



Carbon dots and polyurethane composite for photo-induced elimination of uranium under air atmosphere

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ABSTRACT

Uranium is the main fuel of nuclear power and elimination uranium from nuclear wastewater is significant both in environmental protection and fuel recycle. Here we report for the first time the synthesis of carbon dots/polyurethane (CDs/PU) composite materials for the photoinduced elimination of uranium from water. Irradiated with visible light, CDs/PU could eliminate uranium efficiently with the generation of $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ as solid products in air. The further investigated mechanism showed that the addition of CDs/PU could produce more H_2O_2 under visible light, which reacted with uranyl ions to form $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. Importantly, the sponge-like CDs/PU could be easily removed from water with high reusability as the elimination efficiency remained above 95% after 5 cycles. CDs/PU also displayed good selectivity in the presence of other metal ions. Our work affords exciting strategies for developing photocatalysts and eliminating uranium from water.

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Nuclear power has become an irreplaceable technology with low greenhouse gas emission and high efficiency. It plays a significant role in overcoming the energy shortage and climate change issues. During the nuclear fuel cycle, waste water containing uranium has been regarded as a hazardous contaminant with both radioactivity and chemical toxicity. It is highly desirable and important to eliminate uranium from water for environmental protection and energy supply. Various advanced methods have been studied for uranium elimination and adsorption is considered as the efficient method in uranium capture [1]. While, the limited binding sites and poor selectivity of many adsorbents impeded their further application.

Recently, researchers are interested in the photocatalyst assisted method to extract uranium because it could generate less soluble uranium species instead of soluble U(VI) in water to realize the solidification and elimination of uranium [2,3]. Besides, the photocatalytic method could break the adsorption equilibrium to enhance the elimination capacity [4]. Researchers have focused on develop-

ing novel photocatalysts for uranium extraction, including $g\text{-C}_3\text{N}_4$ [5–8], TiO_2 [9,10], functionalized graphene [11,12], MOFs [13–15], COFs [16–18]. While, the applications of many photocatalysts are still limited for the tedious synthesis process, inconvenient separation with water, poor selectivity and reusability. Moreover, most of them could only work with the protection of inert gas, because in the presence of oxygen, the reduced product such as UO_2 is unstable and the removal performance decrease dramatically [19–21]. For practical application, it is required to develop photocatalysts that could work under air atmosphere, and new photoinduced elimination mechanism should be studied as well.

Carbon dots (CDs) are a novel kind of carbon material with abundant characteristics such as low cost, easy preparation, high photo-stability and have intriguingly aroused much attention of researchers in various fields [22–26]. Besides, the unique optical and electronic properties make CDs in favorable for the development of photocatalysts, which have been applied in the degradation of organic pollutants [27], extraction of heavy metal ions [28], hydrogen evolution [29] and other areas [30–33]. While few studies have applied CDs for the photoinduced elimination of uranium from water.

As the small size and hydrophilic property of CDs make them hard to be separated from water, CDs should combine with other solid materials. In this work, we have decorated CDs into sponge

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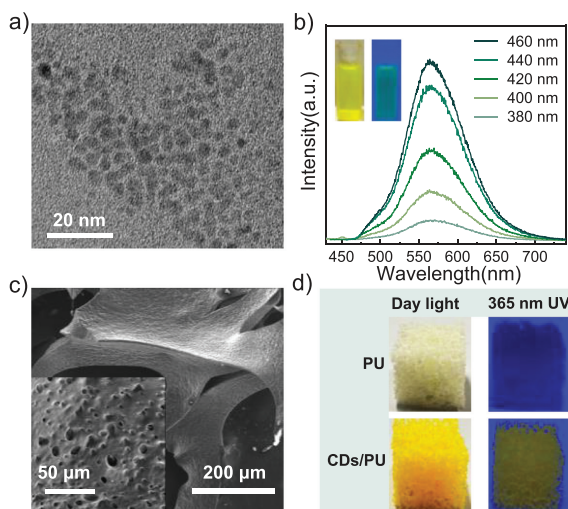


Fig. 1. (a) TEM image of CDs. (b) Fluorescent spectra of CDs and insert was the picture of CDs under day light and 365 nm UV light. (c) SEM image of polyurethane. (d) Picture of PU and CDs/PU under day light and 365 nm UV light.

like polyurethane (PU) for the photocatalytic elimination of uranium from water. With swell method [34], the CDs/PU composite material could be prepared easily with the yellow fluorescent property of CDs. It could eliminate uranium from water efficiently when irradiated with visible light under air atmosphere and the solid products of $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ could be obtained. The elimination mechanism was further investigated with various designed experiments. The reusability and selectivity of CDs/PU were also measured to fulfill the real application environment. This work applies CDs in the photoinduced elimination of uranium for the first time and provides a novel mechanism for uranium extraction under air atmosphere.

