

Supplementary Information for “New Insight of Fe Valence State Change Using Leaves: A Combined Experimental and Theoretical Study”

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Table of contents:

PS1. Materials and methods

PS2. The morphology and elements mapping of Fe-Cl@leaves by SEM and EDS

PS3. The Partial XPS spectrum of C1s and Fe 2p peaks of Fe-Cl@leaves

PS4. The partial XPS spectra of the Fe 2p peaks of other Fe-Cl@leaves samples

PS5. The partial XPS spectra of the Fe 2p peaks of Fe-Cl@reduced leaves samples

PS6. Adsorption configurations of different $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ @catechin clusters, obtained by DFT calculations

PS1. Materials and Methods

Materials. FeCl_3 (CP, $\geq 97.0\%$) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (AR, $\geq 98.0\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Catechin hydrate ($\text{C}_{15}\text{H}_{14}\text{O}_6$, AR, $\geq 98\%$) was purchased from Hefei Bomei Biotechnology Co., Ltd. (Hefei, China). Green tea leaves and other leaves were obtained at Shanghai Institute of Applied Physics, CAS.

Sample preparation. Fe-Cl@leaves. The Fe-Cl@leaves sediments were prepared by vacuum filtration method. 2.0 g of leaves were ground into powder and then dispersed into 40 mL of newly prepared deionized water (18.2 M Ω , produced by ultra-pure water machine system ULUPURE, UPHW-I-90 T). Next, 20 mL of supernatant of leaves powder dispersion was added into a bottle containing 20 mL of FeCl_3 aqueous solution (120 mM). The mixture was sealed and stored still at ambient conditions (20°C) for 3 h for the Fe^{3+} adsorption on leaves and then vacuum filtered onto an ultrafilter membrane (25/50 mm diameter, 0.22 μm pore size). The Fe-Cl@leaves sediments were dried in a dry chamber (DZF-6020, Xiren, China) at 50 °C for 12 h.

Fe-Cl@reduced leaves. The reduced leaves were obtained by the thermal reduction method. The thermal reduction of leaves was performed at 180 °C for 1 h in the dry chamber. Adopting the same preparation procedure of Fe-Cl@leaves, 2.0 g of reduced leaves were dispersed into 40 mL of newly prepared deionized water to prepare reduced leaves dispersion.

Fe-Cl@catechin. Fe-Cl@catechin was prepared by vacuum filtration method. 20 mg of catechin hydrate was dispersed into 20 mL of deionized water to obtain catechin solution. The catechin solution was then added to 20 mL of 120 mM FeCl_3 aqueous solution. The mixture was sealed and stored still at ambient conditions (20°C) for 3 h and then vacuum filtered onto an ultrafilter membrane. The filtration sample was dried in a dry chamber at 50°C for 12 h.

Experimental measurements. X-ray photoelectron spectroscopy (XPS) experiments were performed on Imaging X-ray Photoelectron Spectrometer (AXIS Ultra DLD, Kratos, Japan) in Shanghai Jiaotong University. UV-visible absorption spectroscopy was carried out on UV-Visible Spectrophotometer (UV-2600, Shimadzu, Japan). Fourier transform infrared spectroscopy was performed using Infrared Spectrometer (PE-Frontier, Perkin-Elmer, USA). Scanning Electron Microscopy (SEM) morphology and Energy Dispersive Spectroscopy (EDS) mapping was conducted on a scanning electron microscope (LEO 1530VP, Germany).

Theoretical calculation methods. The M06-2X method in the framework of DFT, which has been widely used in the study of water molecules on solid surfaces or inside CNTs was used to study the intermolecular interactions. For geometry optimizations, the double- ζ basis was employed, and a d-polarization function was added (marked with 6-31 G(d,p)). All calculations were carried out using the Gaussian-09 package.^[1] The multiplicity for the whole $\text{Fe}(\text{6H}_2\text{O})_6^{3+}$ @catechin cluster is 6 (due to the 3d5 valence electron orbital on Fe^{3+}), which performs as the lowest

total system energy.

