Achieving the evolution of radiation protection materials by integrating the merits of leather

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Achieving the evolution of radiation protection materials by integrating the merits of leather

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Abstract

The widespread applications of ionizing radiations such as X/γ-rays in industrial production as well as daily life call urgently for lightweight, high-efficiency and high-strength wearable radiation protection materials. In the recent years, we have designed and fabricated the first-generation natural leather-based radiation protection material, and evolved it into the third generation by integrating the merits of leather.

The first generation of leather-based radiation protection materials focus on the loading and dispersion of the functional component, *i.e.* elements with high atomic number (Z). The structural and chemical merits of leather is preferable to reduce the particle size of high-Z elements, and therefore to enlarge the radiation performance. In this regard, an “impregnation–desolvation” strategy has been developed to introduced the high-Z elements following the process of tanning, which loaded high-Z element ions *via* coordination, hydrogen bond and electrostatic interaction. The resultant materials demonstrated good radiation protection performances stemming from the uniform dispersing capability of leather to high-Z elements.

The second generation of leather-based radiation protection materials are devoted to offset the drawback of weak absorption in certain energy region. To this end, three approaches have been carried out including the loading the bis-high-Z element salts, loading the mixture of two high-Z element oxide nanoparticles as well as applying a thin polyurethane layer containing the second kind high-Z element. All methods were able to successfully introduce the second high-Z element into leather, thus complemented the weak absorption region of the material by the synergistic effect of bis-high-Z elements, and elevated the radiation protection performance to a large extent.

The third generation of leather-based radiation protection materials are committed to further levitate the radiation protection capability without increasing the material density. To achieve this goal, advanced structural design has been carried out, and Barbican-inspired core-shell nanoparticles comprised of bis-high-Z elements are fabricated and incorporated into natural leather. By regulating the interaction between X/γ-ray photons with high-Z elements, the attenuation and absorption of photon energy have been maximized, and the radiation protection performances have been raised to a new stage.

In a word, by integrating the merits of leather, we have fabricated advanced leather-based radiation protection materials, and have achieved the evolution of radiation protection materials with light weight, high efficiency and high strength.

Keywords: natural leather, synthetic leather, regenerated leather, tanning, retanning, coating, radiation protection

1. **Introduction**

With the continuous advancement of nuclear science and technology, ionizing radiation such as X/γ-rays has found extensive applications in various fields including clean energy, medical diagnostics and therapy, aerospace exploration, as well as industrial and research circumstances. However, X/γ-rays are double-edged swords, providing convenience to daily life and industrial production while also posing risks to human health and the environment. Due to its ability to break chemical bonds and generate free radicals, prolonged exposure to X/γ-rays can lead to tissue carcinogenesis; additionally, X/γ-rays can interact with electrons, posing significant hazards to precision electronic instruments. Hence, developing novel radiation protection materials featuring excellent shielding performances, light weight and high flexibility is crucial to effectively safeguard both human health and electric instruments.

So far, several attempts have been reported to obtain lightweight X-ray shielding materials by combining synthetic polymers with metal oxide nanoparticles containing high-Z elements; however, as it is nearly unable to stably load and well disperse large amounts of high-Z components in such matrices, the prepared materials suffer from either poor X-ray shielding performance or insufficient mechanical strength. To our knowledge, simultaneously achieving excellent shielding performances and outstanding physiomechanical properties remains a critical problem till then.

Natural leather (NL), as an abundant natural polymer, has long been regarded as a kind of traditional material for manufacturing wearable products, yet its capability is far beyond this. It features a multistage supramolecular assembled structure in which the hierarchical subunits of NL are favorable to binding to metal nanoparticles due to abundant functional groups including −OH, −COOH, $-CONH_2$ and $-NH_2$, which demonstrates its potential ability to load, disperse, and stabilize high-Z element nanoparticles by coordination and other nonvalent interactions to provide great X-ray attenuation efficiency. Besides, a 3D fibrous woven network endows NL with great tensile and tear strength along with outstanding water-vapor permeability. Furthermore, the superior flexibility, tailorability and solvent resistance make NL favorable for diverse shielding garment manufacture aiming at various kinds of applications.

Herein, we carried out brief introduction to the design and manufacture of the first-generation leather-based radiation protection materials by integrating the merits of leather. Aim to supplement the weak absorption region resulted from the single high-Z element and gain enhanced radiation protection performance, the second high-Z element is introduced and the Barbican-inspired core-shell structure has been designed, respectively, achieving the evolution to the second-generation and the third-generation leather-based radiation protection materials. The iterated materials feature excellent shielding performances, light weight and high flexibility, and are perfect choice for the fabrication of advanced radiation protection clothes or garments.