CDs were synthesized by solvothermal method with neutral red as raw materials [35]. After centrifugal washing, the upper clear CDs solution was collected. The TEM image in Fig. 1a displayed that CDs were well dispersed with a narrow size distribution and the average size was about 3 nm (Fig. S1 in Supporting information). CDs could emit yellow fluorescence under 365 nm UV light irradiation as shown in the picture insert in Fig. 1b. The UV-vis adsorption property of CDs was presented in Fig. S2 (Supporting information). CDs solution possessed an obvious adsorption band at 400–500 nm and the fluorescent spectra in Fig. 1b also displayed the strongest excitation wavelength was at about 460 nm. Besides, CDs had an excited-independent property and the maximum emission at about 520 nm, which confirmed the successfully preparation of the yellow fluorescent CDs.

Due to the small size of CDs, they suffer from separation difficulties when applied alone for application and thus need to be combined with other solid-phase materials to synthesize composite materials. Polyurethane sponge is a kind of commercialized material with low cost and porous structure, and the hydrophilic PU has been applied in wastewater treatment areas. Fig. 1c presented the surface morphology of PU. The porous structure enhanced its surface area and make it easy to be functionalized. After immersed in CDs solution, CDs could be easily decorated on PU with the swelling method. As listed in Fig. 1d, the cream-colored PU showed no fluorescence under 365 nm UV light. After functionalized with CDs, PU changed to golden yellow under day light and it also emit yellow fluorescence under UV light, indicating that CDs have been decorated on PU to form the CDs/PU composite material.

In our previous work [36], we found uranium itself possessed good photocatalytic property and it could degrade methanol with H-abstraction reaction under irradiation to generate H_2O_2 in air

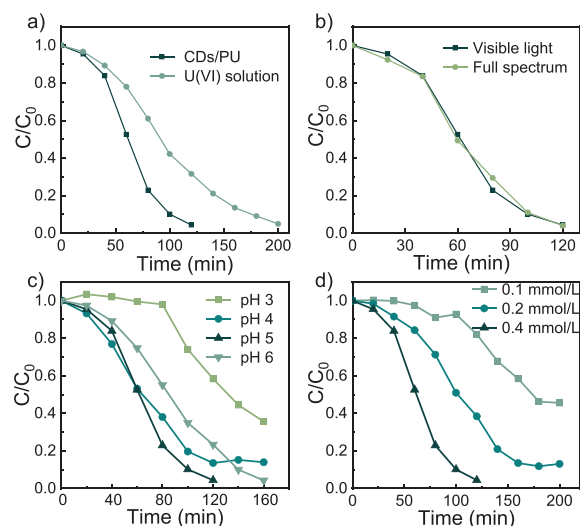


Fig. 2. The photocatalytic elimination property of CDs/PU (a) compared with pure uranium solution, (b) irradiated with visible light and full spectrum light after reached to adsorption equilibrium, (c) in uranium solution with different pH and (d) different concentration.

condition. Abundant H_2O_2 could combine with uranium to form solid products to realize the solidification and separation of uranium. Then the photocatalytic experiments of CDs/PU compared with pure uranium solution was studied under visible light first. As shown in Fig. 2a, pure uranium solution could also accomplish the elimination of uranium in solution. While, the addition of CDs/PU accelerated the uranium solidification process. More than 97% uranium could be eliminated in 120 min with CDs/PU compared with 200 min of pure uranium solution. The elimination rate of uranium was enhanced from 0.015 min^{-1} to 0.027 min^{-1} as shown in Fig. S3 (Supporting information), indicating CDs/PU played a vital role in the solidification of uranium. Then more batch experiments were carried out to optimize the photoreaction condition of CDs/PU. As tested in Fig. 2b and Fig. S4 (Supporting information), we found both the visible light and the simulated sunlight presented the same elimination tendency of uranium, which could attribute to the emission wavelength of CDs. CDs was mainly excited by 460 nm and emitted mainly at 520 nm, which made the light at UV band invalid in the photoreaction of uranium. Then the pH and concentration of uranium solution was optimized as shown in Figs. 2c and d, respectively. The elimination rate enhanced as the pH increased, which might because more hydrogen ions competed with uranium on the surface of CDs at lower pH. And the existing form of uranium at different pH may also affect the elimination rate. As reported in our previous study, the hydrolytic uranium ions were more easily to form solid products in the photocatalytic process. Besides, the fluorescent property of uranium itself may be quenched at lower pH, resulting in the decreased activity of uranium in the whole photocatalytic process. And a faster elimination rate was observed at higher concentration of uranium, which was reasonable because the enhanced concentration of the reactant was benefit for the generation of the products.