Charge decomposition analysis (CDA) was calculated by Mulltiefn software package 3.8. The adsorption configuration of the $\text{Fe}(\text{6H}_2\text{O})_6^{3+}$ @catechin cluster was divided into two parts as the $\text{Fe}(\text{6H}_2\text{O})_6^{3+}$ and the catechin. Both parts have the same structure as they were in the adsorption configuration obtained by DFT calculations. The two parts were performed single-point calculations to get the data of the orbital wave functions, respectively. Then, the CDA data can be calculated through the Multiwfn software package.

PS2. The morphology and elements mapping of Fe-Cl@leaves by SEM and EDS

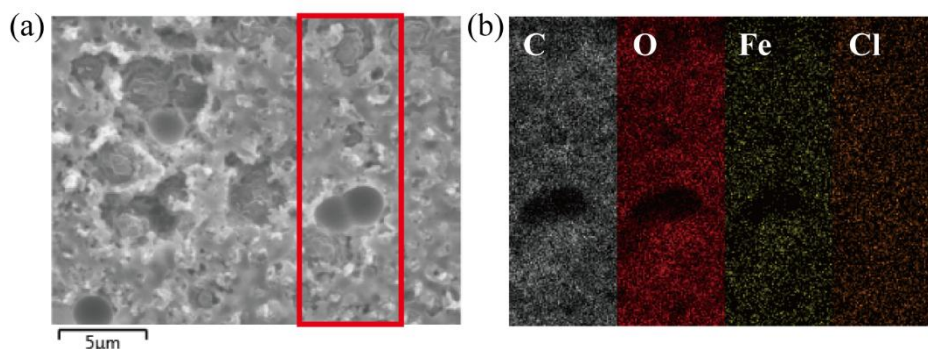


Fig. S1. (a) SEM surface morphology of Fe-Cl@leaves. (b) Elements mappings of Fe-Cl@leaves based on SEM-EDS analysis in the red rectangular region in (a).