2. **Material and Methods**

The materials and preparation methods are provided in our previous publications in detail, thus are not contained in this manuscript. For the first-generation leather-based radiation protection materials, please see references [1,2]; for the second-generation leather-based radiation protection materials, please see references [3–7]; for the third-generation leather-based radiation protection materials, please see reference [8].

3. **Results and Discussion**

Since X- and γ-rays mainly interact with matters with photoelectric effect, Compton scattering and pair production effect, the elements with high atomic number (Z) are regarded as functional components that could effectively reduce the energy of radiations [9]. Therefore, the design of the radiation protection materials includes the combination of the high-Z elements and leather matrix.

3.1. The first-generation leather-based radiation protection materials

According to the previous research, under the same high-Z element loading, reducing the particle size and increasing the dispersity of the functional components are beneficial for enhancing the shielding efficiency against X/γ-rays [10]. Therefore, in designing the first-generation radiation protection material, our goal was to stabilize and disperse high-Z elements into the natural leather, increasing the accessibility to the high-Z elements, thus enhancing the material's shielding capability against X/γ-rays.

To achieve such goal, the parameters influencing the attenuation coefficient (μ) in eq. 1 have been thoroughly analyzed, where h is the Plank constant, c the light speed, ρ the material density, Z the atomic number, A the mass number, E the energy of photons, and λ the wavelength of the photons [11]. The Z is fourth-power exponential to the attenuation coefficient, so increasing Z is an effective method to elevate μ. However, there is a clear upper limit to choose high-Z elements, as elements with atomic numbers greater than 83 (bismuth) have naturally radioactivity. Additionally, increasing density to enhance the attenuation coefficient is not as effective as increasing the Z, and will inevitably compromise the material's light weight and wearability, making it an unfavorable strategy. Finally, we considered constructing highly dispersed amorphous high-Z elements to enable repeated Compton scattering during the photon propagation in the material, enlarging the wavelength of the X/γ photons (λ), and gradually reducing the photons' energy (E). By this means, a cubic exponential improvement can also be achieved.

$$\mu = \frac{\rho Z^{4}}{AE^{3}} = \frac{1}{h^{3}c^{3}}\frac{\rho Z^{4}\lambda^{3}}{A} \quad (1)$$

Hence, taking the advantages of natural leather into account including hierarchical fibrous structure, abundant functional groups as well as hydrophilic yet insoluble in water, the "impregnation–desolvation" strategy (Figure 1) is developed to fabricate radiation protection materials [1]. The concept behind this strategy involves preparing highly concentrated solutions of soluble high-Z element salts and introducing them into the natural leather using an equal-volume impregnation method; subsequently, an appropriate method is employed to rapidly remove the solvent, facilitating the rapid precipitation and stabilization of high-Z element salts on the various fiber surfaces of natural leather. Due to the exceptionally high osmotic pressure of high-concentration solutions, high-Z elements can penetrate the most channels within natural leather more swiftly and efficiently.

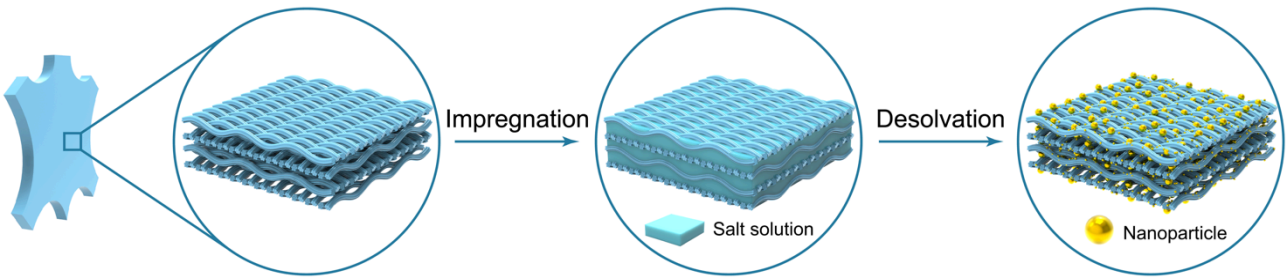


Figure 1. Schematically illustration of the "impregnation–desolvation" strategy for the fabrication of natural leather-based radiation protection materials.

The natural leather–tungsten composites (WNP_x-NL, where x is the loading amounts in g_W cm_{NL}^{-3}) were prepared by introducing sodium tungstate into the natural leather. As seen in the SEM images (Figure 2), the original collagen fibrils exhibit a corn kernel-like D-periodicity; after the introduction of the high-Z element, the D-periodicity in fibrils dissipates and the fiber diameter increases. This phenomenon serves as clear evidence that high-Z element have been successfully loaded onto the surface of the collagen fibers. Notably, there is no substantial aggregations of high-Z element particles observed at higher scales, indicating the superior stabilization and dispersion of high-Z elements enabled by the natural leather.

