literature.^[46] In the EPR spectrum of the irradiated NaNO_3 /aniline solution, there was no $\cdot\text{OH}$ signal, which was replaced by a typical signal of carbon-centered radical with six characteristic peaks (1:1:1:1:1:1). The above results indicate that aniline can react rapidly with $\cdot\text{NO}_3$, $\cdot\text{OH}$, and other free radicals in this system to produce carbon-centered radical intermediates that are captured by DMPO; however, no polymer is formed. In comparison, the EPR spectrum of the irradiated HNO_3 /aniline solution was consistent with the paramagnetic resonance signal of proton-doped PANI reported in the literature.^[47] This also proves that aniline undergoes rapid reactions with all free radicals produced in HNO_3 solution under γ -ray radiation to generate PANI. Fig. 3(b) shows the change in the pH of the HNO_3 /aniline solution as a function of the absorbed dose. At the beginning of the irradiation (<1.7 kGy), the pH value of the system decreased rapidly with the absorbed dose, that is,

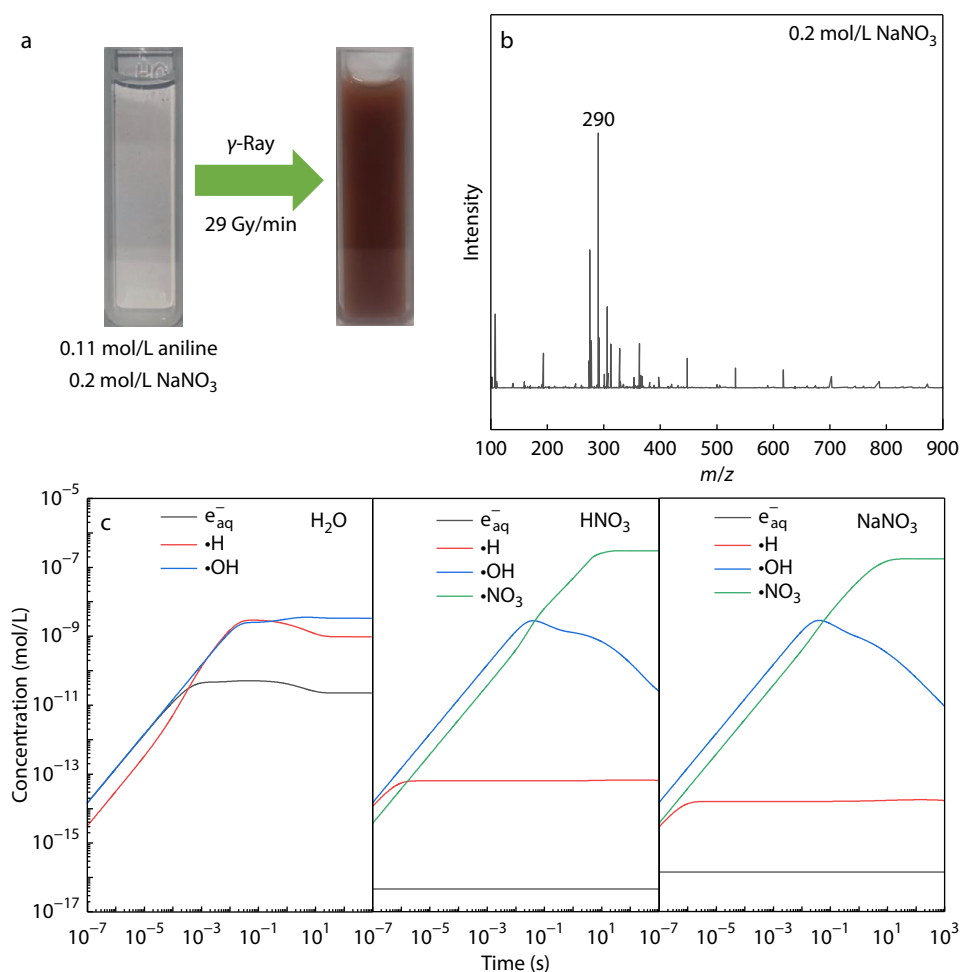


Fig. 2 (a) Digital photos of an aqueous solution containing aniline (0.11 mol/L) and NaNO₃ (0.2 mol/L) before and after γ -ray irradiation (dose rate: 29 Gy/min, absorbed dose: 41.8 kGy); (b) MS spectrum of the product from the irradiated NaNO₃/aniline system; (c) the simulated time-dependence of the concentrations of e_{aq}^- , $\cdot H$, $\cdot OH$, and $\cdot NO_3$ produced in H₂O, 0.2 mol/L of HNO₃ and NaNO₃ solutions under γ -ray radiation by MCAP-FACSIMILE software.

Table 2 Main radiation chemical reactions and the corresponding rate constants in NaNO₃ aqueous solution in an inert atmosphere ([NaNO₃]=0.2 mol/L).

System	pH	Reaction	k_p (M ⁻¹ ·s ⁻¹)	Ref.
NaNO ₃ /H ₂ O	6.80	H ₂ O → e_{aq}^- , $\cdot H$, $\cdot OH$, HO ₂ ·, H ₂ , H ₂ O ₂	—	[41]
		NO ₃ ⁻ → $\cdot NO_3$ + e^-	—	[32]
		NO ₃ ⁻ + e_{aq}^- → $\cdot NO_3^{2-}$	9.7×10 ⁹	[44]
		$\cdot NO_3^{2-}$ + H ₂ O → NO ₂ + 2OH ⁻	5.5×10 ⁴	[44]
		NO ₃ ⁻ + $\cdot H$ → $\cdot NO_2$ + OH ⁻	1.0×10 ⁷	[32]
		$\cdot NO_2$ + $\cdot H$ → HNO ₂	1.0×10 ¹⁰	[32]

the radiation time, and then almost leveled off, which is similar to the phenomenon observed during the chemical oxidative polymerization of aniline.^[36] It means that the radiation-induced polymerization reaction of aniline should be accompanied by the oxidative dehydrogenation of aniline units to lower the pH of the reaction system. For comparison, the EPR spectra of the irradiated H₂SO₄ and H₂SO₄/aniline solutions are also shown in Fig. 3(a). It can be seen that there is only a signal of $\cdot OH$, and no signal of $\cdot SO_4$ can be found in the irradiated H₂SO₄ solution because the rate constants of the reaction between $\cdot SO_4^-$ and $\cdot H$, as well as HO₂· and $\cdot OH$, are so large (see Table 1) that they cannot be captured by DMPO.

