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# Selective electrochemical removal of cesium ion based on nickel hexacyanoferrate/reduced graphene oxide hybrids

Xiaolan Jin[a], Lu Huang[a], Shuai Yu[a], Mengna Ye[a], Junhua Yuan[a,b,*], Jianfeng Shen[c,*], Keming Fang[a], Xuexiang Weng[a]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Life Sciences and Chemistry, College of Geography and Environmental Science, Zhejiang Normal University, Jinhua, Zhejiang 321004, China
[b] School of Pharmacy, Hubei University of Science and Technology, Xianning, Hubei 437100, China
[c] Center of Special Materials and Technology, Fudan University, Shanghai 200433, China

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ABSTRACT

A co-precipitation strategy is developed to prepare the reduced graphene oxides (RGOs) supported nickel hexacyanoferrate (NiHCF) nanoparticles. The NiHCF nanoparticles were uniformly deposited on RGOs with a size distribution of 60 nm. The NiHCF/RGO hybrids exhibit a reversible current response to alkali ion, and the ion exchange can be controlled by the applied potentials. As an electrochemical-switched ion exchange (ESIX), NiHCF/RGO hybrids show a high selectivity toward $Cs^+$ ion in the presence of $K^+$ ion. Their $Cs^+$ uptake capacity ($Q_e$) can reach up to be 320 $mg\,g^{-1}$ with a $Cs^+$ distribution coefficient ($K_d$) of 625 $L\,g^{-1}$ in 1 $mol\,L^{-1}$ KCl solution. The Cs removal performance of NiHCF/RGO hybrids is superior to that of the pure NiHCFs ($Q_e$ 235 $mg\,g^{-1}$, 376 $L\,g^{-1}$), comparative to or better than those of state-of-the-art metal HCF sorbents or ESIXs reported recently. In addition, NiHCF/RGO hybrids show a high cycling stability with 92% ion-exchange capability after 160 cycles of $Cs^+$ separation.

## 1. Introduction

Nuclear power, a carbon-free alternatives to fossil fuels, is already in widespread use [1]. As an important source, nuclear power has account for 13% of the world's energy in 2012 [2]. However, the operation of nuclear plant will produce a substantial waste with high levels of radioactivity [3]. Worse still, the release of these massive radioisotopes in the accident of nuclear leakage as a result from an earthquake or human error will cause ecological disaster [4,5]. A tremendous amount of radioactivity was discharged because of the damage to cooling systems of nuclear reactors in the Fukushima No. 1 nuclear power plant in March 2011. Fukushima and its adjacent prefectures were contaminated with fission products from the accident [6–8].

Among these radioisotopes, $^{137}Cs$ is a dominant radioactive component in waste, and it poses a significant hazard to human health as a strong γ-ray emitter with a long half-life (30.4 years) [9]. In addition, $^{137}Cs$ salt is highly soluble in water, leading to a fast migration through groundwater to the biosphere [10,11]. In addition, similar to K and Na, $^{137}Cs$ is easily assimilated by terrestrial and aquatic organisms. It will be accumulated inside body tissue and organ through food chains [12]. Moreover, $^{137}Cs$ can travel in airborne dust and contaminate food and water supplies. Thyroid cancer is one of the worst case scenarios under exposure to $^{137}Cs$ in high dose [13]. Therefore, given the risk of nuclear contamination, radioactive cesium should be removed efficiently and selectively from nuclear waste for public health and environmental preservation.

Recently, many strategies have been used to remove $^{137}Cs$ from nuclear waste effluent [14], such as micro-filtration [15], solvent extraction [16], adsorption/ion-exchange [17–19], membrane processes [20] and coagulation/sedimentation [21]. Among those available technologies, adsorbents/ion-exchangers, such as titanates [22], polyoxometalates [23], and mesoporous silicate [24], are most used in $^{137}Cs^+$ separation in the treatment of nuclear water due to its low cost [25], thermal stability and good compatibility [26]. Unfortunately, a large amount of secondary waste will be generated in the process of adsorption/ion-exchange. In order to minimize the secondary waste, an electrochemical-switched ion exchange (ESIX) was proposed to separate $^{137}Cs$ from the nuclear waste effluent with high selectivity and efficiency [26].

Over the past decade, metal hexacyanoferrate (MHCF) has been

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* Corresponding authors at: Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Life Sciences and Chemistry, College of Geography and Environmental Science, Zhejiang Normal University, Jinhua, Zhejiang 321004, China (J. Yuan).

*E-mail addresses:* jhyuan@zjnu.cn (J. Yuan), jfshen@fudan.edu.cn (J. Shen).

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emerged as the electrochemical-switched ion exchanger (ESIXr) in the radioactive Cs removal [27,28]. The open zeolite-type cubic network of MHCF offers a large volume pore to accommodate alkali ion. But not all hydrated alkali ion can diffuse into the limited channel of MHCFs, such as $Li^+$ and $Na^+$, will get blocked, leading to a high selectivity for Cs separation [28,29]. In addition, ion exchange is concurrent with electron transfer of iron center in MHCFs to maintain charge neutrality [10,26,29,30].

$$A_xM_y[Fe^{III}(CN)_6]_z + zA^+ + ze = A_{x+z}M_y[Fe^{II}(CN)_6]_z$$

where A is alkali ion, such as $Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$, M is transition metal, such as Ni, Cu, Zn and Co.

