

Supporting Information

Bio-Inspired Preparation of Clay-Hexacyanoferrate Composite Hydrogels as Super Adsorbents for Cs⁺

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1. Adsorbent Fabrication

Table S1. Fabrication sequence for the different adsorbents tested.

Sample	1 st step		2 nd step
	1 st addition	2 nd addition	Crosslinker
DHG(Cu)	KHCF	CuSO ₄	Cu ²⁺
DHG(Cu-eq)	KHCF	CuSO ₄	/
DHG(Fe)	KHCF	FeCl ₃	
DHG(step-Cu)	CuSO ₄	KHCF	Cu ²⁺
DHG(step-Fe)	CuSO ₄	KHCF	Fe ³⁺
DG(Cu)	/	CuSO ₄	Cu ²⁺

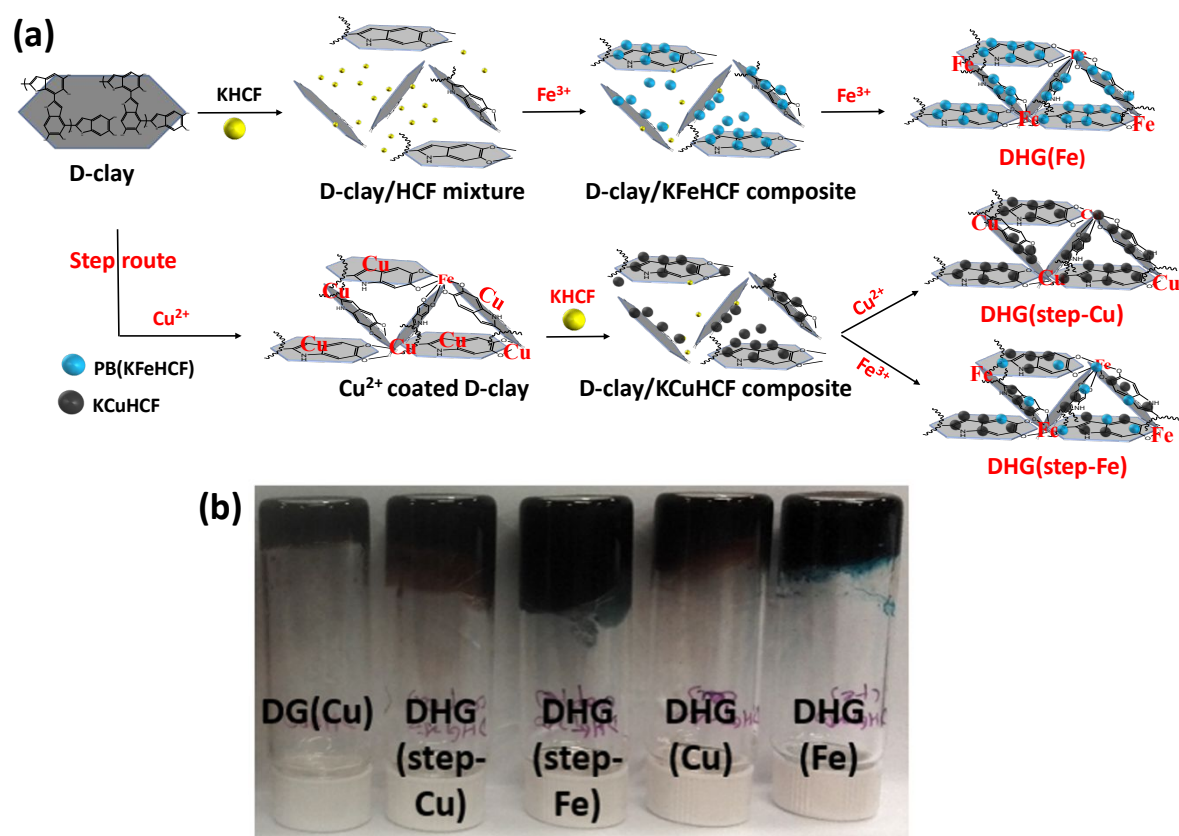


Figure S1. (a) Schematic of the fabrication routes to prepare DHG(step-Cu), DHG(step-Fe) and DHG(Fe). Route to prepare DHG(Cu) is shown in the manuscript (Fig. 1). (b) Images of samples (from left to right): DG(Cu), DHG(step-Cu), DHG(step-Fe), DHG(Cu) and DHG(Fe).