However, in the EPR spectrum of the irradiated H₂SO₄/aniline solution, only the $\cdot OH$ signal was present, but the intensity was significantly weakened. These results indicate that the polymerization of aniline under γ -ray radiation should be initiated by the radiolysis product of NO₃⁻ under acidic conditions rather than the $\cdot OH$ produced by the radiolysis of H₂O.

According to the radiolysis reactions in HNO₃ and NaNO₃ aqueous solutions, the oxidative active species in the system include not only $\cdot NO_3$ but also NO₂⁻ and H₂O₂. NO₂⁻ can be detected using the chromogenic method with sulfanilamide and *N*-(1-naphthyl)ethylenediamine dihydrochloride.^[25] As shown in Fig. 3(c), the UV-Vis spectra of the irradiated HNO₃

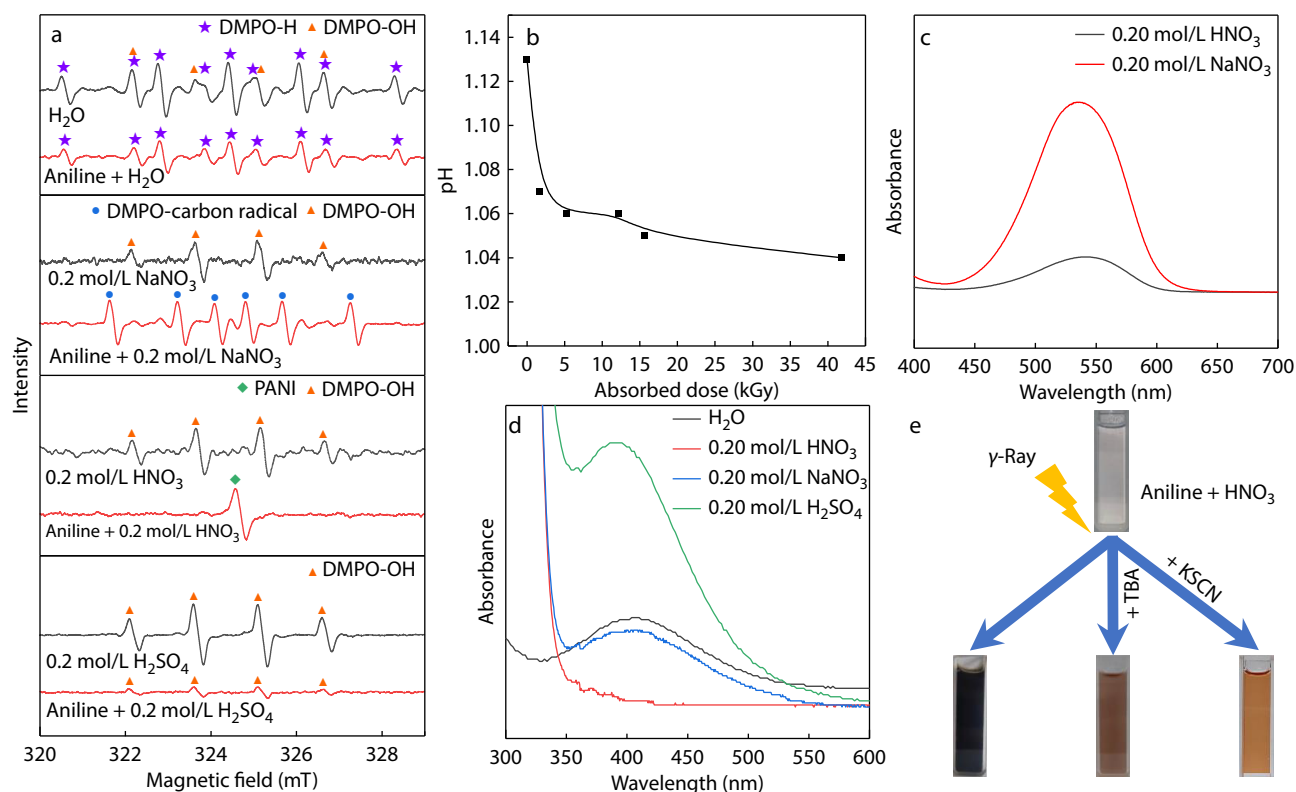


Fig. 3 (a) EPR spectra of the irradiated H₂O, H₂O/aniline, NaNO₃, NaNO₃/aniline, HNO₃, HNO₃/aniline, H₂SO₄, H₂SO₄/aniline solutions containing DMPO (dose rate: 29 Gy/min, absorbed dose: 1.7 kGy); (b) the change of pH value of the irradiated HNO₃/aniline solution with the absorbed dose; (c) UV-Vis spectra of NO₂⁻ in the irradiated aqueous solutions detected by sulfanilamide and *N*-(1-Naphthyl) ethylenediamine dihydrochloride; (d) UV-Vis spectra of H₂O₂ in irradiated aqueous solution quantified by titanium sulfate; (e) digital photos of the irradiated HNO₃/aniline, HNO₃/aniline/TBA, and HNO₃/aniline/KSCN solutions.

and NaNO₃ solutions showed characteristic absorption at 543 nm, corresponding to the presence of azo compounds with chromophores. This indicates that NO₂⁻ was formed in the irradiated system, and the concentration of NO₂⁻ in the irradiated NaNO₃ solution was much higher than that in the irradiated HNO₃ solution. NO₂⁻ is the product of the reaction between NO₃⁻ and e_{aq}⁻ or ·H. Thus, the concentration of ·NO₃ in the NaNO₃ solution was comparatively lower than that in the HNO₃ solution.^[32,44] The result indicated that the radiation-induced polymerization of aniline is independent of the concentration of NO₂⁻. H₂O₂ can be quantified using the colorimetric method with titanium sulfate.^[24] In the UV-Vis spectra shown in Fig. 3(d), the characteristic absorption at 410 nm corresponding to TiO₂H₂O₂ was observed in the irradiated H₂O, NaNO₃ and H₂SO₄ solutions, but no absorption was detected in the HNO₃ solution. This was due to the consumption of H₂O₂ reacting with NO₂⁻ in the acidic system.^[32] However, the polymerization of aniline does not occur in H₂SO₄ solution. This result suggests that the radiation-induced polymerization of aniline in HNO₃ solution is not related to H₂O₂.