Lilga et al first theorized ESIX in Cs separation based on NiHCF [26]. Chen et al had developed ESIX technology in selective removal of $Cs^+$ from waste water with CuHCF film [10,29]. However, pure MHCF is not an efficient in ESIX for Cs removal due to its low conductivity, poor stability and limited surface area. A feasible solution is to introduce carbon support in MHCF ESIX. The carbon support can act as nanocollector to accelerate electron transfer. In addition, the advantage of introducing carbon support can better the dispersion of MHCF nanoparticles and reduce the detachment of MHCF nanoparticles from the electrode [31,32].

Among carbon materials, graphene is used widely as an atomic carbon support because of its low cost, excellent conductivity and huge surface area [33,34]. In our previous work, NiHCF nanocubes can be uniformly deposited on the reduced graphene oxide (RGO) with poly (diallyldimethylammonium chloride) (PDDA). NiHCF/PDDA/RGO hybrids show two redox couplets, corresponding to NiHCF and the complex between PDDA and $[Fe(CN)_6]^{3-}$ ion, respectively [33]. Herein, we develop a facile in-situ co-precipitation strategy to synthesize NiHCF/RGO hybrids using polyvinylpyrrolidone (PVP). The NiHCF nanoparticles were uniformly dispersed on the reduced graphene oxides (RGOs) with a size of about 60 nm. Differently, NiHCF/RGO show only one redox couplet associated with NiHCF, and PVP did not affect ion exchange within NiHCF. Moreover, NiHCF/RGO hybrids are highly selective in response to $Cs^+$ ion, and exhibit high Cs removal efficiency in the interference of $K^+$ ion.

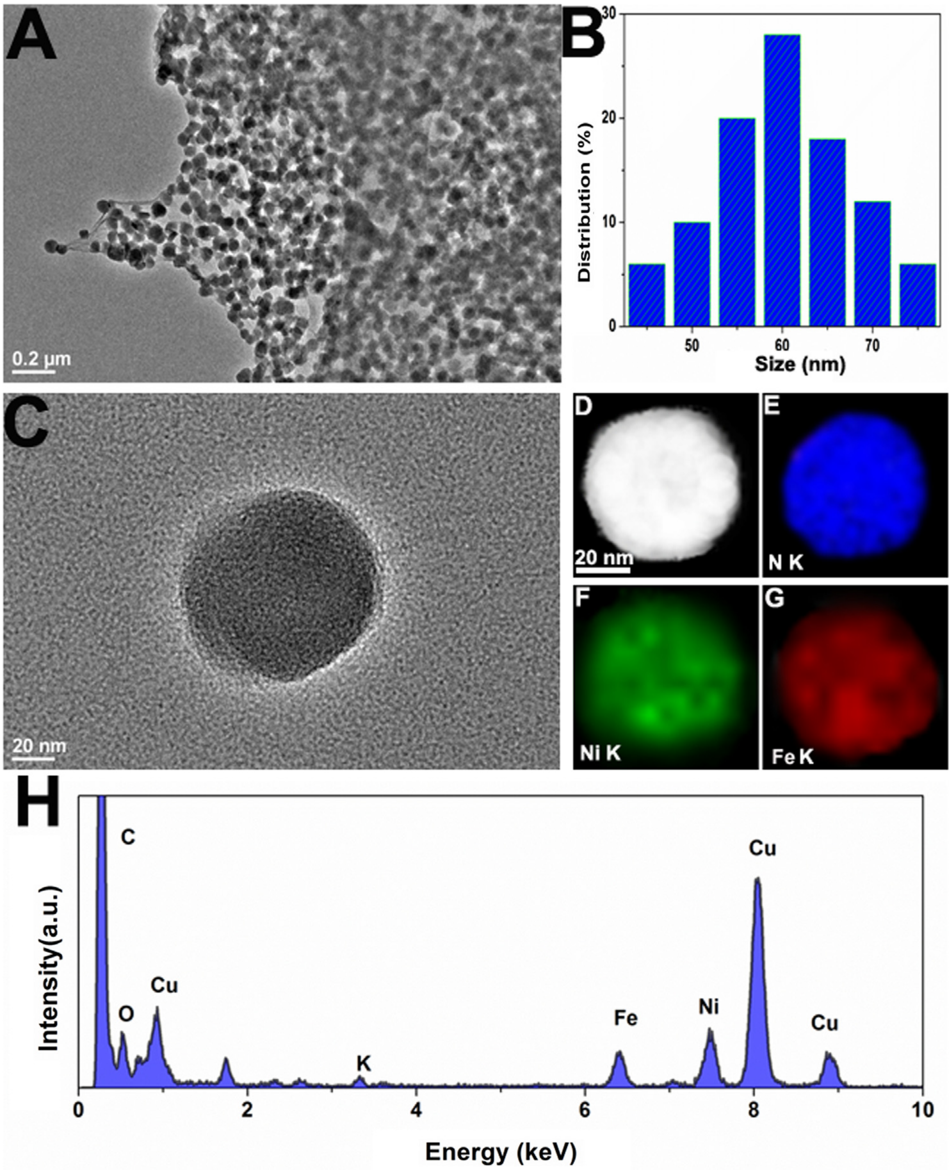

**Fig. 1.** (A) TEM images of NiHCF/RGO hybrids, scale 0.2 μm. (B) The size distribution of NiHCF nanoparticles on RGOs. (C) The high revolution of TEM images of a single NiHCF nanoparticles, scale 20 nm. (D, E, F and G) HAADF-STEM images of a single NiHCF nanoparticles. (H) The EDS curve in area-scanning mode.