

Supporting Information

Self-assembly preparation of lignin-graphene oxide composite nanospheres for highly efficient Cr(VI) removal

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Precipitation conditions of KL

The lignins used in this experiment are derived from the black liquors which were produced in the kraft pulping process. The experimental conditions in the pulping process are as the following: 2000g of dry eucalyptus woods were put into a 10L vertical cooking pot, sulphidity is 25%, solid-liquid ratio is 1:4, and the dosage of Na₂O is 17.5%. After the reaction, the black liquors were collected for later use. H₂SO₄ was added to the black liquors and the pH value was adjusted to 6, the precipitate and the supernatant were obtained after separation. Continue to add H₂SO₄ to the above supernatant and adjust the pH to 4, the precipitate and the supernatant were obtained after separation. Add H₂SO₄ to the second supernatant and adjust the pH to 2, precipitate was collected as raw material.

Nanospheres prepared by different ratios of KL/GO

Apart from the nanospheres prepared by KL/GO=1/1 which described in the manuscript, we also prepared adsorbents at the ratio of KL/GO=2/1 and 1/2. It can be seen from Figure S1 that regular spherical structures can be formed when KL/GO=2/1. While when KL/GO=1/2, spherical structures cannot be formed and the dispersion is poor. Additionally, the maximum adsorption capacity of the adsorbents were measured with the conditions at 318k and concentration of Cr(VI) being 500mg/L. The adsorption efficiency is shown in Figure S2, and we can see that Cr(VI) adsorption capacity of nanospheres prepared by KL/GO=2/1 and 1/2 is 135.88mg/g and 153.63mg/g respectively.

In addition, the results showed that the adsorption capacity of pure GO in a 500mg/L Cr(VI) solution is only 55.61mg/g. Additionally, we also measured the adsorption capacity of KL under the same conditions and it is only 23.06mg/g. These results indicate that LGNs have good adsorption capacity and the Cr(VI) removal of LNs has also been greatly improved compared to KL.

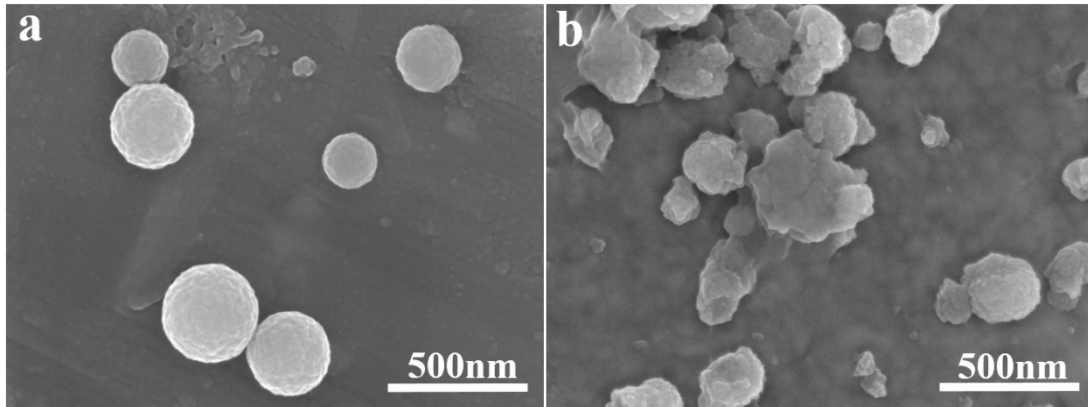


Figure S1. SEM images of different ratios by KL and GO mixed: (a) KL/GO=2/1; (b) KL/GO=1/2.