Furthermore, the HNO₃/aniline/TBA and HNO₃/aniline/KSCN systems were selected to investigate the effect of ·NO₃ on the radiation-induced polymerization of aniline. TBA is an effective scavenger of ·OH and ·H, whereas KSCN is an effective scavenger of ·NO₃.^[32,48] As shown in Fig. 3(e), brown precipitates appeared in the HNO₃/aniline/TBA system, similar to the color of oligomers, while the product obtained from the

irradiated HNO₃/aniline/KSCN system was lighter in color and dissolved in water. TBA can clear the ·OH produced by water radiolysis and inhibit the reaction of HNO₃ with ·OH to generate ·NO₃, thereby reducing the concentration of ·NO₃ in the system and making aniline polymerization difficult. However, KSCN completely removes all ·NO₃ in the solution, the polymerization reaction of aniline cannot be carried out, and no polymers or oligomers are formed. This result proves that radiation-induced polymerization of aniline in HNO₃ solution is primarily associated with ·NO₃ rather than ·OH.

The Effect of pH on Radiation-induced Polymerization of Aniline and the Morphology of PANI

The concentration of HNO₃

The pH of the system was adjusted by changing the HNO₃ concentration at a fixed [aniline]. Figs. 4(a)–4(d) show digital photos of the irradiated HNO₃/aniline solution with different [HNO₃] and [aniline] of 0.11 mol/L, as well as SEM images of the products. When [HNO₃] is 0.08 mol/L, the pH of the solution is 4.14, the irradiated system appears brown and the products are microspheres with a particle size of ca. 636 nm (Fig. 4a). When [HNO₃] exceeds 0.2 mol/L, the pH of the system drops below 1.13, all the irradiated systems appear dark green and the morphology of the products are strip-like PANI with a length of micrometers (Figs. 4b–4d), which is similar to the morphology of PANI prepared by chemical oxidation using (NH₄)₂S₂O₈ as an oxidant in HNO₃ or HCl system (Fig. S1 in the electronic supple-

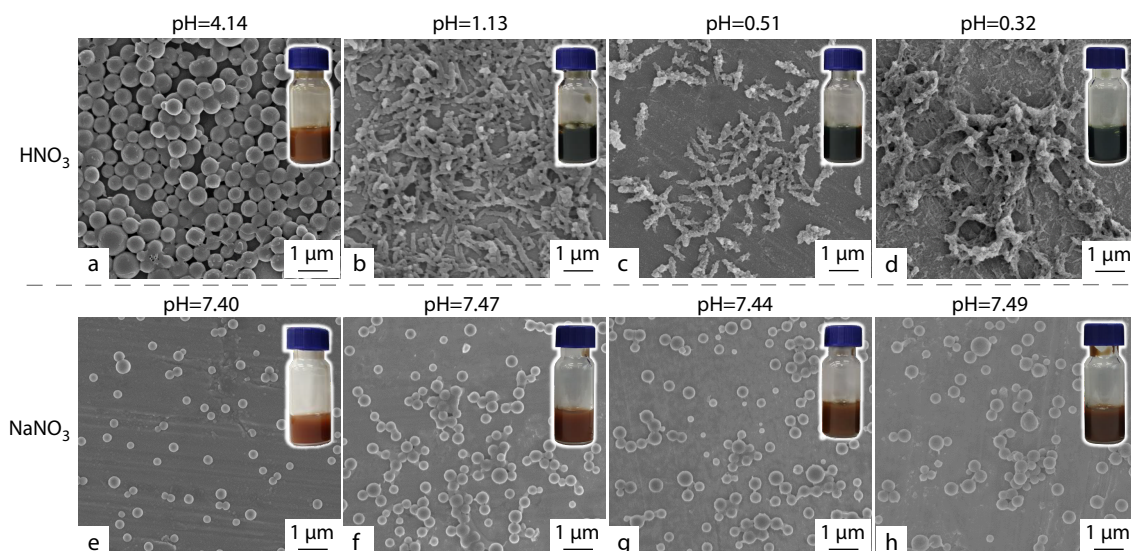


Fig. 4 SEM images of the products in the irradiated HNO_3 /aniline and NaNO_3 /aniline solutions with different $[\text{NO}_3^-]$: (a, e) 0.08 mol/L, (b, f) 0.2 mol/L, (c, g) 0.5 mol/L, and (d, h) 0.7 mol/L; the insets are the digital photos of the corresponding reaction systems ($[\text{aniline}] = 0.11$ mol/L, dose rate: 29 Gy/min, absorbed dose: 41.8 kGy).

mentary information, ESI). The concentration of HNO_3 has a significant impact on the degree of protonation of aniline and the amount of oxidative $\cdot\text{NO}_3$ produced by the radiolysis of NO_3^- . Increasing the HNO_3 concentration was conducive to the radiation-induced polymerization of protonated aniline to form polyaniline. It indicates that the radiation-induced polymerization of aniline in HNO_3 solution is closely related to the NO_3^- concentration of the solution.

As a contrast, the digital photos of the irradiated weakly alkaline NaNO_3 /aniline solution with the same concentration of NO_3^- are shown in Figs. 4(e)–4(h), and SEM images of the products are displayed accordingly. All products were microspherical oligoanilines with particle sizes of 300–500 nm. The

results show that radiation-induced polymerization of aniline requires not only NO_3^- but also a certain concentration of protons.

The concentration of aniline

In order to further demonstrate the effect of pH on the radiation-induced polymerization of aniline, pH was also adjusted by changing the concentration of aniline at a fixed $[\text{HNO}_3]$ of 0.08 mol/L, as shown in Figs. 5(a)–5(f). It can be seen clearly that when $[\text{aniline}] \geq 0.10$ mol/L, i.e., $\text{pH} \geq 3.62$, the irradiated solutions become brown and all products are microspherical oligoanilines. When $[\text{aniline}] \leq 0.08$ mol/L, i.e., $\text{pH} \leq 2.13$, the irradiated solutions are nearly dark green and all products are strip-like PANI.