PS3. The Partial XPS spectrum of C 1s and Fe 2p peaks of Fe-Cl@leaves

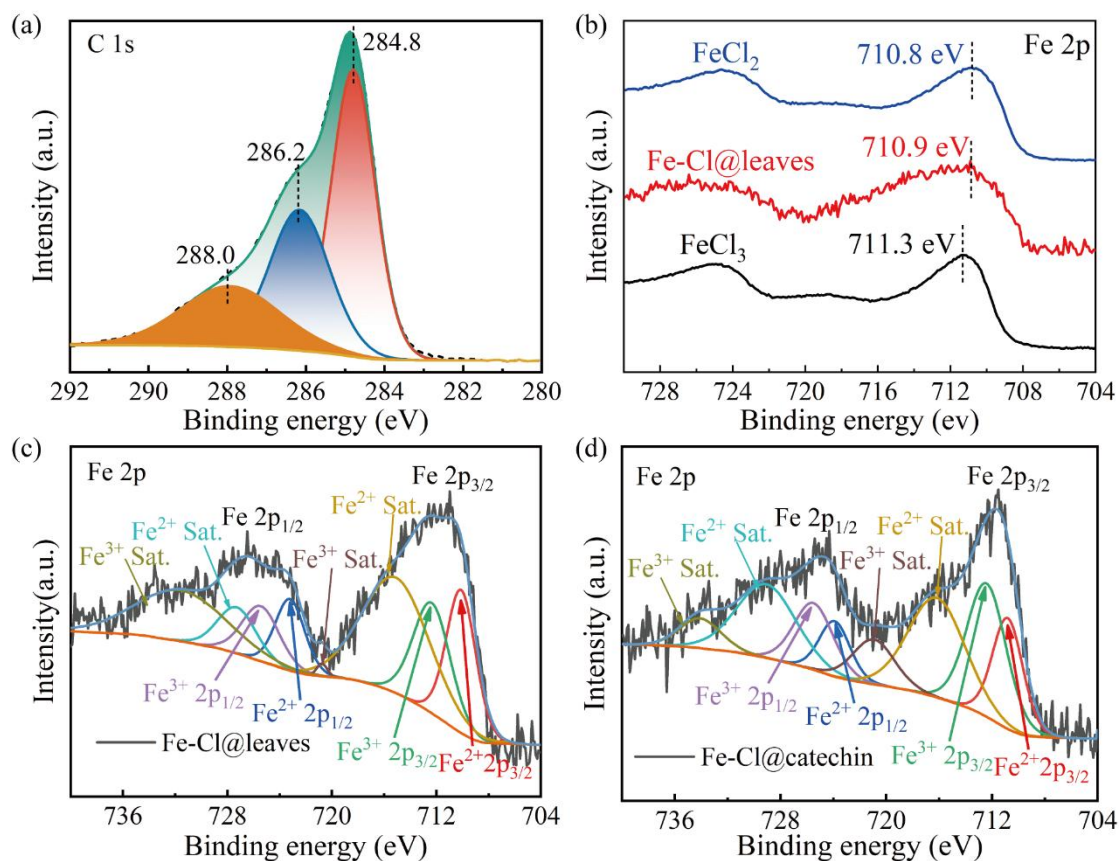


Fig. S2. (a) XPS partial spectrum of C 1s peak of Fe-Cl@leaves. (b) Partial spectra of Fe 2p peaks for FeCl₃ crystals, Fe-Cl@leaves sediments, and FeCl₂ crystals, respectively. (c) Partial spectra of Fe 2p peaks of Fe-Cl@leaves. (d) Partial spectra of Fe 2p peaks of Fe-Cl@catechin. The peaks of Fe-Cl@leaves and Fe-Cl@catechin are fitted with two contributions, one from the Fe²⁺ component and the other from the Fe³⁺ component.

PS4. The partial XPS spectra of the Fe 2p peaks of other Fe-Cl@leaves samples

As shown in Fig. S3, similar binding energy shifts of Fe 2p in other Fe-Cl@leaves samples, such as wintersweet leaves (710.7 eV) and ginkgo biloba (710.8 eV) were observed by XPS surface analysis.

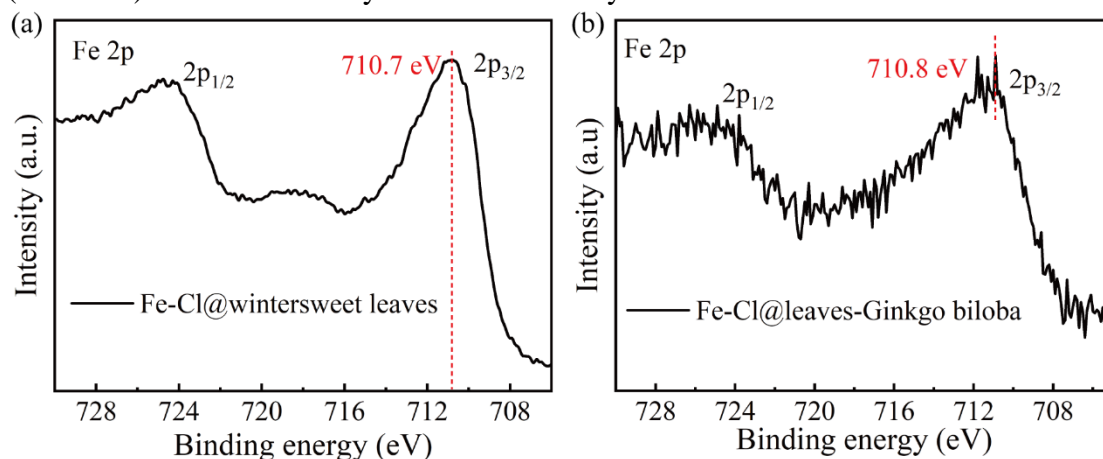


Fig. S3. Partial XPS spectra of the Fe 2p of (a) Fe-Cl@wintersweet leaves and (b) Fe-Cl@Ginkgo biloba leaves.

PS5. The partial XPS spectra of the Fe 2p peaks of Fe-Cl@reduced leaves samples

The thermal reduction of leaves was performed in a dry chamber at 180 °C for 1 h. The valence state of the Fe element changed from Fe³⁺ to Fe²⁺ could also be detected by XPS after reduced leaves dispersion was added into FeCl₃ dilute solution, shown in Fig. S4.

