

1 Brief History

At the very beginning of the foundation of the University of Science and Technology of China (USTC) in Beijing in 1958, the Department of Radiochemistry and Radiation Chemistry was one among 13 departments. In the early 1970s, that is, during the cultural revolution, USTC was moved to Anhui Province and finally settled down in Hefei city. The research in radiochemistry had to be given up due to the external environment, but the research in radiation chemistry has continued in the Teaching and Research Laboratory of Radiation Chemistry in the Department of Applied Chemistry.

In the early 1980s, a ^{60}Co γ -rays source with a radioactivity of about 1.87×10^{15} Bq was introduced as is the basic condition for radiation chemistry research. The staff members were about 10 with only several graduate students, while it was the only university in China that had radiation chemistry majors for undergraduate students. As being the aftermaths of the cultural revolution, it was a rather difficult period for the scientists all over the country. The grant-in-aid for scientific research was quite limited, and the scientific instruments were too old and far behind that in the developed countries. But the professors were struggling with great courage to do some 'useful' research. The ^{60}Co γ source was even used for radiation sterilization of medical devices and Chinese traditional medicines, and so on. At that time, the research themes were radiation chemistry of polymers, for example, radiolytic synthesis of hydrogen gels and resins for medical uses or else. It is worth mentioning that some of those studies have finally come

out with industrial production, for example, the radiolytic synthesized textile adhesives and poly(acrylic acid) thickeners have been being successfully used in the dyeing and printing industries with an annual output of about 200 million RMB in recent years. The situation changed little by little and became much better at the beginning of this century.

In 2001, the group of radiation chemistry was incorporated into the Department of Polymer Science and Engineering and became today's Radiation Chemistry Laboratory.

2 Recent Research Activities

Now 3 professors and 3 associated professors, with more than 30 (M.S. and Ph.D.) graduate students are involved in radiation chemistry related studies. The radioactivity of the ^{60}Co γ source is about 5.6×10^{14} Bq (the building, control room and irradiation room of the ^{60}Co γ source are shown in Fig. 1), but it might be increased to 2.2×10^{15} Bq in the near future.

The recent research activities are radiolytic polymerization of functional materials, radiation grafting or crosslinking of polymers, synthesis of polymeric nanocomposites, modeling of water radiolysis for nuclear spent fuel reprocessing and fusion water, etc. In general, the major research themes (as shown in Fig. 2) and some examples are briefly introduced as below:

2.1 Basic and practical studies

The basic and practical studies in radiation chemistry have been developed: (a) Radiation induced polymerization, especially radiation induced emulsion polymerization of acrylic acid and its ester monomers, (b) the mechanism and application of radiation grafting, radiation crosslinking of polymer materials, and (c) according to particular features of the effect of high energy radiation on the medium system, *i.e.*, homogeneous distribution and the

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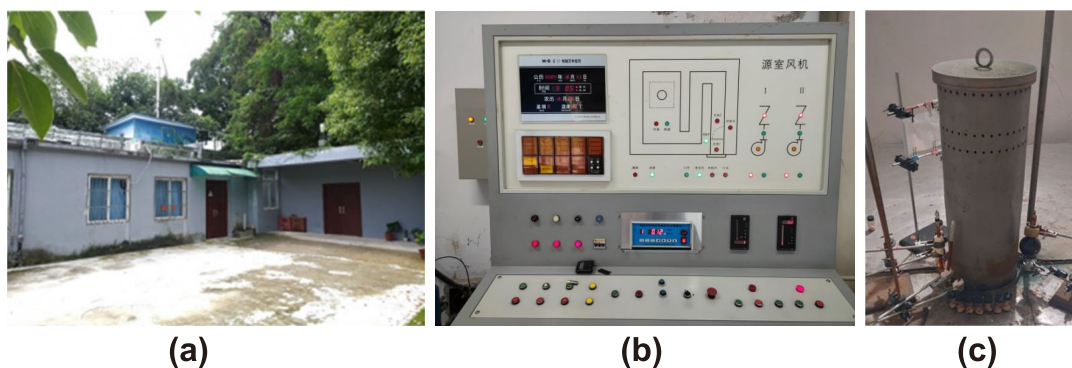


Figure 1. (a) Building, (b) control room, and (c) irradiation room of the ^{60}Co γ source.