The photocatalytic product of CDs/PU was gathered and its structure was verified with various methods in Fig. 3. The morphology of the photocatalyzed products on CDs/PU were first characterized with SEM in Fig. 3a. The micrometer-sized particles fully covered on the surface of CDs/PU composites and they appeared to be identical and short rod shapes. Some of the particles fell off the surface of CDs/PU composite and they were collected and measured with XRD, Raman and XPS to figure out the composition and structure. As displayed in Fig. 3b, the crystallized products

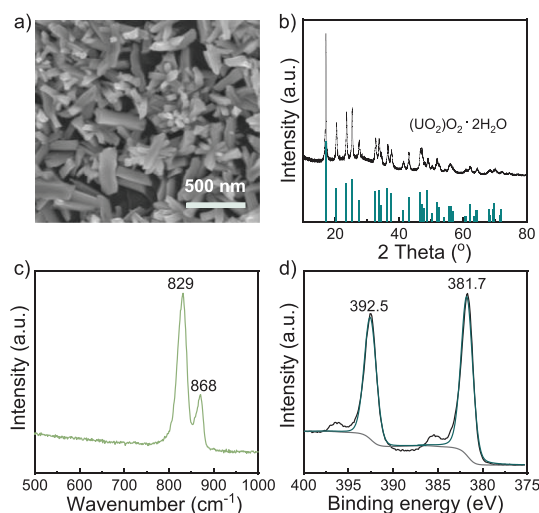


Fig. 3. (a) SEM image, (b) XRD pattern, (c) Raman spectra and (d) XPS spectra of uranium solid products.

were assigned as metastudtite ($(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, JCPDS 01-081-9033) [37], which was one of the existing uranium peroxide species in nature. The Raman spectroscopy of the product in Fig. 3c showed two characteristic peaks at 829 and 868 cm^{-1} , which indicated the product was uranium peroxide and it was consistent with the XRD results. Moreover, the XPS spectra of the product was measured and the U 1s spectra was presented in Fig. 3d. Two characteristic peaks at 392.5 and 381.7 eV were identified as the U $4f_{5/2}$ and U $4f_{7/2}$ of U(VI), respectively. And no peaks of U(IV) were observed, confirming the valence state of uranium in the product was mainly U(VI) and $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ was generated during the photocatalytic process with CDs/PU composites.

Combined with the characterization results and our previous study [36], the possible mechanism was presented in Fig. 4a. Uranium was first stimulated to excited state ($^*\text{[UO}_2^{2+}]$) with high oxidation activity and then abstracted H atom on methanol. Fig. 4b showed that without methanol the concentration of uranium remained the same as initial, verifying the necessity of methanol. And then H_2O_2 was generated under air atmosphere and reacted with uranium to form $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$, thus to eliminate uranium

ions from water. The existing of CDs/PU composites may enhance the yield of H_2O_2 and the titration experiment with KMnO_4 was carried out to quantify the generation of H_2O_2 (Fig. 4c). Because of the photochemical property of uranium itself, H_2O_2 was produced during the photoreaction of pure uranium solution and more H_2O_2 was obtained after the addition of CDs/PU composites, which confirmed the function of the composites and it also explained the higher elimination rate of CDs/PU compared with pure uranium solution in Fig. 2a. As the photo-induced extraction strategy, especially that could work under air atmosphere has great application potential in uranium extraction from seawater, furthermore, the influence of chloride ions in the photocatalytic process was investigated in Figs. 4d and e. According to our previous work, chloride ion might coordinate with uranyl to quench the excited state of $^*\text{[UO}_2^{2+}]$ and then decrease the elimination rate of uranium. The experiment results in Fig. 4d and Fig. S5 (Supporting information) verified this phenomenon. The elimination rate declined along with the increased concentration of NaCl, which was agreed well with our previous study [9]. Then uranyl acetate was employed to substitute uranyl nitrate because CH_3COO^- owned a stronger complexation affinity than Cl^- and the influence of Cl^- on elimination process was weakened in Fig. 4e. Besides, the elimination rate was slightly increased after changed uranyl nitrate to uranyl acetate in Fig. S6 (Supporting information). This could be attributed to the acetate ions in solution, which may act the same role with methanol.