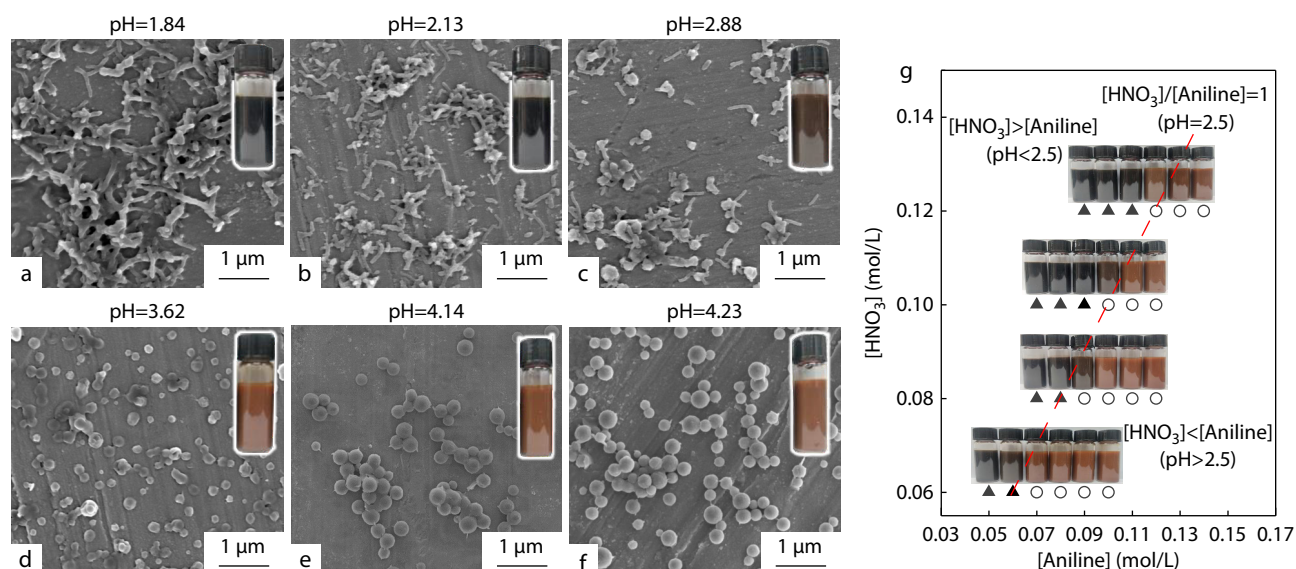


Fig. 5 SEM images of the products in the irradiated HNO_3 /aniline solutions with different $[\text{aniline}]$: (a) 0.07 mol/L, (b) 0.08 mol/L, (c) 0.09 mol/L, (d) 0.10 mol/L, (e) 0.11 mol/L, and (f) 0.12 mol/L; the insets are the digital photos of the corresponding reaction systems ($[\text{HNO}_3] = 0.08$ mol/L, dose rate: 29 Gy/min, absorbed dose: 41.8 kGy). (g) The summary of the radiation-induced polymerization activity of aniline at different concentrations of HNO_3 and aniline (▲: polymer; ○: non-polymer).

When [aniline]=0.09 mol/L, that is, pH=2.88, the irradiated solution was brown-black. Both strip-like and microspherical products were present simultaneously. The findings unequivocally demonstrate that the successful radiation-induced polymerization of aniline in HNO₃ solution has an upper pH limit. The radiation-induced polymerization activity of aniline at different concentrations of HNO₃ and aniline is summarized in Fig. 5(g). PANI can be successfully obtained only when [HNO₃] > [aniline], i.e., pH < 2.5. These results are consistent with the reaction conditions required for the chemical oxidative polymerization of aniline widely reported in the literature.^[11,36,49] It is also confirmed that the radiation-induced polymerization of aniline in HNO₃ solution requires the involvement of both H⁺ and NO₃⁻.

Radiation-induced Polymerization Mechanism of Aniline

Based on the above experimental and characterization results, a radiation-induced polymerization mechanism of aniline was proposed, as illustrated in Fig. 6. When γ -ray radiolysis of water molecules occurs, a large number of active species can be produced, such as $\cdot\text{H}$, e_{aq}^- , $\cdot\text{OH}$, etc. In strongly acidic solutions (pH < 2.5), e_{aq}^- produced by water radiolysis is immediately neutralized by H⁺ to form $\cdot\text{H}$, subsequently, $\cdot\text{H}$ reacts with NO₃⁻ to generate HNO₂, and as a result, the DMPO-H signals were absent in the EPR spectrum of the irradiated HNO₃ aqueous solution. NO₃⁻ is converted to strongly oxidative $\cdot\text{NO}_3$ through direct ionization and a reaction with $\cdot\text{OH}$. The consumption of reductive e_{aq}^- and $\cdot\text{H}$, along with the generation of oxidative $\cdot\text{NO}_3$, makes the entire system full of an oxidizing atmosphere. Subsequently, $\cdot\text{NO}_3$ reacts with protonated aniline to generate aniline cationic free radicals, which can undergo electron rearrange-

ment to form quinone imide carbon free radicals, thereby initiating the polymerization of aniline. In the chain growth stage, these two free radicals react with each other to form an unstable dimer with two positive charges (reaction ①). This dimer quickly removed protons from imide N to generate a new secondary amine cation (reaction ②). The latter is then oxidized by $\cdot\text{NO}_3$ to a secondary amine cation radical, which rearranges into a dimer possessing a quinone imide carbon radical (reaction ③). Reaction ①, ②, and ③ repeats over and over again, PANI macromolecular free radicals are eventually formed. Owing the strongly acidity and oxidation of the system, some phenylenediamine units in macromolecular free radicals may be oxidized to a quinoid structure, and quinone imine is easily protonated. Furthermore, the benzene ring unit in the PANI chain was electrophilically replaced by $\cdot\text{OH}$ in the solution into the phenol structure. Macromolecular free radicals can be terminated by the normal double-group reaction or the reaction with $\cdot\text{OH}$, ultimately yielding PANI salt with a specific degree of oxidation.

Electrochemical Property of Radiation-Synthesized Polyaniline

The polymerization method, doping process of proton acid, and electrolyte type have a great influence on the electrochemical properties of PANI.^[50–52] The electrochemical properties of the radiation-synthesized PANI were characterized using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The samples were labelled as PANI-R_{0.2}, PANI-R_{0.5} and PANI-R_{0.7}, respectively, based on the [HNO₃] of the preparation systems. Figs. 7(a)–7(c) show the CV curves of the PANI-R_{0.2}, PANI-R_{0.5}, and PANI-R_{0.7} systems. Three redox peaks at 0.31 V (A/A'), 0.49 V (B/B') and 0.70 V