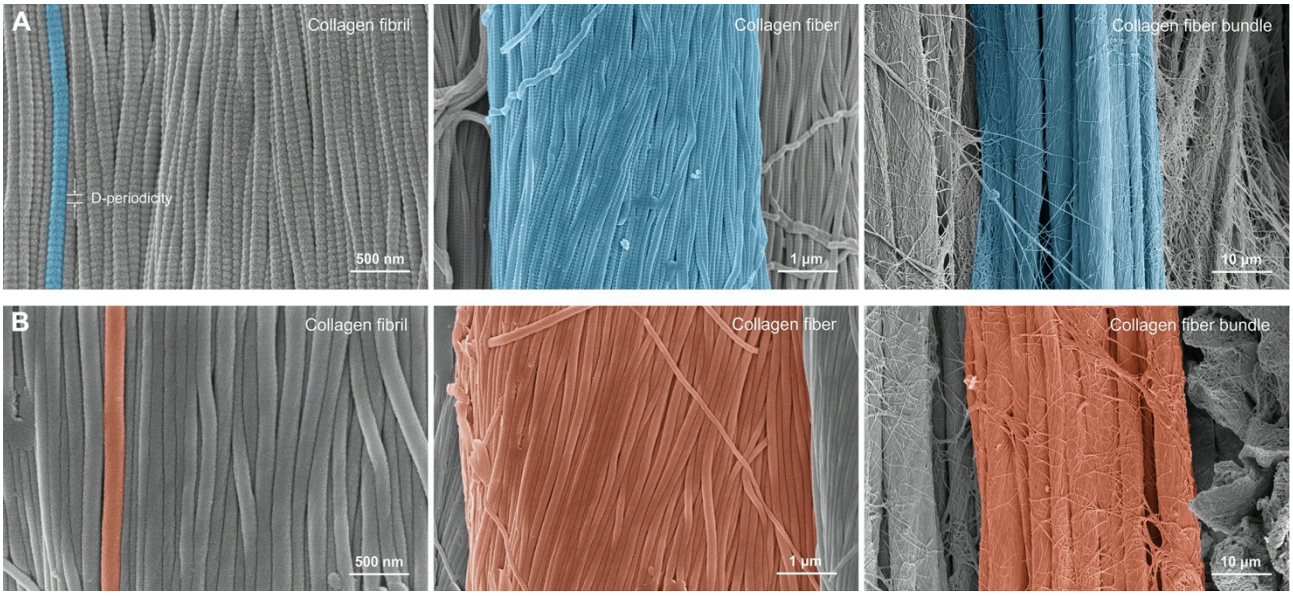


Figure 2. Morphologies of the hierarchical structures of (A) pristine natural leather and (B) natural leather–high-Z element composite.

According to the X-ray shielding performance test, when the loading density of tungsten element reaches 0.42 g cm^{-3}, the attenuation efficiency of 1.0 mm WNP-LM against 100 keV X-rays reaches 32% (Figure 3A). Furthermore, this efficiency can be increased to 50% through multiple impregnations with sodium tungstate (Figure 3B) and further elevated to 80% by increasing the material thickness to 5.0 mm (Figure 3C).

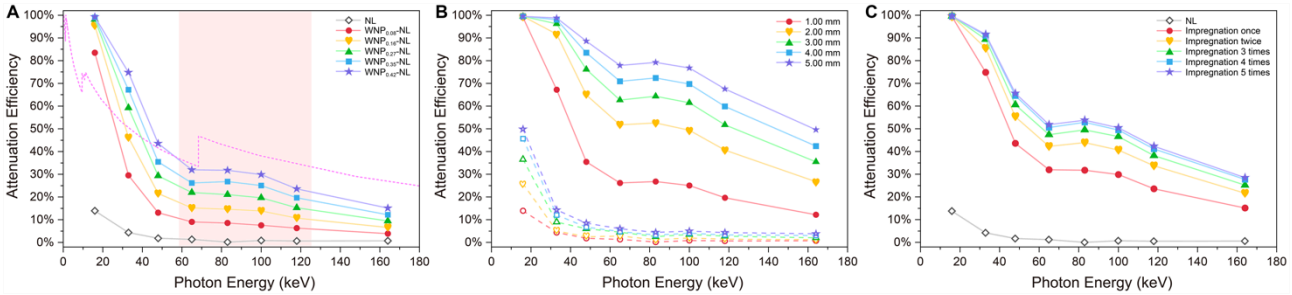


Figure 3. X-ray attenuation efficiencies of WNP-NL with different (A) tungsten loading amounts, (B) material thicknesses and (C) times of impregnation.