To fabricate the adsorbents, several routes were explored as shown in Table S1. DHG(Cu-eq) is an intermediate product of the composite hydrogel DHG(Cu), and DG(Cu) is the D-clay hydrogel without KCuHCF nanoparticles. DHG(Fe), DHG(step-Cu) and DHG(step-Fe) were three control samples fabricated (see Fig. S1a) to assess if the order of adding reactant and crosslinker had any affect on adsorbent performance. Different from DHG(Cu), DHG(Fe) was prepared by replacing CuSO₄ with FeCl₃ throughout the fabrication route. That is, adding 2 mL of 0.25 M FeCl₃ into 16 mL D-clay suspension (solid content = 7.55 g/L), and 2 mL of 0.25 M K₄Fe(CN)₆ in the first-step before adding 0.4 mL 1.0 M FeCl₃ in the second-step for crosslinking enhancement. For DHG(step-Cu) and DHG(step-Fe), 2 mL of 0.25 M CuSO₄ was added before 2 mL of 0.25 M K₄Fe(CN)₆ into the D-clay suspension, and in the second-step, DHG(step-Cu) was crosslinked with 0.4 mL of 1.0 M CuSO₄, while DHG(step-Fe) was crosslinked with 0.4 mL of 1.0 M FeCl₃.

For DHG(Fe), Fe³⁺ was used to synthesise HCF nanoparticles (nanoparticles being Prussian Blue KFe[Fe(CN)₆]), with D-clay nanosheets assembled into the hydrogel by the Fe³⁺-catechol complexation mechanism. For DHG(step-Cu) and DHG(step-Fe), since CuSO₄ was added first to D-clay before KHCF, the D-clay nanosheets were initially assembled to form the 3D network before formation of KCuHCF nanoparticles. Upon forming the KCuHCF nanoparticles, the 3D network was partially destroyed since Cu²⁺ is released from the crosslinking point to complex with K₄Fe(CN)₆ for HCF nanoparticle synthesis, along with growth of the nanoparticles further separating the clay nanosheets due to space occupation. Further addition of 0.4 mL of 1.0 M CuSO₄ or FeCl₃ enhanced the strength of the hydrogel framework, but remained weaker than DHG(Cu) (see Fig. 6b). The appearance of the fabricated gels in inverted glass vials are shown in Fig. S1a, highlighting the different degrees of flowability.

2. UV-vis Absorption

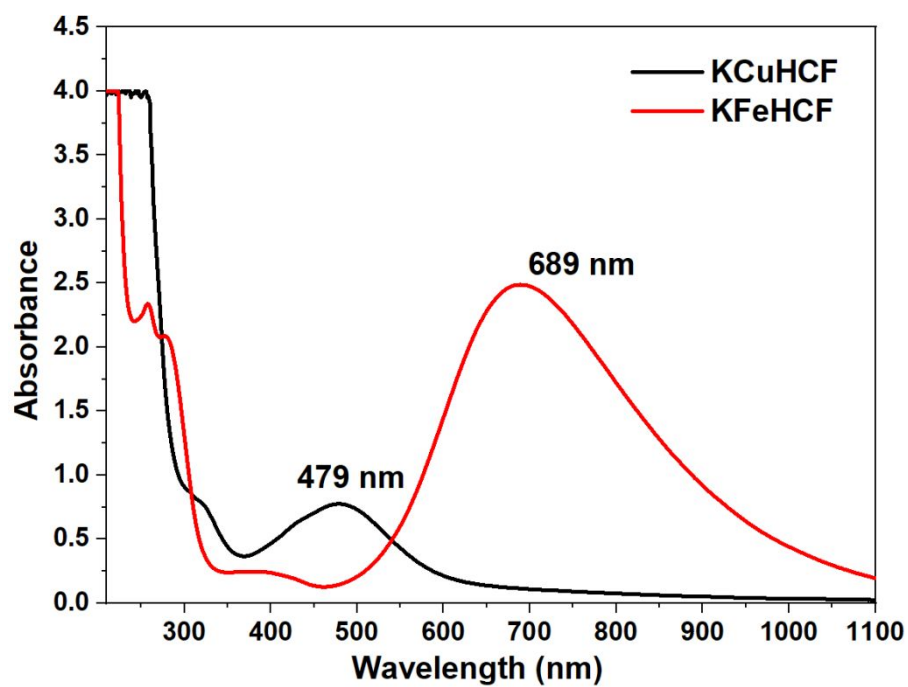


Figure S2. UV-vis adsorption bands of KCuHCF and KFeHCF particle suspensions.