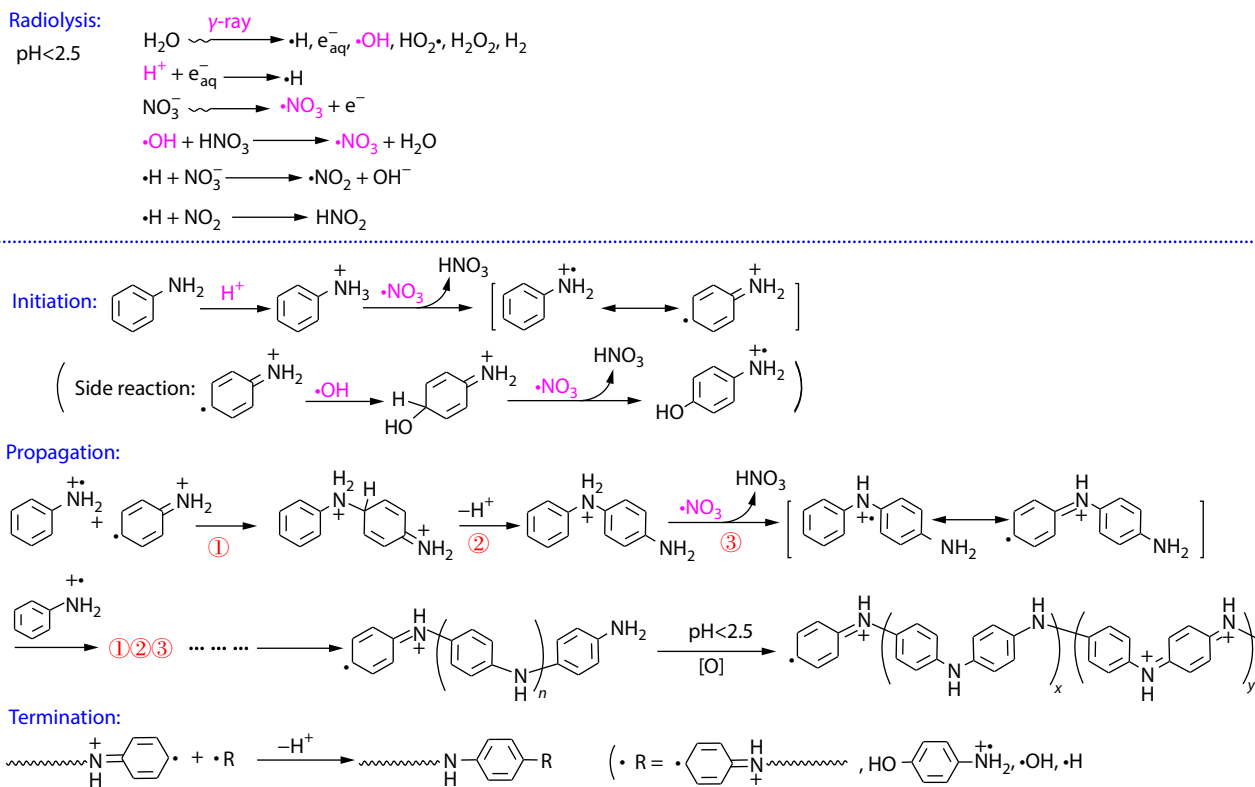


Fig. 6 Proposed radiation-induced polymerization mechanism of aniline in this work.

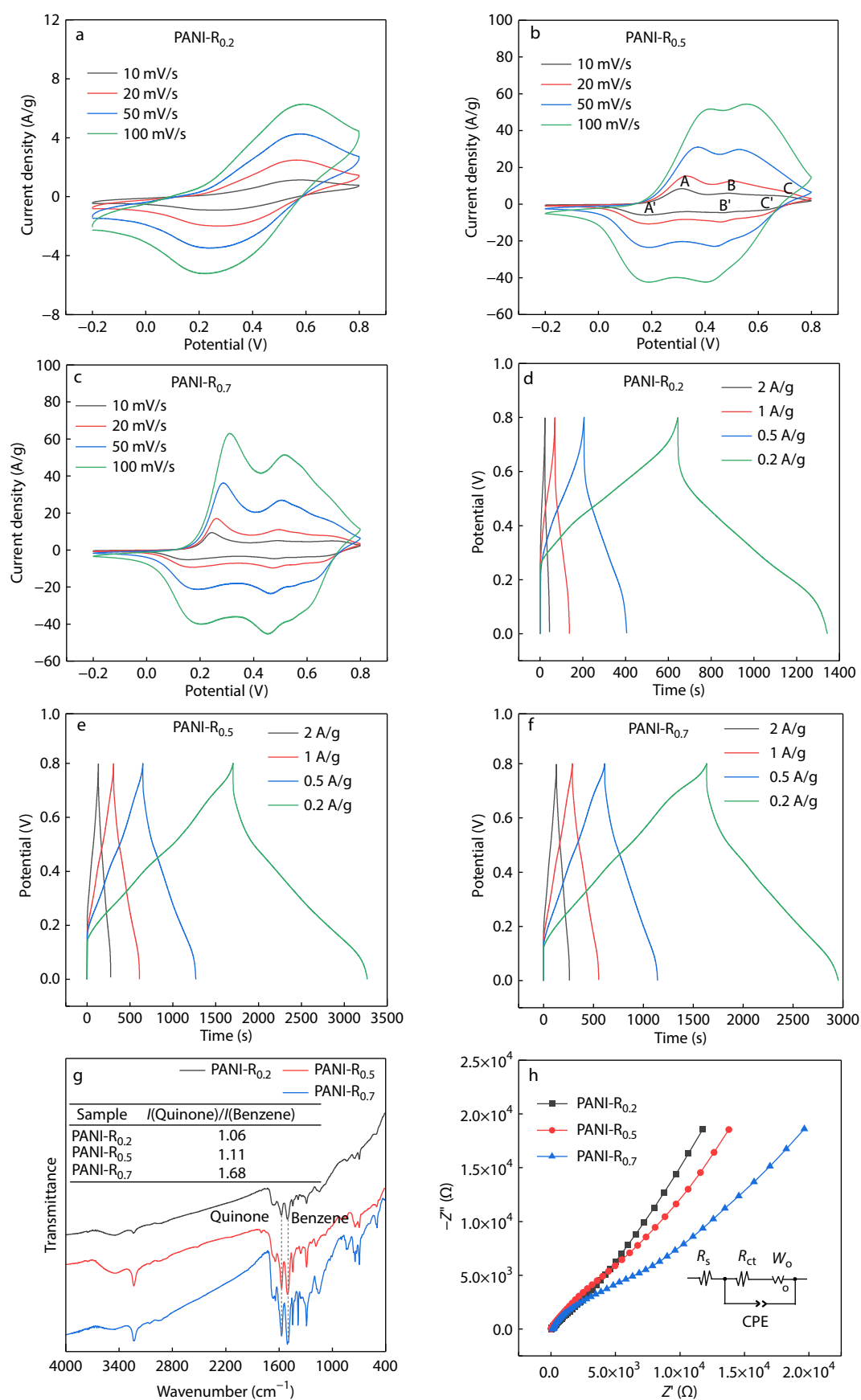


Fig. 7 (a–c) CV curves, (d–f) GCD curves, (g) FTIR spectra, and (h) EIS Nyquist plots of the radiation synthesized PANI-R_{0.2}, PANI-R_{0.5}, and PANI-R_{0.7}.