Furthermore, the materials prepared *via* the “impregnation–desolvation” strategy disrupt the crystalline state of the high-Z element salt during the rapid precipitation step. As a result, sodium tungstate in the material is loaded in an amorphous form (Figure 4A, B). This amorphous state effectively reduces the material’s susceptibility to X-ray directional diffraction, redirecting radiation scattering into the internal space of the material. Within the material, repeated Compton scattering and photoelectric effects occur, efficiently dissipating the energy of photons rather than scattering them outside of the material [1]. According to the measurements, the secondary radiation of $WNP_{0.42}$-NL is exceptionally low, accounting for only about 30% of a 0.25 mm lead plate (Figure 4C). This minimalized secondary radiation contributes to a reduction in environmental radiation doses, mitigating the radiation hazards to both humans and precision instruments.

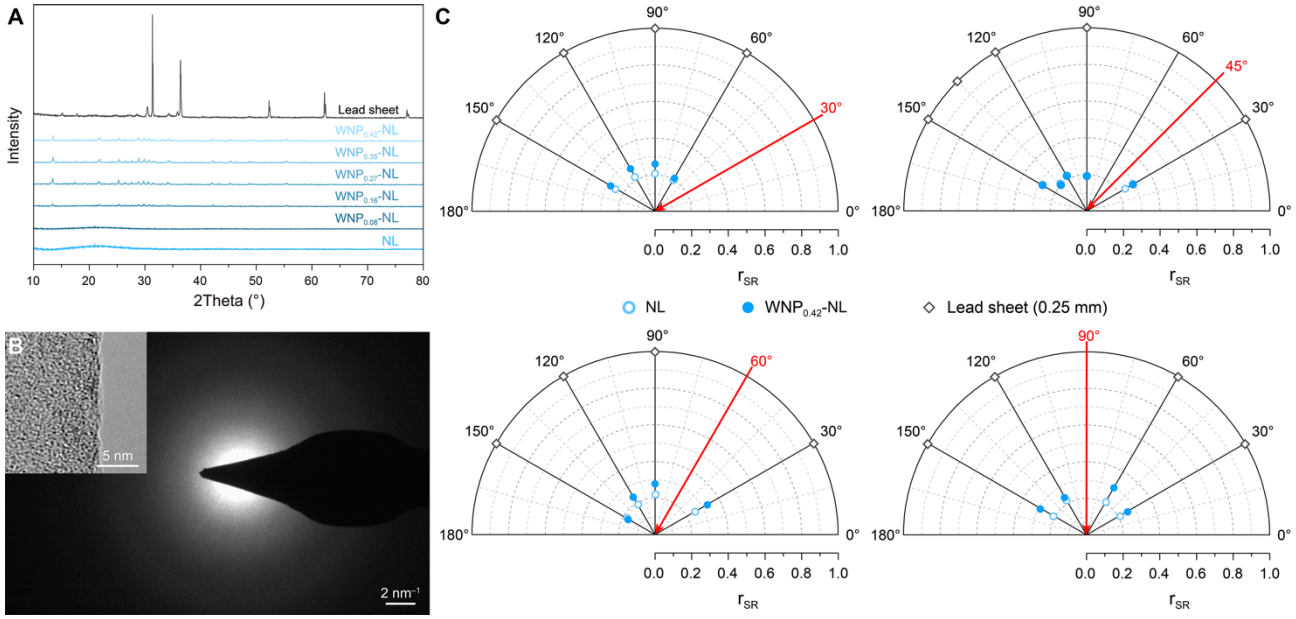


Figure 4. (A) XRD patterns of NL, WNP_x-NL and lead sheet. (B) HRTEM and SAED images of $WNP_{0.42}$-LM. (C) Secondary radiation generation ratio of NL and $WNP_{0.42}$-NL corresponding to lead sheet at different angles.

3.2. The second-generation leather-based radiation protection materials

After successfully fabricating the first-generation leather-based radiation protection materials, we aim to solve the weak absorption region stemming from the K/L-absorption edge of single high-Z element. When a single high-Z element is used as the functional component, the material exhibits a weak absorption region within a specific energy range. Consequently, it was necessary to improve the material's radiation protection performance over a wide energy range by material iteration. The strategy to achieve this goal is straightforward – introduce the second high-Z element to complement the existing weak absorption region of the first high-Z element, thus achieving high attenuation efficiency across a broad energy spectrum.

Regarding the methods for introducing the second high-Z element, three approaches have been explored. The first method is mixing oxide nanoparticles of both high-Z elements and loading them into natural leather [4]; the second measure is introducing bis-high-Z element salts containing both anionic and cationic components of high-Z elements into natural leather [3]; the third approach is applying a thin coating layer containing the second high-Z element onto the surface of the first-generation material [6,7]. As displayed by the morphological and elemental mapping characterizations (Figure 5), whether the high-Z elements are originated from soluble high-Z element salts or oxide nanoparticles, natural leather can effectively stabilize and disperse the functional components taking advantages of its hierarchical structure and abundant functional groups. Among these three methods, using bis-high-Z element salts offers the advantage of reducing the loading of non-high-Z elements, thus effectively lowering the material's overall mass while maintaining its radiation protection performances.

