

A Mesoporous Titanium Glycolate with Exceptional Adsorption Capacity to Remove Multiple Heavy Metal Ions in Water

Wei Han,^{†,‡,#} Xiulin Yang,^{‡,#} Fuwen Zhao,[‡] Xiaofeng Shi,[‡] Taishan Wang[‡],

Xiangdong Zhang,^{*†} Li Jiang,^{*‡} Chunru Wang[‡]

[†] College of Chemistry, Liaoning University, Shenyang 110036, PR China

[‡] Beijing National Laboratory for Molecular Sciences, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190

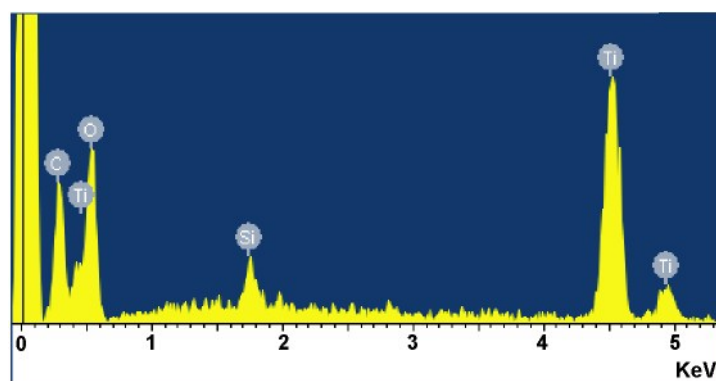


Figure S1. EDS analysis of titanium glycolate.

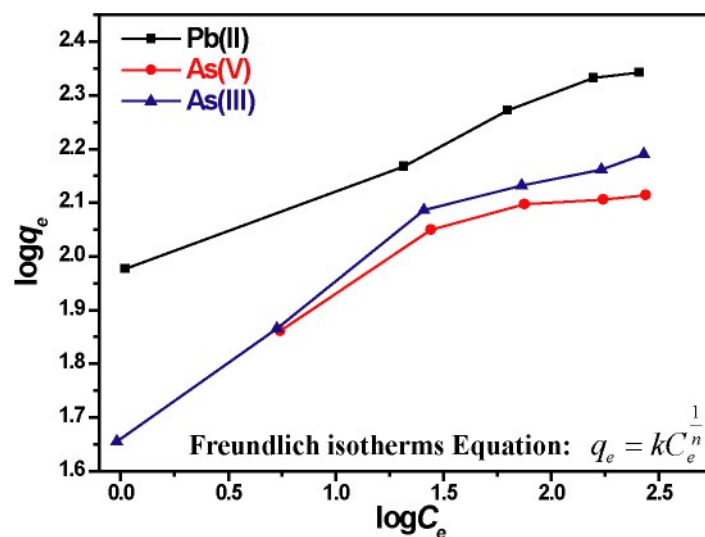


Figure S2. Freundlich isotherms model of titanium glycolate adsorbed Pb(II), As(V) and As(III). The initial ion concentration is 10~200 mg·L⁻¹ and sample dose is 5 mg/25 mL.

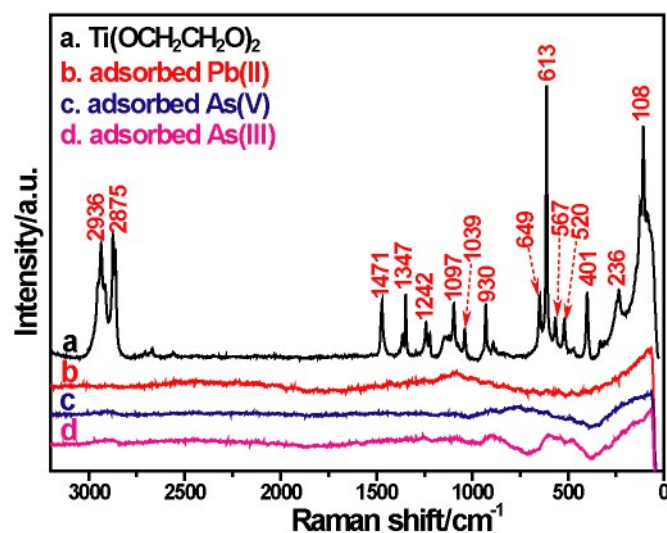


Figure S3. Raman spectrum of (a) titanium glycolate, (b) Ti(OCH₂CH₂O)₂-adsorbed Pb(II), (c) Ti(OCH₂CH₂O)₂-adsorbed As(V) and (d) Ti(OCH₂CH₂O)₂-adsorbed As(III).

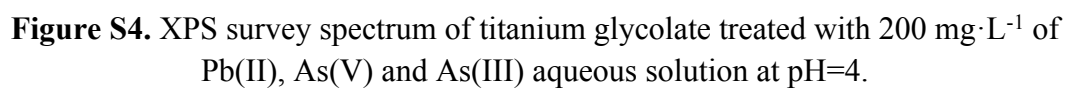


Figure S4. XPS survey spectrum of titanium glycolate treated with 200 mg·L⁻¹ of Pb(II), As(V) and As(III) aqueous solution at pH=4.