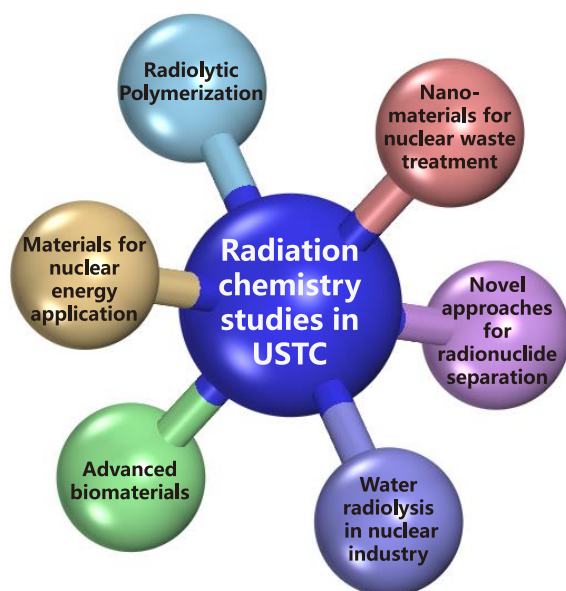


Figure 2. The research themes in the USTC.

fast reaction rate in ambient temperature and pressure, various methods on the fabrication of nano/micro-structured materials with controllable morphology and structure, such as porous and hollow polymeric microspheres, anisotropic particles and organic/inorganic nanocomposites,

Novel porous sulfonated polystyrene (SPS) / reduced graphene oxide (rGO) composite microspheres loaded with Au nanoparticles (AuNP@SPS/rGO) were synthesized through γ irradiation on a simple one-pot system, *i.e.* an aqueous solution containing cage-like porous

SPS microspheres, GO, and HAuCl_4 . rGO and AuNPs with a size of about 12 nm were formed in water simultaneously under γ -irradiation, and *in situ* loaded on cage-like porous SPS microspheres. The prepared cage-like AuNP@SPS/rGO microspheres showed far better catalytic performance than the conventional non-supported AuNP catalysts, which completed the reduction of *o*-nitroaniline by NaBH_4 within only 15 s. Moreover, the prepared AuNP@SPS/rGO microspheres can be easily recycled from the reaction system by centrifugation without loss of the catalytic activity¹⁾.

A novel method was proposed to construct hierarchically porous microspheres with inner macropores and a mesoporous wall (Macro@Meso-SPS) through two consecutive phase separation processes²⁾. Based on this method, swelling-osmosis and polymerization-induced phase separation (PIPS) in solid sulfonated polystyrene (SPS) seed microspheres which were prepared by the sulfonation of polystyrene (PS) microspheres synthesized *via* γ -ray-radiation initiated dispersion polymerization with polyvinylpyrrolidone (PVP) as a stabilizer. The pore size of the Macro@Meso-SPS microspheres could be tuned from 3.1 nm to over 50 nm by adjusting the absorbed dose during the synthesis of PS microspheres, the amount and the conversion of MMA in PIPS. The Macro@Meso-SPS microspheres with surface mesopores around 3.1 nm showed better controlled-release performance of the loaded small molecules like methyl orange, whose cumulative release ratio was merely 45.3 % after 24 h, compared to those with larger surface pores above 11.2 nm.

2.2 Materials related to nuclear energy application

We have been working on the fundamental study involving the materials related to nuclear energy application, such as the physical properties, lifetime, and radiation effect of materials in extreme radiation conditions. It aims to provide technical reserves for the future science related to nuclear energy.

To study the radiation resistant of epoxy (EP) resins, boron nitride (*h*-BN)/EP resin composites were fabricated by solution blending. The results showed that the addition of *h*-BN improved the mechanical property and the glassy transition temperature of the resin. The presence of low-level *h*-BN was favorable to enhance the radiation resistance of EP. For the composites with the 0.05 % mass percentage of *h*-BN, the absorbed dose required to decrease relative tensile strength by 50 % was about 300 kGy, which was higher than that of neat EP. Benefiting from the absorbing neutrons capability of boron atoms, an addition of 0.55 % *h*-BN to the EP resin could reduce the neutron transmittance of the resin by 5.6 %³⁾.

A new radiation-induced reduction-exfoliation method is developed to achieve the one-step exfoliation of *h*-BN to form Ni-nanoparticle-(NiNP)-bound boron nitride nanosheet (BNNS) (Ni/BNNS) in a binary isopropanol/water medium using γ -ray radiation at ambient temperature and pressure⁴⁾. The prepared magnetic Ni/BNNS exhibits good catalytic performance, excellent structural stability, and reusability toward the reduction of 2-nitroaniline (2-NA). After 5 cycles, the conversion of 2-NA still reaches 95.9 % within 500 s. More interestingly, when Ni/BNNS was dispersed in water/methanol solution at a content of 0.17 mg mL⁻¹ followed by exposure to simulated sunlight irradiation, H₂ evolution of 8404.3 $\mu\text{mol g}_{\text{Ni}}^{-1}$ within 2 h can be detected.

2.3 Multi-functional and high-efficient nano-medicine

We have been developing novel, multi-functional, and high-efficient nano-medicine platforms based on the preparation technique on versatile stimuli-response microsphere materials, which aims to push the applications of the fundamental research findings of radiation chemistry in the field of advanced biomaterials.