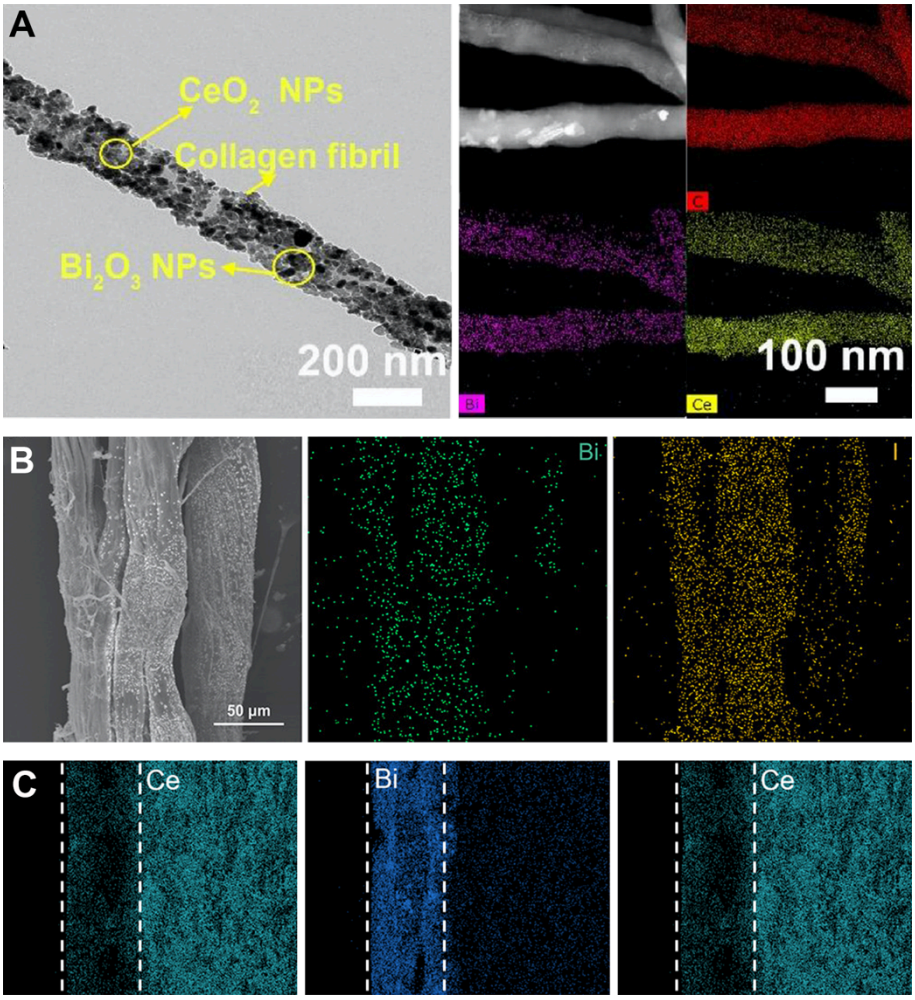


Figure 5. (A) TEM and elemental mappings of the natural leather–bismuth–cerium composites prepared by oxide nanoparticles mixing. (B) SEM and elemental mappings of the natural leather–bismuth–iodine composites prepared by loading bis-high-Z element salts. (C) Crosssectional SEM and elemental mappings of the natural leather–bismuth–cerium composites prepared by applying additional thin coating layer.

Herein, the natural leather–bismuth–iodine composite prepared by loading bis-high-Z element salts is selected as examples to demonstrate the X-ray shielding performance of the second-generation leather-based radiation protection materials. After optimizing the preparation parameters, a 1.00 mm natural leather–bismuth–iodine composite exhibits an average X-ray attenuation efficiency that is 3% higher than a 0.25 mm lead plate and 5% higher than a 0.65 mm commercial lead apron in the energy range of 16–83 keV (Figure 6A). Due to its lower density, the mass attenuation coefficient of natural leather–bismuth–iodine composite is significantly higher than that of the commercial lead apron (Figure 6B). Based on the estimations, wearing the natural leather–bismuth–iodine protective garment can extend the annual safe radiation exposure time to 18.77 hours, which represents a 32% improvement over commercial lead apron (Figure 6C). These results highlight the superior performance of the natural leather–bismuth–iodine composite in X-ray shielding applications, making it a promising choice for radiation protection, particularly when considering both high radiation protection performance and light weight.