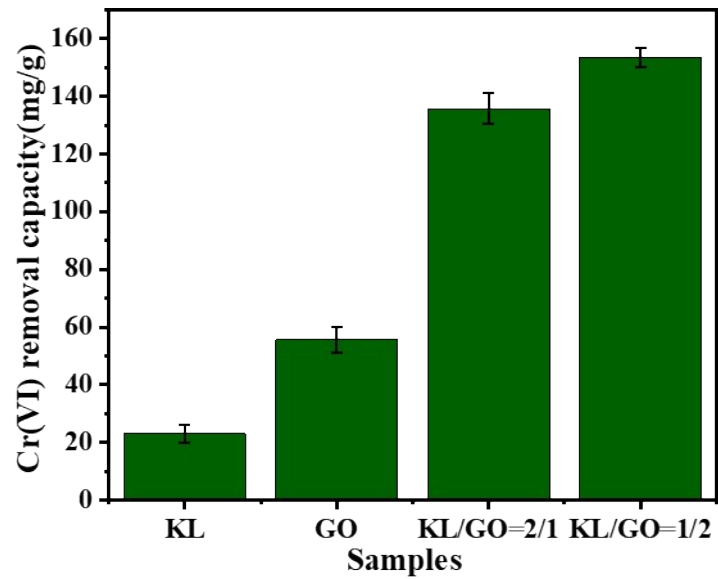


Figure S2 Cr(VI) adsorption capacity of KL, GO, nanospheres prepared by KL/GO=2/1 and 1/2.

Characterization of graphene oxide

We measured XRD and XPS of GO and the results showed there are many oxygen-containing functional groups such as -OH, -COOH and C=O. The peak of XRD is at 12° , corresponding to a layer spacing of 0.71nm. The layer spacing of GO becomes larger compared with graphene, indicating that GO has more oxygen-containing functional groups on the surface.¹ Additionally, the carboxyl groups of GO was determined by Boehm titration,²⁻⁴ and its content is 2.93mmol/g.

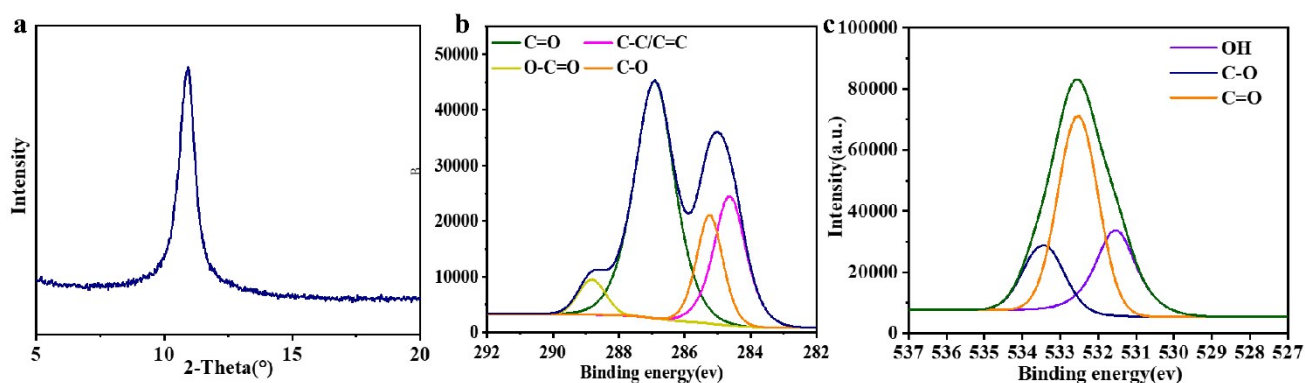


Figure S3. Characteristics of GO:(a) XRD; (b) C1 XPS peaks;(c) O1 XPS peaks.

Phenolic hydroxyl content

Determination of phenolic hydroxyl content is shown by aqueous phase potentiometric titration.⁵ The results show that the phenolic hydroxyl content of LNs is 1.13mmol/g, and that of KL is 1.25 mmol/g. This may be due to some phenolic hydroxyl groups being encapsulated during the self-assembly process.