To study the functionalized nanoparticles as gene carriers, novel glutathione (GSH) triggered degradable organosilica nanoparticles grafted with guanidinated

fluorinated α -polylysine (*o*-SiNP-GF) are prepared⁵⁾. The cytotoxicity and DNA-binding ability of *o*-SiNP-GF, as well as *in vitro* gene transfection performance of DNA/*o*-SiNP-GF complexes, have been investigated using enhanced green fluorescent protein plasmid (pEGFP) as the DNA model. 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay (a colorimetric assay for assessing cell metabolic activity) shows that the cytotoxicity of *o*-SiNP-GF is very low even at a concentration up to 800 mg mL⁻¹. The *in vitro* transfection efficiency of pEGFP/*o*-SiNP-GF complexes in 293T cells: human embryonic kidney cells, is up to 94.7 % at the N/P ratio: molar ratios of nitrogen (N) in poly((2-dimethylamino) ethyl methacrylate) (PDMAEMA) to phosphate (P) in DNA, of 10, much higher than that of pEGFP/PEI complexes. This work not only provides a way to prepare novel GSH-triggered degradable organosilica nanoparticles of size less than 50 nm but also proves that the modification of guanidinated-fluorinated α -polylysine is an effective method to improve the efficiency of gene carriers⁵⁾.

A novel approach was developed to prepare near-infrared (NIR) light response inverse-opal lysozyme (Lyz) - imprinted polydopamine/polypyrrole (IO-PDA/PPy-MIP (molecularly imprinted polymer)) composite microspheres using micron-sized SiO₂ colloidal crystal microspheres as the sacrificed template⁶⁾. The IO-PDA/PPy-MIP microspheres show a rapid, selective adsorption ability for Lyz due to the inverse-opal macroporous structure. The adsorption capacity exceeds 800 mg g⁻¹ within 20 min, and the imprinting factor is as high as 24. The bound Lyz molecules can be released rapidly from IO-PDA/PPy-MIP microspheres triggered by the irradiation of NIR laser and remain enough bioactivity to decompose *Escherichia coli* efficiently. The adsorption capacity can remain up to 90 % of the initial value after 5 times recycle, exhibiting excellent structure stability and good recyclability.

2.4 Functional low dimensional materials

We have been synthesizing, with ionizing radiations, functional low dimensional materials such as graphene, boron nitride nanosheets, or hierarchically bimodal mesoporous silica for the separation of metallic ions, particularly for the radionuclides of fission products, such as Sr²⁺, Cs⁺, U(VI), Re (Tc) and platinum group metals (PGMs).

A high-efficient sorbent was successfully prepared by functionalization of graphene oxide with phenanthroline diamide (GO-PDA), which exhibited excellent selectivity towards actinides over lanthanides. The sorption isotherms of both U(VI) and Th(IV) coincided with the Langmuir model, while the maximum sorption capacities of U(VI) (pH 5.5) and Th(IV) (pH 4.0) at 298 K were 718 mg g⁻¹ and 703 mg g⁻¹ respectively, being much higher than most of the previously reported graphene oxide (GO) based sorbents. GO-PDA also possessed significantly enhanced selectivity for U(VI) and Th(IV) over Eu(III), Nd(III), and Sm(III) compared to pristine GO at ultra-low pH (0–2), with separation factors larger than 23 at pH 0⁷⁾.

A functional fibrous hierarchically bimodal mesoporous silica (F-SiO₂-DP) as a high efficient adsorbent for selective adsorption of uranium and thorium, which had hierarchically bimodal mesoporous structure and specific surface area of *ca.* 474.1 m² g⁻¹, was prepared by a post-modification method using 2,9-diamide-1,10-phenanthroline. The selectivity coefficient of U(VI) and Th(IV) over Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Y(III), and Yb(III) is all larger than 9 at pH 3.8, indicating that F-SiO₂-DP possesses a good simultaneously selective adsorption performance for U(VI) and Th(IV)⁸⁾.

Non-metal photocatalysts, carbon-doped BN (BCN) nanosheets were used to extract the uranium by the photocatalytic reduction technique, and the doping in the form of carbon rings can regulate the bandgap and electronic structure by manipulating carbon amount⁹⁾. Benefiting from the porous structure and strong visible-light absorption, the U(VI) separation ratio of 97.4 % could be achieved after 1.5-hour visible irradiation with an apparent rate value of 2.97 h⁻¹. The prepared BCN displayed good reusability and stability with the U(VI) separation ratio > 90 % even after five cycles.