(C/C') are clearly observed in PANI-R_{0.5} and PANI-R_{0.7} systems, respectively. Among them, the A/A' and C/C' peaks are associated with the mutual transition between the reductive and oxidizing states of PANI, while the B/B' peak is attributed to the hydrolyzed products of the quinoid units in the molecular chain.^[53,54] However, a prominent redox peak of B/B' was detected in PANI-R_{0.2}. Based on the proposed polymerization mechanism in Fig. 6, the molecular units of radiation-synthesized PANI are easily oxidized to form quinoid units, and aniline units are more easily oxidized with the increase in pH owing to the strongly oxidizing atmosphere caused by the radiolysis of HNO₃ solution. Therefore, the intensity of the B/B' peak in the CV curve of PANI-R_{0.2} was higher than those of PANI-R_{0.5} and PANI-R_{0.7}. Figs. 7(d)–7(f) show the GCD curves of the PANI-R_{0.2}, PANI-R_{0.5}, and PANI-R_{0.7} systems, all of which exhibit nonlinear charge-discharge processes.^[55] According to the GCD curve at a current density of 1 A/g, the specific capacitances of PANI-R_{0.2}, PANI-R_{0.5} and PANI-R_{0.7} were calculated to be 88.8, 384.2 and 357.9 F/g, respectively. The electrochemical properties of PANI are related to its degree of protonation and oxidation, and optimizing the appropriate levels of protonation and oxidation can significantly enhance the specific capacitance of PANI.^[13] The synthetic system of PANI-R_{0.2} has the lowest concentration of HNO₃, its protonation degree is relatively low. According to the ratio of the characteristic peaks at 1576 cm⁻¹ (quinoid ring) and 1502 cm⁻¹ (benzene ring) in the FTIR spectra of the three samples (Fig. 7g), the proportions of oxidized/reduced structural units in the molecular chains of PANI-R_{0.2}, PANI-R_{0.5}, and PANI-R_{0.7} are 1.06, 1.11, and 1.68, respectively. The oxidation degree of PANI-R_{0.7} was much higher than that of PANI-R_{0.5} and PANI-R_{0.2}. From a comprehensive perspective, PANI-R_{0.5} has moderate protonation and oxidation levels; thus, the PANI-R_{0.5} system has the highest specific capacitance. For comparison, the GCD curves of the two samples (PANI-C_{HNO3} and PANI-C_{HCl}) prepared by chemical oxidative polymerization initiated by (NH₄)₂S₂O₈ in HNO₃ and HCl solutions, respectively, similar to the synthesis of PANI-R_{0.5}, are shown in Fig. S2 (in ESI). The specific capacitances of the two systems are calculated to be 334.9 F/g (PANI-C_{HNO3}) and 348.8 F/g (PANI-C_{HCl}), respectively, indicating that the radiation-synthesized PANI exhibits a higher specific capacitance under the same conditions. Fig. 7(h) shows the EIS Nyquist plots of the PANI-R_{0.2}, PANI-R_{0.5}, and PANI-R_{0.7} systems. The diameter of the semicircle in the high-frequency region represents the resistance R_{ct} caused by charge transfer between the electrolyte and the electrode interface, which depends on the conductivity and electrochemical active area of the electrode material.^[55,56] R_{ct} of PANI-R_{0.5} is 0.2 Ω , which is significantly lower than of PANI-R_{0.2} (230.2 Ω) and PANI-R_{0.7} (421.1 Ω), indicating its high conductivity, which is consistent with the structural characteristics of the above analysis.

CONCLUSIONS

In this work, radiation-induced polymerization of aniline in HNO₃ solution was successfully achieved at room temperature without the use of chemical oxidants. Through the analysis of the radiation chemical reactions of inorganic acids and nitrate salt solutions, the characterization of the intermediate free radicals in the irradiated systems, and the exploration of the influence of the pH of the aqueous solutions on the polymerization

activity and the product morphologies, it is confirmed that radiation-induced polymerization of aniline requires not only NO₃⁻, but also a certain concentration of protons. In other words, only under the condition of [HNO₃] > [aniline], that is, pH < 2.5, PANI can be successfully obtained. The polymerization begins with the oxidation of aniline cations to aniline cation radicals by ·NO₃ generated by radiolysis reactions, and goes through three repeated steps including recombination, deprotonation, and oxidation reaction of ·NO₃, thus forming PANI macromolecular chain. Along with the polymerization reaction, the aniline units were protonated and oxidized because of the strongly acidity and oxidation of the reaction system under γ -ray irradiation, thus forming chain structural units of different oxidation states. This also means that the molecular chain structure of radiation-synthesized PANI can be regulated by the pH, nitrate concentration, and irradiation conditions. The electrochemical properties of the radiation-synthesized PANI showed that PANI with moderate protonation and oxidation states could be synthesized by the radiation method; thus, a PANI supercapacitor with the highest conductivity and specific capacitance was obtained, and its performance was better than that of PANI synthesized by chemical oxidation under the same conditions. This work presents a new radiation-synthesis method and polymerization mechanism of PANI, which not only expands the application of radiation techniques in the field of polymer synthesis but also provides a new idea for the structural regulation and performance optimization of PANI.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3258-1>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The authors' contact information: pstwmz@ustc.edu.cn; xwge@ustc.edu.cn.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51973205 and 51773189) and the Fundamental Research Funds for the Central Universities (Nos. WK9110000066, WK345000005 and WK345000006).

REFERENCES

- Ćirić-Marjanović, G. Recent advances in polyaniline research: polymerization mechanisms, structural aspects, properties and