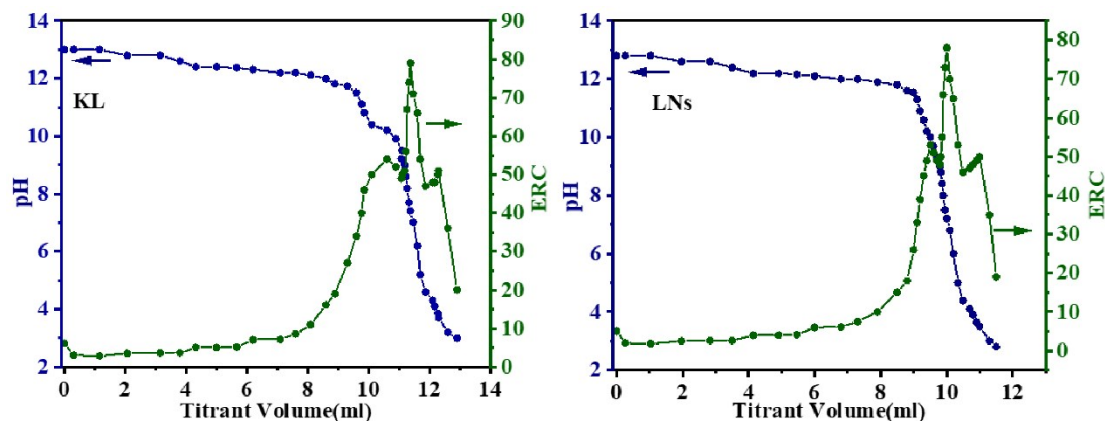


Figure S4. Diagrammatic curve of LNs and KL by aqueous titration.