Magnetic Nb-substituted crystalline silicotitanate (mag-Nb-CST), which can be used for separation of Sr²⁺ and Cs⁺ from aqueous solution, is successfully synthesized by embedding amine-functionalized Fe₃O₄ into the Nb-substituted crystalline silicotitanate (Nb-CST). The adsorption process reaches equilibrium within about 8 h, and the maximum adsorption capacity on mag-Nb-CST is 14.38 mg g⁻¹ at pH 11.00 for Sr²⁺, and 11.18 mg g⁻¹ at pH 4.00 for Cs⁺, respectively. The pH dependence on the adsorption capacity suggests a possibility to separate Sr²⁺ and Cs⁺ from each other by simply adjusting pH.

Mag-Nb-CST is able to remove most of the Sr²⁺ and Cs⁺ at ppb level. Even in real seawater, it is able to remove 94.19 % of Cs⁺. Moreover, mag-Nb-CST shows good acid-resistance and radiation stability¹⁰⁾.

A high efficiency pyridine-functionalized reduced graphene oxide (rGO) adsorbent was prepared for selective separation of Pd(II) from simulated electronic waste leachate by one-pot γ -ray radiation-induced simultaneous grafting polymerization (RIGP) of 4-vinylpyridine (4VP) from graphene oxide (GO) and reduction of GO. The poly(4-vinylpyridine)-grafted reduced graphene oxide (rGO-g-P4VP) exhibits fast adsorption kinetics and high maximum adsorption capacity. The adsorption capacity is 105 mg g⁻¹ in the first minute and reaches equilibrium within 120 min. Other precious metal ions like Pt(IV) and Au(III) can also be recovered easily and selectively by rGO-g-P4VP¹¹⁾.

2.5 Novel methods for nuclear waste treatment

We have been developing photochemical and radiolytic reduction methods for the separation of metallic ions from aqueous solutions under the background of high-level liquid wastes (HLLW) treatment.

The photochemical method was proposed to extract and separate PGMs (Pd, Ru) from simulated HLLW. Pd and Ru metals were extracted from an aqueous solution by photoreduction with high efficiency (reduction ratio > 90 %) in the presence of alcohols. The highly efficient extraction and separation of Pd or/and Ru metal(s) from their mixture with lanthanide (Nd) by selective photoreduction was realized. The results suggest that the photochemical method is a promising method for the efficient extraction and separation of PGMs from HLLW¹²⁾.

γ irradiation was applied to separate rhenium (which is the analogue of technetium) from an aqueous solution in the presence of isopropanol. Re(VII) was reduced by hydrated electrons (e_{aq}⁻) generated from γ -radiolysis of water, leading to the formation and precipitation of Re(0) and rhenium oxides (ReO₂ and ReO₃) nanoparticles. The reduction of Re(VII) by γ irradiation was very fast, and efficient in alkaline conditions, whose separation ratio reached 93.6 % after 2-h irradiation, and the final separation ratio was as high as 98.1 %¹³⁾.

2.6 Applications in nuclear industry

We have been studying the radiolytic effects of novel extractants as well as the solvents in spent fuel reprocessing, and modeling of water radiolysis for pressurized water reactor (PWR) and fusion reactor.

Alpha radiolysis of a nitric acid aqueous solution by a ^{238}Pu source is investigated experimentally and theoretically. A novel kinetic model for the γ -radiolysis of the nitric acid aqueous solution is established by considering the direct and indirect effects. The simulation results agree well with the experimental data. The redox reactions involving Pu cannot be neglected in the γ -radiolysis of the solution¹⁴⁾.

To predict the effects of coolant water radiolysis induced by neutron and γ radiation in the international thermonuclear experimental reactor (ITER), a new model has been developed, by modifying existing models, to evaluate the water radiolysis behaviors in different primary heat transfer systems (PHTSs) in ITER. The new model takes the circulation of coolant and the combined γ and 14 MeV neutron radiation into consideration. We recommend the injection of about 5 cc H_2 under standard temperature and pressure (STP) per kilogram of H_2O into the first wall/blanket (FW/BLKT) PHTS to both efficiently suppress water radiolysis and avoid problems caused by the addition of excessive H_2 ¹⁵⁾.

3 Prospects

In order to meet the demand for carbon reduction and carbon neutralization, an increase in the capacity of nuclear energy in China is inevitable. In fact, according to the 14th five-year plan (2021–2025) for national economic and social development and the long-range objectives through the year 2035, the total nuclear electricity capacity will be increased up to about 70 GW in 2025 and might be increased to 160 GW. At the same time, advanced nuclear systems, such as sodium-cooled fast reactor, high temperature gas-cooled, molten salt reactor, and accelerator driven subcritical reactor system, are being under research and development. And also, the applications of nuclear technology, for example, the radiotherapy of cancer using heavy-ion accelerators, are rapidly growing. There-

fore, in the foreseeable future, the needs of radiation chemistry research in China should be highly required. USTC should continue to take the responsibility to educate the students while doing basic study or application research which are financially supported by the government or industries.

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