- applications. *Synthetic Met.* **2013**, *177*, 1–47.
- 2 Chu, X.; Yang, W.; Li, H. Recent advances in polyaniline-based micro-supercapacitors. *Mater. Horiz.* **2023**, *10*, 670–697.
 - 3 Tarver, J.; Loo, Y. L. Mesostuctures of polyaniline films affect polyelectrochromic switching. *Chem. Mater.* **2011**, *23*, 4402–4409.
 - 4 Zhang, T.; Qi, H.; Liao, Z.; Horev, Y. D.; Panes-Ruiz, L. A.; Petkov, P. S.; Zhang, Z.; Shivhare, R.; Zhang, P.; Liu, K.; Bezugly, V.; Liu, S.; Zheng, Z.; Mannsfeld, S.; Heine, T.; Cuniberti, G.; Haick, H.; Zschech, E.; Kaiser, U.; Dong, R.; Feng, X. Engineering crystalline quasi-two-dimensional polyaniline thin film with enhanced electrical and chemiresistive sensing performances. *Nat. Commun.* **2019**, *10*, 4225.
 - 5 Huang, J.; Wang, Z.; Hou, M.; Dong, X.; Liu, Y.; Wang, Y.; Xia, Y. Polyaniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous zinc-ion battery. *Nat. Commun.* **2018**, *9*, 2906.
 - 6 Yan, L. X.; Chen, L. J.; Zhao, X.; Yan, X. P. pH switchable nanoplatfor for in vivo persistent luminescence imaging and precise photothermal therapy of bacterial infection. *Adv. Funct. Mater.* **2020**, *30*, 1909042.
 - 7 Sapurina, I.; Stejskal, J. The mechanism of the oxidative polymerization of aniline and the formation of supramolecular polyaniline structures. *Polym. Int.* **2008**, *57*, 1295–1325.
 - 8 Wang, B.; Tang, J.; Wang, F. Electrochemical polymerization of aniline. *Synthetic Met.* **1987**, *18*, 323–328.
 - 9 Macdiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. Polyaniline: a new concept in conducting polymers. *Synthetic Met.* **1987**, *18*, 285–290.
 - 10 Stejskal, J.; Hlavatá, D.; Holler, P.; Trchová, M.; Prokeš, J.; Sapurina, I. Polyaniline prepared in the presence of various acids: a conductivity study. *Polym. Int.* **2004**, *53*, 294–300.
 - 11 Zhao, Y.; Tomšík, E.; Wang, J.; Morávková, Z.; Zhigunov, A.; Stejskal, J.; Trchová, M. Self-assembly of aniline oligomers. *Chem. Asian J.* **2013**, *8*, 129–137.
 - 12 Baker, C. O.; Huang, X. W.; Nelson, W.; Kaner, R. B. Polyaniline nanofibers: broadening applications for conducting polymers. *Chem. Soc. Rev.* **2017**, *46*, 1510–1525.
 - 13 Eftekhari, A.; Li, L.; Yang, Y. Polyaniline supercapacitors. *J. Power Sources* **2017**, *347*, 86–107.
 - 14 Wang, H.; Liu, D.; Duan, X.; Du, P.; Guo, J.; Liu, P. Facile preparation of high-strength polyaniline/polyvinyl chloride composite film as flexible free-standing electrode for supercapacitors. *Mater. Design* **2016**, *108*, 801–806.
 - 15 Cao, Y.; Andreatta, A.; Heeger, A. J.; Smith, P. Influence of chemical polymerization conditions on the properties of polyaniline. *Polymer* **1989**, *30*, 2305–2311.
 - 16 Goswami, S.; Nandy, S.; Fortunato, E.; Martins, R. Polyaniline and its composites engineering: a class of multifunctional smart energy materials. *J. Solid State Chem.* **2023**, *317*, 123679.
 - 17 Sharma, N.; Singh, A.; Kumar, N.; Tiwari, A.; Lal, M.; Arya, S. A review on polyaniline and its composites: from synthesis to properties and progressive applications. *J. Mater. Sci.* **2024**, *59*, 6206–6244.
 - 18 Hochanadel, C. J. Effects of cobalt γ -radiation on water and aqueous solutions. *J. Phys. Chem.* **1952**, *56*, 587–594.
 - 19 Marignier, J. L.; Belloni, J.; Delcourt, M. O.; Chevalier, J. P. Microaggregates of non-noble metals and bimetallic alloys prepared by radiation-induced reduction. *Nature* **1985**, *317* (6035), 344–345.
 - 20 Lattach, Y.; Coletta, C.; Ghosh, S.; Remita, S. Radiation-induced synthesis of nanostructured conjugated polymers in aqueous solution: fundamental effect of oxidizing species. *ChemPhysChem* **2014**, *15*, 208–218.
 - 21 Flores-Rojas, G. G.; López-Saucedo, F.; Bucio, E. Gamma-irradiation applied in the synthesis of metallic and organic nanoparticles: a short review. *Radiat. Phys. Chem.* **2020**, *169*, 107962.
 - 22 Wang, J.; Rong, J. L.; Fang, Z.; Wang, M. Z.; Asif, A.; Wu, Q. C.; Zhou, X.; Ge, X. W. Monodisperse polypyrrole nanoparticles prepared via gamma-ray radiolysis of water: an efficient near-infrared photothermal agent for cancer therapy. *Part. Part. Syst. Char.* **2017**, *34*, 1600430.
 - 23 Karaivanov, I.; Christensen, H.; Toftlund, H.; Andersen, P.; Bisgård, P.; Edlund, K.; Eliassen, M.; Herskind, C.; Laursen, T.; Pedersen, P. Radiolysis of aqueous aniline solutions. *Acta Chem. Scand.* **1975**, *29*, 553–557.
 - 24 Meader, V. K.; John, M. G.; Frias Batista, L. M.; Ahsan, S.; Tibbetts, K. M. Radical chemistry in a femtosecond laser plasma: photochemical reduction of Ag^+ in liquid ammonia solution. *Molecules* **2018**, *23*, 532.
 - 25 Sun, J.; Zhang, X.; Broderick, M.; Fein, H. Measurement of nitric oxide production in biological systems by using griess reaction assay. *Sensors* **2003**, *3*, 276–284.
 - 26 Mai, L. Q.; Minhas-Khan, A.; Tian, X.; Hercule, K. M.; Zhao, Y. L.; Lin, X.; Xu, X. Synergistic interaction between redox-active electrolyte and binder-free functionalized carbon for ultrahigh supercapacitor performance. *Nat. Commun.* **2013**, *4*, 2923.
 - 27 Ma, J.; Wang, F.; Mostafavi, M. Ultrafast chemistry of water radical cation, H_2O^+ , in aqueous solutions. *Molecules* **2018**, *23*, 244.
 - 28 Jiang, P. Y.; Katsumura, Y.; Ishigure, K.; Yoshida, Y. Reduction potential of the nitrate radical in aqueous solution. *Inorg. Chem.* **1992**, *31*, 5135–5136.
 - 29 Matthews, R. W.; Mahlman, H. A.; Sworski, T. J. Elementary processes in the radiolysis of aqueous sulfuric acid solutions. Determinations of both G_{OH} and $\text{G}_{\text{SO}_4^-}$. *J. Phys. Chem.* **1972**, *76*, 1265–1272.
 - 30 Atinault, E.; De Waele, V.; Schmidhammer, U.; Fattahi, M.; Mostafavi, M. Scavenging of e_s^- and $\text{OH}^\cdot$ radicals in concentrated HCl and NaCl aqueous solutions. *Chem. Phys. Lett.* **2008**, *460*, 461–465.
 - 31 Jiang, P. Y.; Katsumura, Y.; Domae, M.; Ishikawa, K.; Nagaishi, R.; Ishigure, K.; Yoshida, Y. Pulse radiolysis study of concentrated phosphoric acid solutions. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 3319–3322.
 - 32 Katsumura, Y.; Jiang, P. Y.; Nagaishi, R.; Oishi, T.; Ishigure, K.; Yoshida, Y. Pulse radiolysis study of aqueous nitric acid solutions: formation mechanism, yield, and reactivity of $\text{NO}_3^\cdot$ radical. *J. Phys. Chem.* **1991**, *95*, 4435–4439.
 - 33 Christensen, H. Pulse radiolysis of aqueous solutions of aniline and substituted anilines. *Int. J. Radiat. Phys. Chem.* **1972**, *4*, 311–333.
 - 34 Zhou, C.; Gong, X.; Han, J.; Guo, R. Controlled synthesis of tower-like aniline oligomers with excellent adsorption properties. *New J. Chem.* **2015**, *39*, 2202–2208.
 - 35 Zhou, C.; Ren, Y.; Han, J.; Gong, X.; Wei, Z.; Xie, J.; Guo, R. Controllable supramolecular chiral twisted nanoribbons from achiral conjugated oligoaniline derivatives. *J. Am. Chem. Soc.* **2018**, *140*, 9417–9425.
 - 36 Stejskal, J.; Sapurina, I. Y.; Trchová, M.; Konyushenko, E. N. Oxidation of aniline: polyaniline granules, nanotubes, and oligoaniline microspheres. *Macromolecules* **2008**, *41*, 3530–3536.
 - 37 Koval'chuk, E. P.; Whittingham, S.; Skolozdra, O. M.; Zavalij, P. Y.; Zavalij, I. Y.; Reshetnyak, O. V.; Błazejowski, J. Copolymers of aniline and nitroanilines: part II. Physicochemical properties. *Mater. Chem. Phys.* **2001**, *70*, 38–48.
 - 38 Zhou, C.; Ren, Y.; Han, J.; Xu, Q.; Guo, R. Chiral polyaniline hollow nanotwists toward efficient enantioselective separation of amino acids. *ACS Nano* **2019**, *13*, 3534–3544.
 - 39 Zhang, Z.; Deng, J.; Wan, M. Highly crystalline and thin