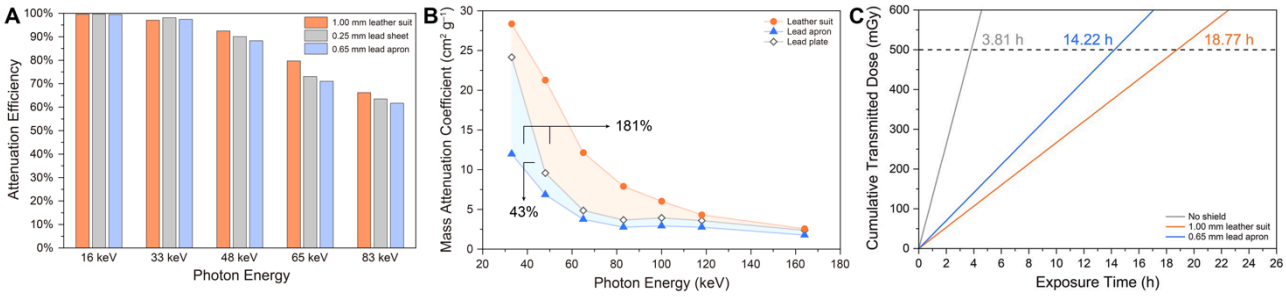


Figure 6. Comparisons of (A) X-ray attenuation efficiency, (B) mass attenuation coefficient and (C) annual safe exposure time among 1.00 mm leather–bismuth–iodine composite, 0.25 mm lead sheet and 0.65 mm 0.25 mmPb lead apron.

3.3. The third-generation leather-based radiation protection materials

The development of the second-generation leather-based radiation protection material successfully addressed the weak absorption region issue by utilizing the synergy of two high-Z elements. However, this synergy was achieved through a simple mixture of the two high-Z elements and did not fully exploit the differences in their strong absorption regions to optimize the material's radiation protection performance. Therefore, in preparing the third-generation leather-based radiation protection materials, our objective is to design the material's structure in such a way that, without increasing the material density, the interaction sequence between photons and high-Z elements be regulated more effectively. By this means, the material's radiation protection capabilities are expected to be further elevated by making better use of the strong absorption regions of the bis-high-Z elements.

But how could we approach the structural design? During our research, we came across the ingenious design of ancient Wengcheng (also called Barbican defense system in English), which was used to surround enemies in a confined space outside the city walls, maximizing the enemy damage with minimal manpower. Inspired by the concept of Barbican defense system, we intend to assemble the two high-Z elements into a core-shell nanostructure (Figure 7). This design will trap X-ray photons to undergo repeated collisions within the region composed of the core and shell elements, thereby effectively attenuate and absorb the energy of the photons [8].

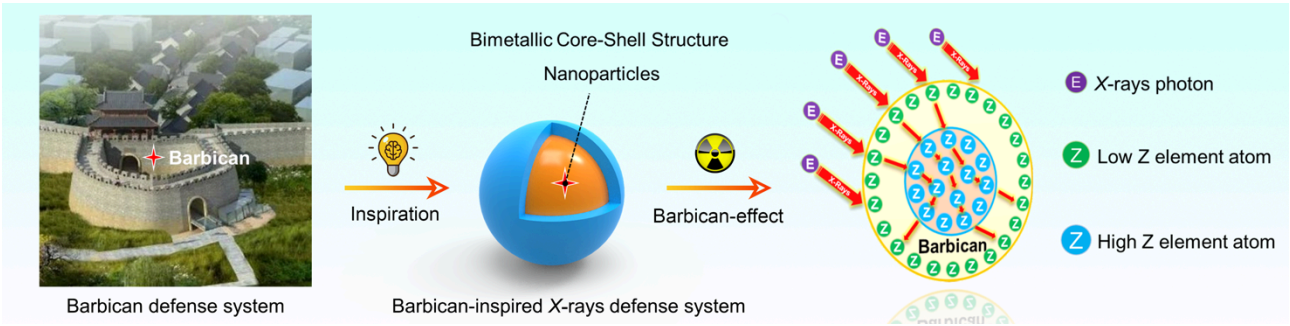


Figure 7. The structural design of Barbican-inspired X-ray shielding functional components.

The process of preparing the third-generation leather-based radiation protection materials involved the assembly of tin into a shell layer on the surface of bismuth oxide nanoparticles *via* the coordination of tannic acid and tin cations. This assembly resulted in the formation of Bi@Sn core-shell nanoparticles. Subsequently, the core-shell nanoparticles were loaded into natural leather using the affinity between tannic acid and collagen fibers. TEM images confirm the successful synthesis of Bi@Sn core-shell nanoparticles as well as the effective loading of these nanoparticles onto the surface of collagen fibers (Figure 8). This approach allows for precise control over the structure and composition of the radiation protection material, thus enables the enhanced performance in attenuating X-ray radiation.