3. SEM image of pristine-MMT

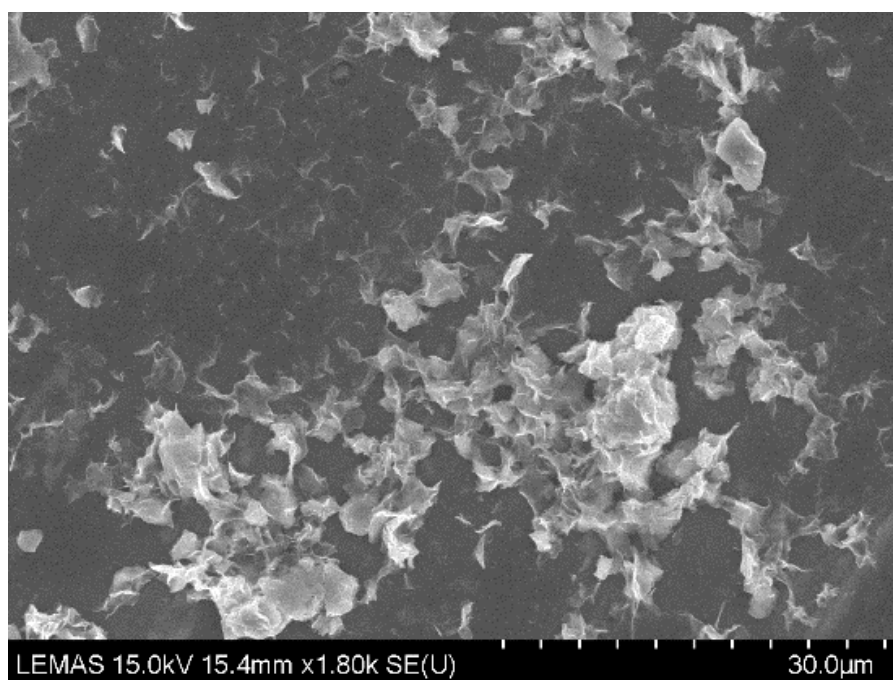


Figure S3. SEM image of pristine-MMT particles.

4. Thermalgravimetric Analysis

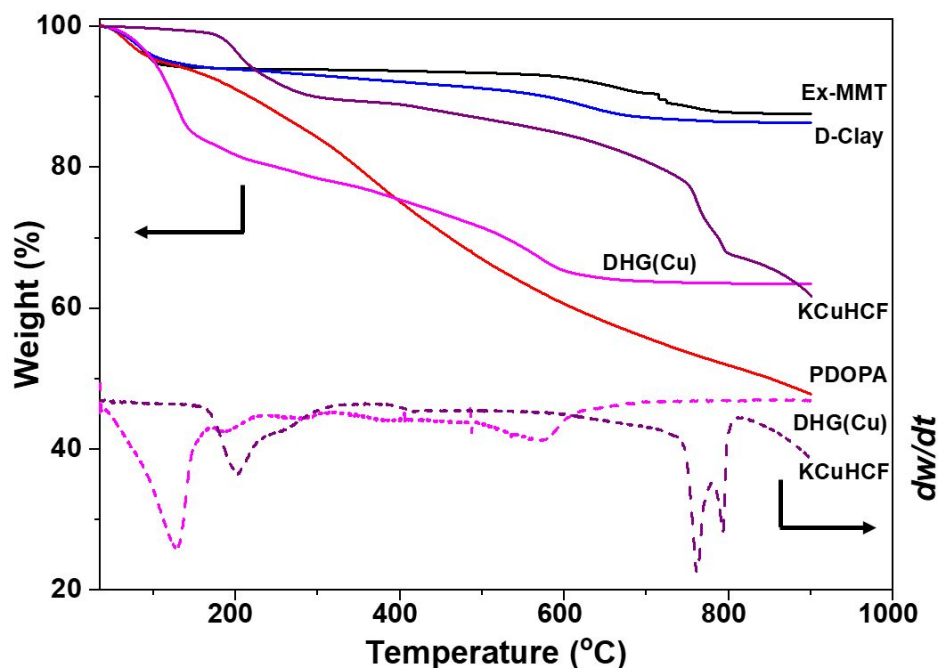


Figure S4. TGA of Ex-MMT, D-clay, DHG(Cu) and pure KCuHCF and PDOPA. Heating rate = 10°C/min.