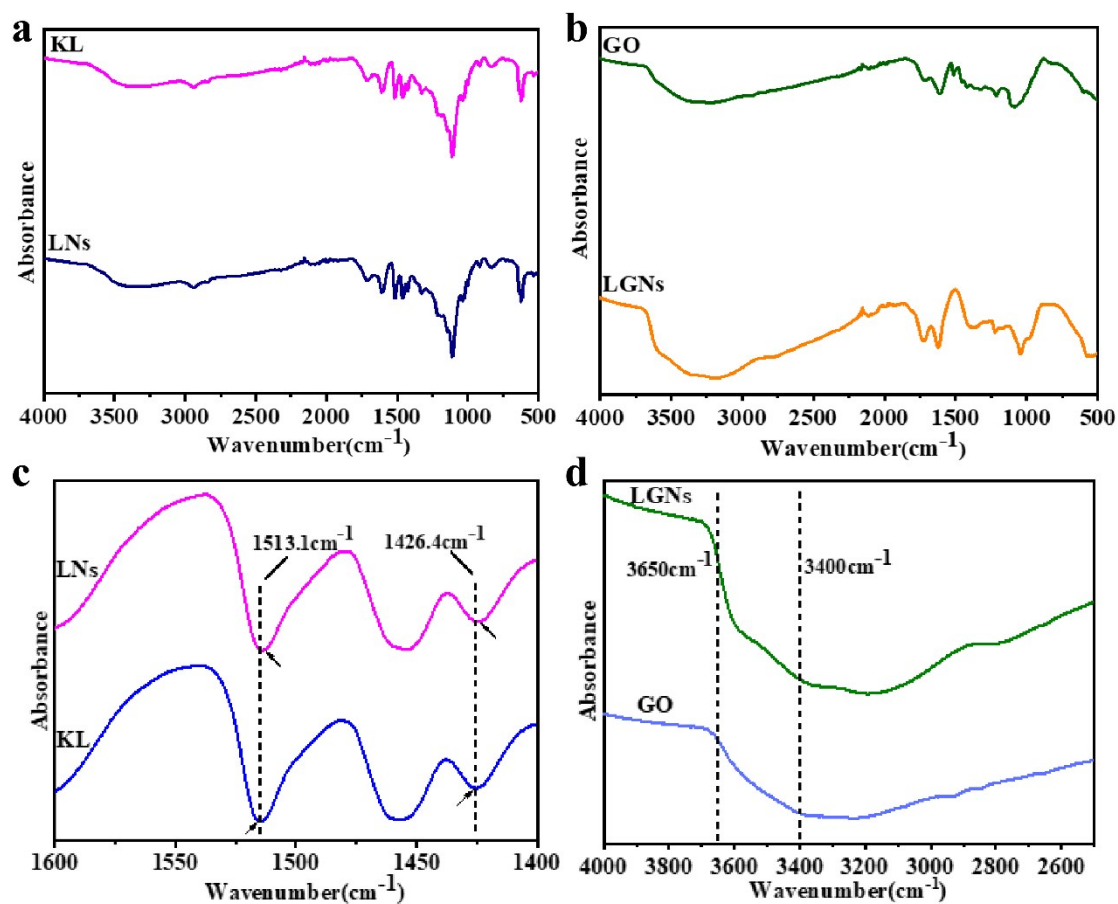


Figure S5 FTIR spectra of (a) KL and LNs; (b) GO and LGNs; and local magnification of (c) LNs and KL; (d) LGNs and GO.

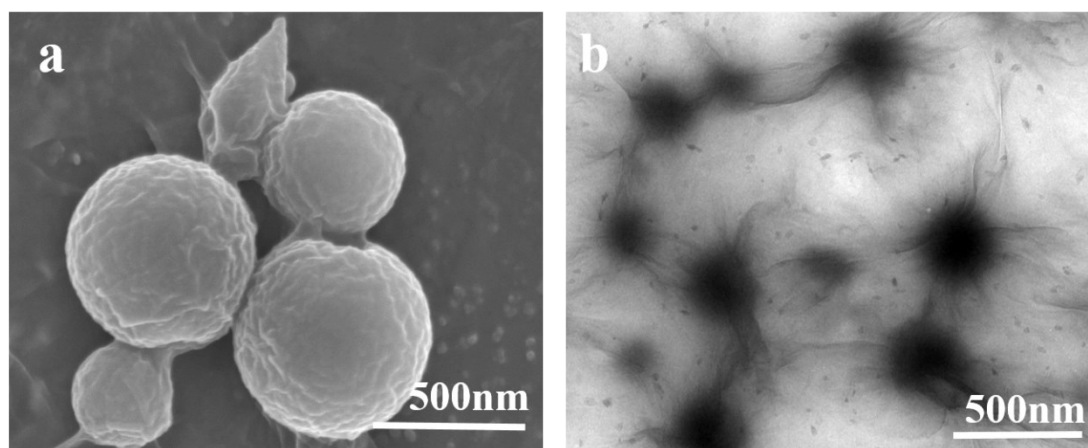


Figure S6 SEM and TEM images of LGNs.