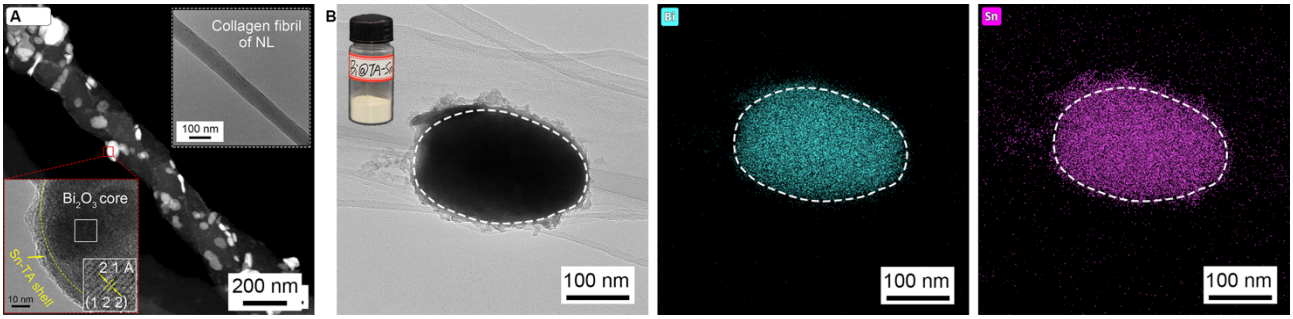


Figure 8. (A) TEM images of the collagen fibril after loaded Bi@Sn nanoparticles. (B) The corresponding TEM morphology and elemental mappings of the Bi@Sn nanoparticles.

Afterwards, the radiation protection performance of natural leather–Bi@Sn core-shell nanoparticles composite (Bi@Sn-NL) was carried out, with sample loaded direct mixture of bismuth and tin into natural leather (Bi+Sn-NL) as a control reference. Compared to Bi+Sn-NL, structuring bismuth and tin into a core-shell configuration significantly improves the material's attenuation efficiency (Figure 9A). It is worth mentioning that this enhancement was gradually pronounced at higher photon energies. Additionally, due to the amorphous nature of tin in the shell layer, this strategy also reduces the secondary radiation generated from the material (Figure 9B).

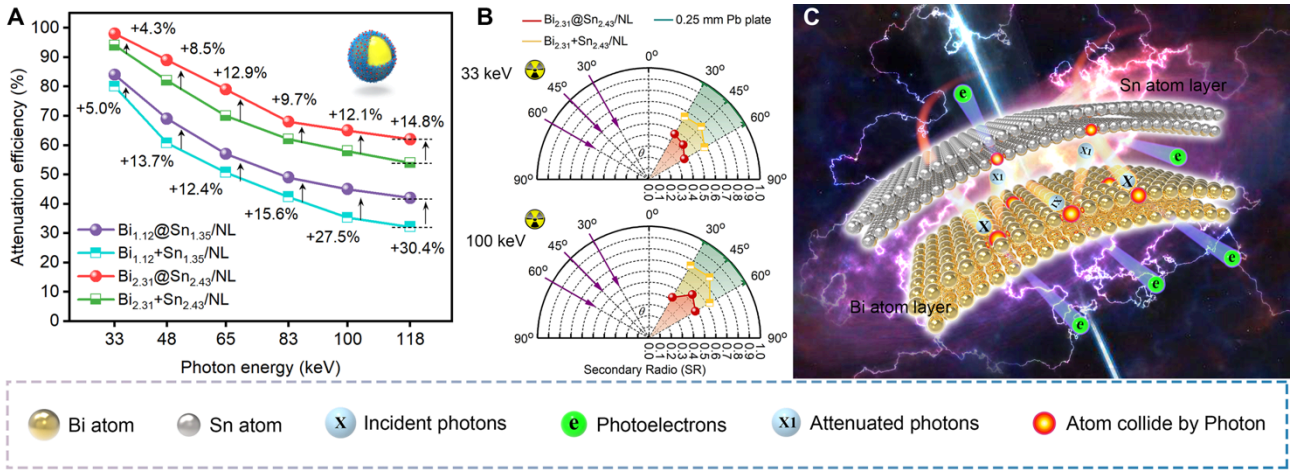


Figure 9. (A) Comparison of attenuation efficiency of Bi@Sn-NL and Bi+Sn-NL. (B) Comparison of secondary radiation ration of Bi@Sn-NL and Bi+Sn-NL. (C) Illustration of the proposed Wengcheng effect.

When the loading amounts of bismuth and tin are held constant, the Bi@Sn core-shell structure features lower radiation dose penetrating through the material and lower secondary radiation dose scattered to the front of the material, as compared to Bi+Sn-NL. This raises a provoking question of where the remaining energy went. According to our presumption, the Bi@Sn core-shell structure could effectively capture photons, trap them within the structure and induce multiple attenuations and absorptions, thus efficiently dissipating radiation energy (Figure 9C). This phenomenon is named the "Wengcheng effect".