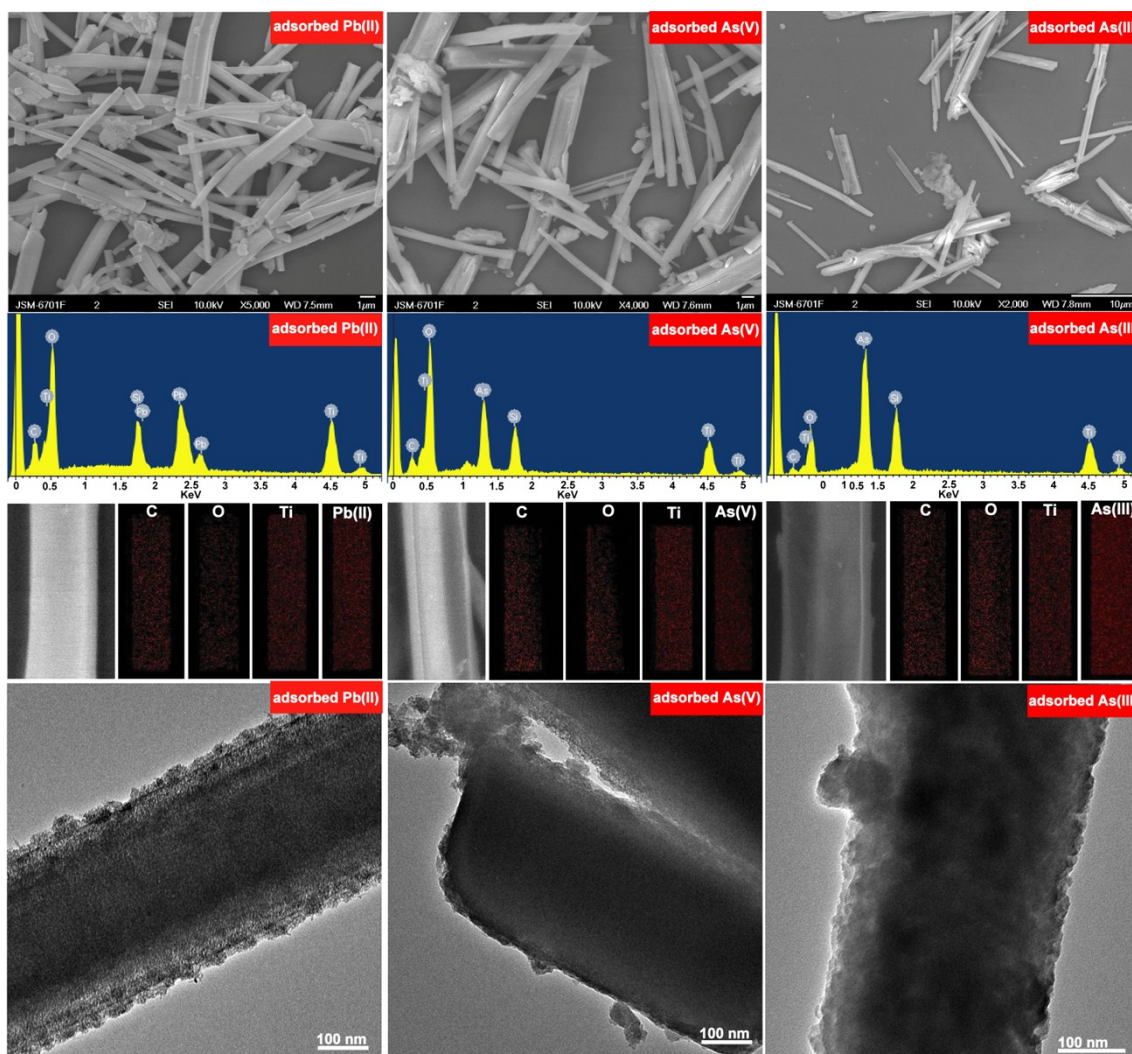


Figure S5. SEM, TEM, EDS and element mapping of titanium glycolate treated with 200 mg·L⁻¹ of Pb(II), As(V) and As(III) aqueous solution at pH=4.

Table S1. The binding energy of C1s, O1s, Ti2p and heavy metal ions (Pb4f and As3d) of titanium glycolate and after adsorbed heavy metal ions.