Recyclability and selectivity are important criterion of photocatalyst and have been conducted in this study. Uranium was first gathered on the surface of CDs/PU composites and then reacted with H_2O_2 generated from the photocatalytic process to form $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. The solid crystals grew to bigger particles and then fell off the surface of CDs/PU to the solution and the active sites on CDs/PU were exposed for the following reaction. This kind of self-regeneration of the active sites provided CDs/PU a good recyclability in Fig. 5a. After each photocatalytic cycle, CDs/PU was taken out and immersed into 0.1 mol/L HNO_3 solution to regenerate the active sites. The desorption rate was higher than 90% and the elimination efficiency remained higher than 95% after 5 cycles. Besides, the sponge like polyurethane made the solid-liquid separation quite convenient and one can take out the CDs/PU from the solution and then it could be used in the next photoreaction. Finally, the selectivity of CDs/PU towards uranium was tested in the

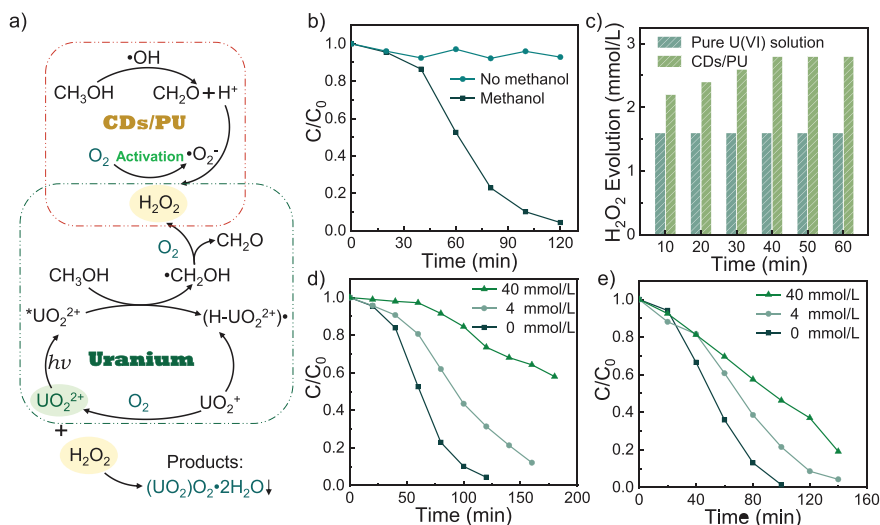


Fig. 4. (a) The illustration of the possible mechanism for photocatalytic elimination of uranium with CDs/PU. (b) The photocatalytic elimination property of uranium with and without methanol. (c) The H_2O_2 evolution of CDs/PU and pure uranium solution under visible light irradiation. The photocatalytic elimination property of CDs/PU in different concentration of NaCl: (d) uranyl nitrate and (e) uranyl acetate.

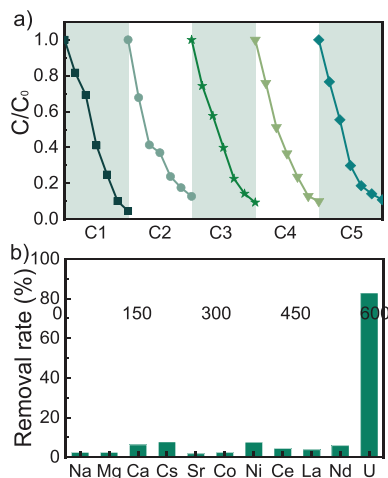


Fig. 5. (a) The recyclability and the (b) selectivity tests of CDs/PU in the photocatalytic elimination of uranium.

presence of other metal ions. As presented in Fig. 5b, more than 80% uranium and less than 10% other metal ions could be eliminated during the photocatalytic process, which could be attributed to the unique photocatalytic property and chemical reaction of uranium. And the high selectivity of CDs/PU towards uranium make it a good photocatalyst in real application area.

In conclusion, we have synthesized CDs with yellow fluorescent and decorated them onto sponge like polyurethane with swell method. The as prepared CDs/PU composite material could eliminate uranium from solution to form solid products and it presented higher elimination rate than pure uranium solution. The higher pH and higher concentration of uranium could enhance the photocatalytic process. The sediments were characterized with various methods and the results showed they were $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ with short rod-like shapes. The CDs/PU could generate more H_2O_2 in air atmosphere to react with uranium to form $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ under visible light irradiation. The CDs/PU could be easily separated from the solution due to the sponge shapes and it still possessed high photocatalytic activity after used for five times, appearing high recyclability. In the presence of other metal ions, over 80% uranium could be eliminated from the solution. The good recyclability and high selectivity make CDs/PU a good photocatalyst in uranium elimination in water.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccllet.2023.108146.

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