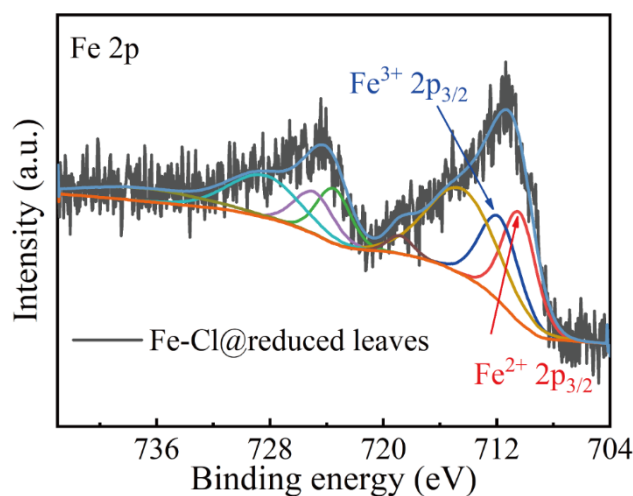


Fig. S4. Partial XPS spectra of Fe 2p peak of Fe-Cl@reduced leaves.

PS6. Adsorption configurations of different $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ @catechin clusters, obtained by DFT calculations

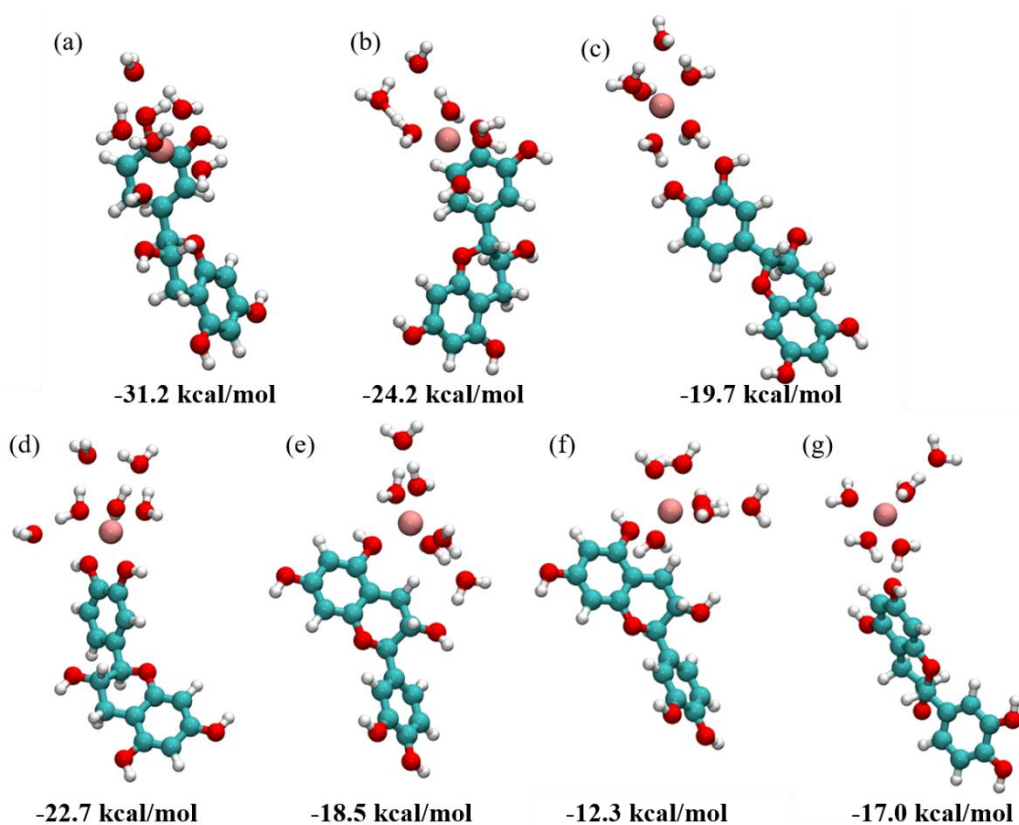


Fig. S5. Adsorption configurations of different $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ @catechin clusters, and the adsorption energies, respectively. (a) $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ adsorbs at the region where the aromatic ring and two -OH groups coexist; (b) $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ adsorbs at the region where the aromatic ring and one -OH group coexist; (c, d, e) $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ adsorbs at the region between two -OH groups of the catechin. (f, g) $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ adsorbs at the region on one -OH groups of the catechin. Where spheres in white, red, cyan, and pink represent the H, O, C, and Fe atoms or cation.

References:

- [1] Frisch M J *et al.*, 2009 *Gaussian 09 Revision D.01* (Wallingford, CT)