Thanks to the Wengcheng effect, we successfully enhanced the radiation protection performance of the material without increasing its density through structural design. This achievement marks the development of the third-generation leather-based radiation protection materials, revealing the innovation and effectiveness of this approach in radiation protection manufacture.

4. **Conclusion**

In a word, by integrating the merits of hierarchical structure and abundant functional groups from leather, we have fabricated advanced leather-based radiation protection materials by stabilizing and dispersing high-Z elements within the substrate. This led to the development of the first-generation leather-based radiation protection materials. Additionally, by introducing a second high-Z element to address the weak absorption region in specific energy ranges, the second-generation leather-based radiation protection materials have been successfully iterated. Building upon these advancements, we designed a core-shell structure with two high-Z elements, utilizing the Wengcheng effect which features gradient attenuation and absorption to the radiation energy. This design allows us to further enhance the radiation protection performance of the material without increasing its density, resulting in the evolution to the third generation of leather-based radiation protection materials. These achievements underscore the versatility and superiority of natural leather as a substrate for fabricating radiation protection materials and demonstrate the potential for innovation in the field of radiation protection, catering to a wide range of applications in nuclear plants, radiation therapy and beyond.

5. **Acknowledgements**

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6. **References**

[1] Y. Wang, R. Zhong, Q. Li, J. Liao, N. Liu, N.S. Joshi, B. Shi, X. Liao, J. Guo, Lightweight and Wearable X-Ray Shielding Material with Biological Structure for Low Secondary Radiation and Metabolic Saving Performance, Adv. Mater. Technol. 5 (2020) 2000240. https://doi.org/10.1002/admt.202000240.

[2] Q. Li, P. Ding, Y. Wang, X. Liao, B. Shi, Preparation of a Rare Earth Natural Leather X-ray Protection Material and Its Properties, Acta Phys.-Chim. Sin. 37 (2021) 2001046. https://doi.org/10.3866/PKU.WHXB202001046.

[3] Y. Wang, P. Ding, H. Xu, Q. Li, J. Guo, X. Liao, B. Shi, Advanced X-ray Shielding Materials Enabled by the Coordination of Well-Dispersed High Atomic Number Elements in Natural Leather, ACS Appl. Mater. Interfaces. 12 (2020) 19916–19926. https://doi.org/10.1021/acsami.0c01663.

[4] Q. Li, Y. Wang, X. Xiao, R. Zhong, J. Liao, J. Guo, X. Liao, B. Shi, Research on X-ray shielding performance of wearable Bi/Ce-natural leather composite materials, J. Hazard. Mater. 398 (2020) 122943. https://doi.org/10.1016/j.jhazmat.2020.122943.

[5] Q. Li, R. Zhong, X. Xiao, J. Liao, X. Liao, B. Shi, Lightweight and Flexible Bi@Bi-La Natural Leather Composites with Superb X-ray Radiation Shielding Performance and Low Secondary Radiation, ACS Appl. Mater. Interfaces. 12 (2020) 54117–54126. https://doi.org/10.1021/acsami.0c17008.

[6] Y. Shen, J. Zhou, Z. Han, H. Li, L. Yan, X. Liao, B. Shi, Natural leather based gamma-ray shielding materials enabled by the coordination of well-dispersed Bi^{3+}/Ba^{2+} ions and RE_2O_3 coating, J. Leather Sci. Eng. 4 (2022) 15. https://doi.org/10.1186/s42825-022-00090-7.

[7] L. Yan, J. Zhou, H. Li, R. Zhong, J. Zhuang, X. Xu, Y. Wang, X. Liao, B. Shi, Wearable synthetic leather-based high-performance X-ray shielding materials enabled by the plant polyphenol- and hierarchical structure-facilitated dispersion, Collagen Leather. 5 (2023) 12. https://doi.org/10.1186/s42825-023-00119-5.

[8] H. Li, J. Zhou, L. Yan, R. Zhong, Y. Wang, X. Liao, B. Shi, Barbican-inspired bimetallic core–shell nanoparticles for fabricating natural leather-based radiation protective materials with enhanced X-ray shielding capability, Chem. Eng. J. 466 (2023) 143355. https://doi.org/10.1016/j.cej.2023.143355.

[9] N. Lee, S.H. Choi, T. Hyeon, Nano-Sized CT Contrast Agents, Adv. Mater. 25 (2013) 2641–2660. https://doi.org/10.1002/adma.201300081.

[10] C. Xu, G.A. Tung, S. Sun, Size and Concentration Effect of Gold Nanoparticles on X-ray Attenuation As Measured on Computed Tomography, Chem. Mater. 20 (2008) 4167–4169. https://doi.org/10.1021/cm8008418.

[11] H. Lusic, M.W. Grinstaff, X-ray-Computed Tomography Contrast Agents, Chem. Rev. 113 (2013) 1641–1666. https://doi.org/10.1021/cr200358s.