- polyaniline nanofibers oxidized by ferric chloride. *Mater. Chem. Phys.* **2009**, *115*, 275–279.
- 40 Józefowicz, M. E.; Epstein, A. J.; Pouget, J. P.; Masters, J. G.; Ray, A.; Sun, Y.; Tang, X.; Macdiarmid, A. G. X-ray structure of polyanilines. *Synthetic Met.* **1991**, *41*, 723–726.
 - 41 La Verne, J. A. Radical and molecular yields in the radiolysis of water with carbon ions. *Radiat. Phys. Chem.* **1989**, *34*, 135–143.
 - 42 Jiang, P. Y.; Katsumura, Y.; Nagaishi, R.; Domae, M.; Ishikawa, K.; Ishigure, K.; Yoshida, Y. Pulse radiolysis study of concentrated sulfuric acid solutions. Formation mechanism, yield and reactivity of sulfate radicals. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 1653–1658.
 - 43 El Omar, A. K.; Schmidhammer, U.; Rousseau, B.; LaVerne, J.; Mostafavi, M. Competition reactions of H_2O^+ radical in concentrated Cl^- aqueous solutions: picosecond pulse radiolysis study. *J. Phys. Chem. A* **2012**, *116*, 11509–11518.
 - 44 Yakabuskie, P. A.; Joseph, J. M.; Stuart, C. R.; Wren, J. C. Long-term γ -radiolysis kinetics of NO_3^- and NO_2^- solutions. *J. Phys. Chem. A* **2011**, *115*, 4270–4278.
 - 45 Miyaji, A.; Kohno, M.; Inoue, Y.; Baba, T. Hydroxyl radical generation by dissociation of water molecules during 1.65 MHz frequency ultrasound irradiation under aerobic conditions. *Biochem. Biophys. Res. Commun.* **2017**, *483*, 178–182.
 - 46 Nash, K. M.; Rockenbauer, A.; Villamena, F. A. Reactive nitrogen species reactivities with nitrones: theoretical and experimental studies. *Chem. Res. Toxicol.* **2012**, *25*, 1581–1597.
 - 47 Mu, S.; Chen, C.; Xue, H. ESR properties of polyaniline in a wide pH range. *J. Electroanal. Chem.* **2014**, *724*, 71–79.
 - 48 Mezyk, S. P.; Cullen, T. D.; Rickman, K. A.; Mincher, B. J. The reactivity of the nitrate radical ($\cdot\text{NO}_3$) in aqueous and organic solutions. *Int. J. Chem. Kinet.* **2017**, *49*, 635–642.
 - 49 Gospodinova, N.; Terlemezyan, L. Conducting polymers prepared by oxidative polymerization: polyaniline. *Prog. Polym. Sci.* **1998**, *23*, 1443–1484.
 - 50 Li, H.; Wang, J.; Chu, Q.; Wang, Z.; Zhang, F.; Wang, S. Theoretical and experimental specific capacitance of polyaniline in sulfuric acid. *J. Power Sources* **2009**, *190*, 578–586.
 - 51 Zeng, F.; Xiao, Y.; Shen, Y.; Xu, X.; Qin, Z. Facile template-free fabrication and charge storage behavior of polyaniline nanobelts by using the oxidation–reduction initiation system in various inorganic acids. *Electrochim. Acta* **2021**, *386*, 138516.
 - 52 Senthilkumar, S. T.; Selvan, R. K.; Lee, Y. S.; Melo, J. S. Electric double layer capacitor and its improved specific capacitance using redox additive electrolyte. *J. Mater. Chem. A* **2013**, *1*, 1086–1095.
 - 53 Cui, C. Q.; Ong, L. H.; Tan, T. C.; Lee, J. Y. Extent of incorporation of hydrolysis products in polyaniline films deposited by cyclic potential sweep. *Electrochim. Acta* **1993**, *38*, 1395–1404.
 - 54 Ding, H.; Park, S. M. Electrochemistry of conductive polymers: XXVII. Effects of polystyrene sulfonate on electrochemical behavior of polyaniline. *J. Electrochem. Soc.* **2003**, *150*, E33.
 - 55 Li, T.; Qin, Z.; Liang, B.; Tian, F.; Zhao, J.; Liu, N.; Zhu, M. Morphology-dependent capacitive properties of three nanostructured polyanilines through interfacial polymerization in various acidic media. *Electrochim. Acta* **2015**, *177*, 343–351.
 - 56 Yang, W.; Gao, Z.; Song, N.; Zhang, Y.; Yang, Y. Synthesis of hollow polyaniline nano-capsules and their supercapacitor application. *J. Power Sources* **2014**, *272*, 915–921.