The organic content in D-clay and DHG(Cu), as well as the HCF content in DHG(Cu) was estimated from the mass ratio of the combustion residue (w at 900 °C) to the initial mass of Ex-MMT (x), PDOPA(y), KCuHCF (z), and D-clay (u) (w at 100 °C):

$$x = \frac{w_{Ex-MMT,900^{\circ}C}}{w_{Ex-MMT,100^{\circ}C}}; y = \frac{w_{PDOPA,900^{\circ}C}}{w_{PDOPA,100^{\circ}C}}; z = \frac{w_{KCuHCF,900^{\circ}C}}{w_{KCuHCF,100^{\circ}C}}; u = \frac{w_{D-Clay,900^{\circ}C}}{w_{D-Clay,100^{\circ}C}} \quad (S1)$$

The four parameters were determined from the TGA data of single bulk components. It was assumed the mass loss increase of D-clay compared to Ex-MMT resulted from PDOPA, and the mass loss increase of DHG compared to D-clay resulted from KCuHCF, with the additional fraction of Cu^{2+} added in the second-step as the crosslinker being unchanged during combustion. The organic content (PDOPA) in D-clay is described by, k , hence the fraction of Ex-MMT is $(1 - k)$. Likewise, the HCF fraction in DHG composite is described as l , the fraction of Cu^{2+} added in second-step is described as p , and hence the fraction of D-clay is $(1 - l - p)$. On the basis of the initial ($W_{D-Clay,100^{\circ}C}$) and residual ($W_{D-Clay,900^{\circ}C}$) masses of D-clay from the TGA curve, a mass equivalence equation can be obtained as follows:

$$k W_{DClay,100^{\circ}C} = [W_{DClay,900^{\circ}C} - W_{DClay,100^{\circ}C}(1 - k)x]/y \quad (S2)$$

The left hand side of Eq. S2 describes the initial amount of PDOPA in the composite, and the right hand side describes the value estimated from the PDOPA residue in the composite at 900 °C by subtracting the residue of Ex-MMT from the D-clay residue. The estimation is based on the assumption that the components in D-clay undergo identical decomposition rates (same mass loss ratio) to that in the pure system. k is thus calculated from Eq. S2 to be 4.996%. Likewise, a relationship of mass equivalence equation can be written for the Cu^{2+} added in second step to prepare DHG composites:

$$p W_{DHG,100^{\circ}C} = W_{DHG,900^{\circ}C} - W_{DHG,100^{\circ}C}(1 - l - p) u - W_{DHG,100^{\circ}C} l z \quad (S3)$$

where u and z are the mass ratios of the combustion residue (W at 900 °C) to the initial mass (W at 100 °C) of pure D-clay and pure KCuHCF, respectively: $u = \frac{W_{D-clay,900^{\circ}C}}{W_{D-clay,100^{\circ}C}}$; $z = \frac{W_{KCuHCF,900^{\circ}C}}{W_{KCuHCF,100^{\circ}C}}$.

The left hand side of Eq. S3 describes the initial amount of Cu^{2+} in the composite and the right hand side describes the value of Cu^{2+} estimated from the residue in the composite at 900 °C by subtracting the residues of D-clay and KCuHCF.

Moreover, in the DHG(Cu) preparation, 16mL D-clay (solid content 7.55 g/L) was used and 0.4 mL 1M Cu^{2+} was added in the second step, giving a mass ratio of $m(D-clay)/m(Cu^{2+}) = 4.719$. That is,

$$\frac{1-l-p}{p} = 4.719 \quad (S4)$$

Combining equation (S3) and (S4) gives

$$p = (m - z)/(1 + 4.719u - 5.719z) \quad (S5)$$

with $m = W_{DHG,900^{\circ}C}/W_{DHG,100^{\circ}C}$. Based on the calculation, $p = 0.0271$; $l = 0.8448$; and $1-l-p = 0.1280$. As such, the calculated content of KCuHCF in DHG(Cu) is 84.48%, the content of Cu^{2+} , added in second-step as crosslinker, is 2.71% and the content of D-clay is 12.81%. The organic content in the DHG(Cu), v (%), is given by:

$$v = (1 - l - p)k \times 100\% = 0.6397\% \quad (S6)$$

5. EDX mapping of DHG(Cu)

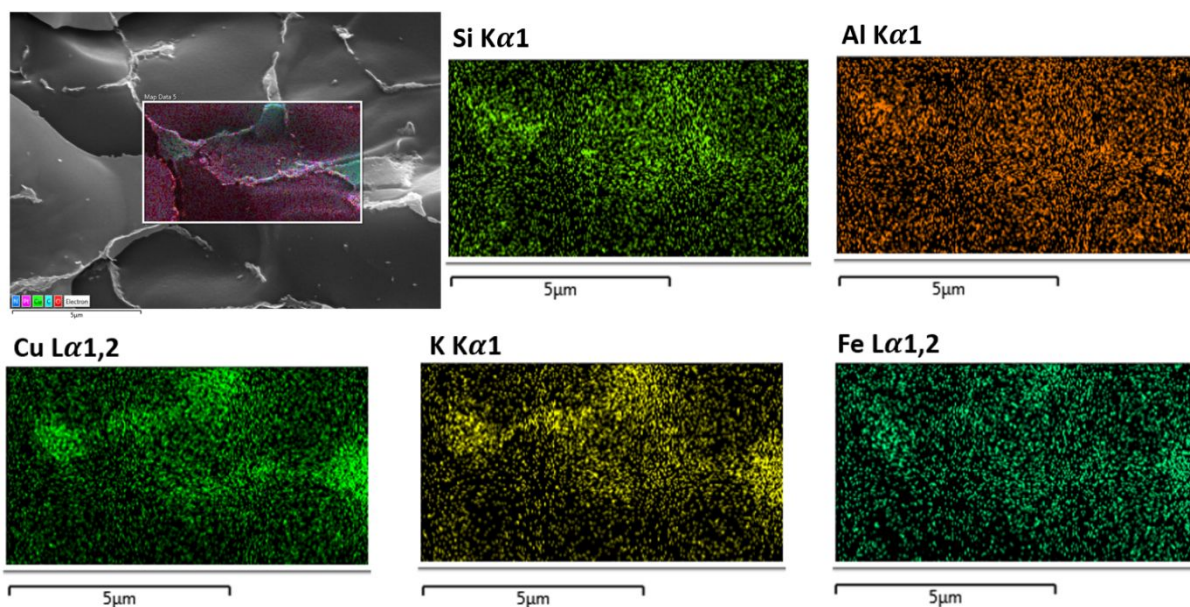


Figure S5. SEM image and EDX map of DHG(Cu).

6. Effect of HCF content on viscoelasticity of DHG(Cu) composite hydrogels

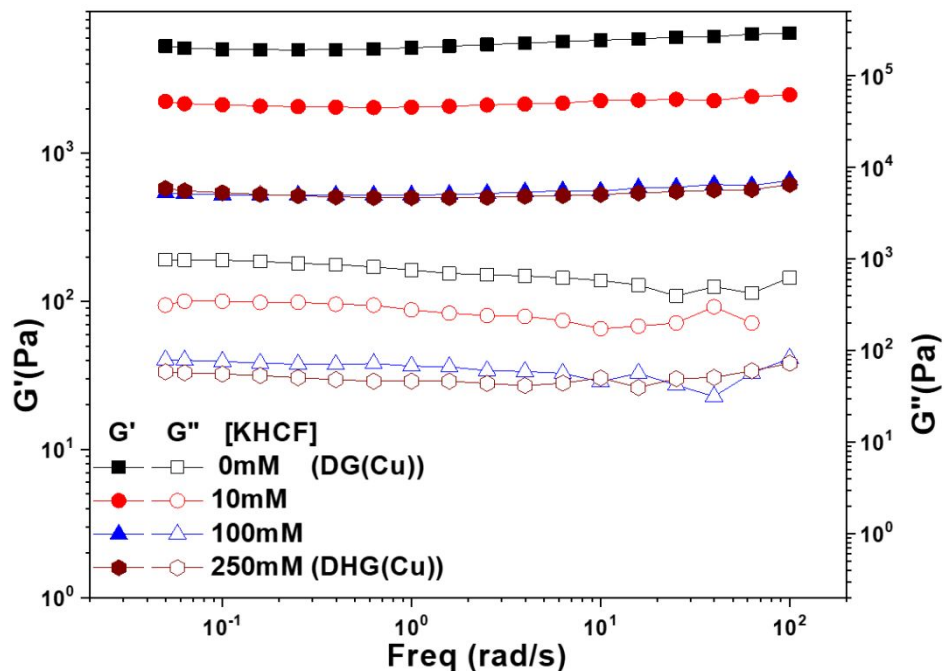


Figure S6. The effect of HCF content on the viscoelasticity of composite hydrogels. [KHCF] represents the concentration of $K_4Fe(CN)_6$ added for $KCuHCF$ nanoparticle synthesis. For DHG(Cu) considered in the study, the concentration of $K_4Fe(CN)_6$ was 250mM.