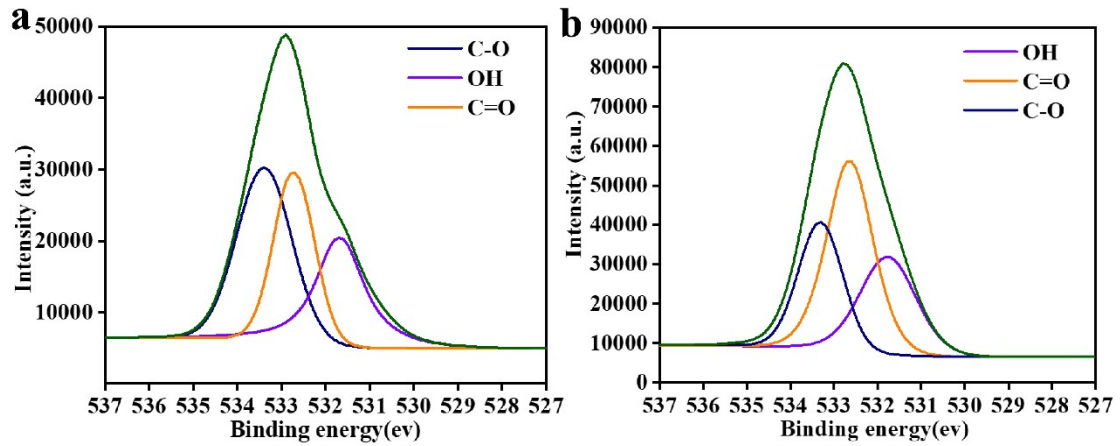


Figure S7. (a) O1 XPS peaks of LNs and (b) O1 XPS peaks of LGNs.

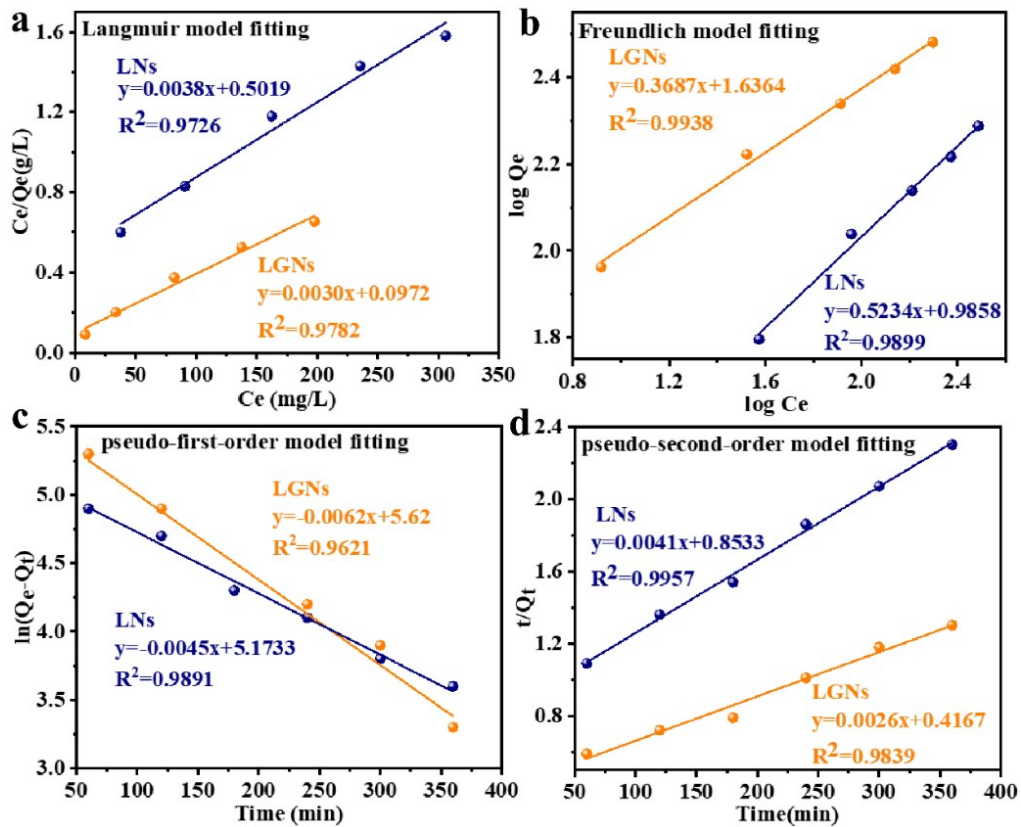


Figure S8. Adsorption isotherm and thermodynamic fitting.

Table S1. Element contents of the samples.

Samples	C (wt %)	H (wt %)	O (wt %)	O/C ratio
KL	52.32	5.16	30.56	0.58
GO	53.50	2.38	42.12	0.79
LN _s	48.28	4.96	36.28	0.75
LGN _s	43.18	3.32	48.70	1.13

References

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