Samples	C1s (eV)	O1s (eV)	Ti2p (eV)	Metal ions (eV)
Ti(OCH ₂ CH ₂ O) ₂	286.1	531.6	458.9	--
Adsorbed Pb(II)	284.8	530.3	458.7	138.7 (Pb4f)
Adsorbed As(V)	284.8	531.2	459.1	45.8 (As3d)
Adsorbed As(III)	284.8	531.0	459.1	44.6 (As3d)

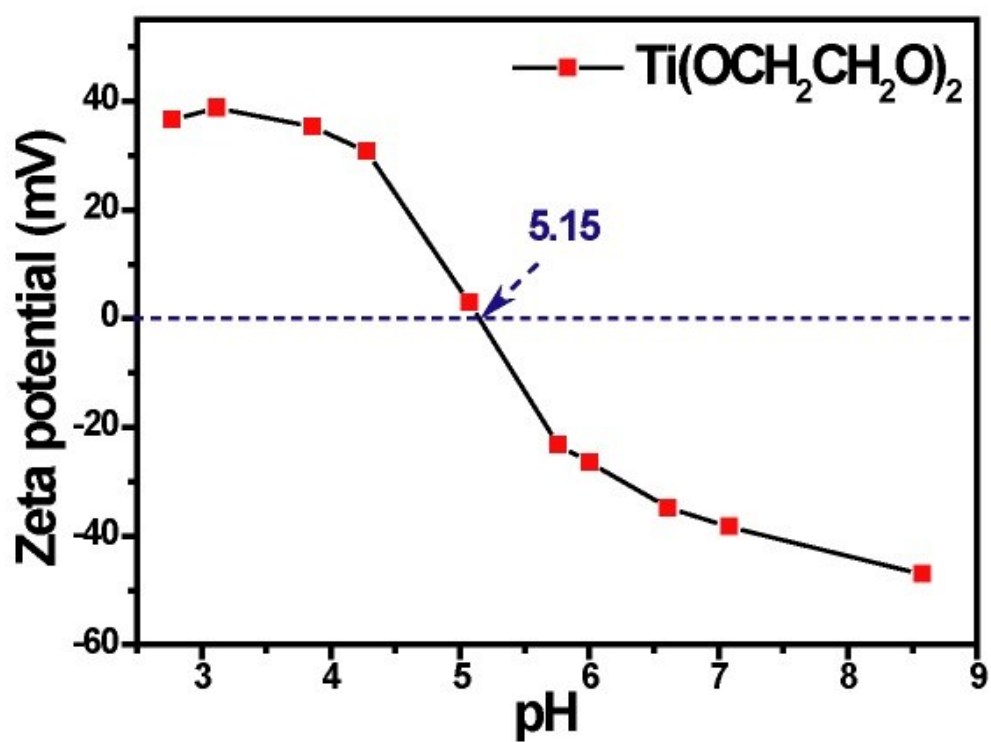


Figure S6. Zeta-potential of $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ As a function of pH, sample dose is $0.2 \text{ g}\cdot\text{L}^{-1}$.

Table S2. Summary of As(V), As(III) and Pb(II) maximum adsorption capacities (q_m) on various adsorbents.

Sorbents	As(V): q_m ($\text{mg}\cdot\text{g}^{-1}$)	As(III): q_m ($\text{mg}\cdot\text{g}^{-1}$)	Pb(II): q_m ($\text{mg}\cdot\text{g}^{-1}$)	BET ($\text{m}^2\cdot\text{g}^{-1}$)
Mesoporous $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ (this study)	131.93	156.01	225.73	246.5
Chrysanthemum-like α -FeOOH microspheres ¹	66.2	--	103	120.8
Ceria Hollow Nanospheres ²	22.4	--	9.2	72
Magnetic gelatin-modified biochar ³	45.8	--	--	--
Flowerlike α -Fe ₂ O ₃ ⁴	51	--	--	130
Cotton-Candy-Like CuO ⁵	--	12.9	--	119
Hollow Nestlike α -Fe ₂ O ₃ ⁶	75.3	--	--	152.42
Flowerlike Magnesium Oxide ⁷	--	--	1980	72
Al(OH)CO ₃ nanospheres ⁸	170	--	--	484
γ -AlOOH@SiO ₂ /Fe ₃ O ₄ ⁹	--	--	214.59	28.6
Magnetic CuO-Fe ₃ O ₄ NPs ¹⁰	118.11	--	--	--
Magnetic binary oxide particles ¹¹	--	16.94	--	--
magnetic carbonaceous NPs ¹²	--	--	123	--
Polyacrylonitrile Nanofiber ¹³	--	--	60.6	--
Porous Magnesium Silicate ¹⁴	--	--	436.68	650.50
Magnesium Oxide Coated Iron ore (IOMO) ¹⁵	--	--	2724	--

1. Li H.; Li W.; Zhang Y.-J.; Wang T.-S.; Wang B.; Xu W.; Jiang L.; Song W.-G.; Shu C.-Y.; Wang C.-R., Chrysanthemum-like α -FeOOH microspheres produced by a simple green method and their outstanding ability in heavy metal ion removal. *J. Mater. Chem.*, **2011**, 21, 7878.
2. Cao, C.-Y.; Cui, Z.-M.; Chen, C.-Q.; Song, W.-G.; Cai, W., Ceria Hollow Nanospheres Produced by a Template-Free Microwave-Assisted Hydrothermal Method for Heavy Metal Ion Removal and Catalysis. *J. Phys. Chem. C*. **2010**, 114(21), 9865-9870.
3. Zhou, Z.; Liu, Y.-G.; Liu, S.-B.; Liu, H.-Y.; Zeng, G.-M.; Tan, X.-F.; Yang, C.-P.; Ding, Y.; Yan, Z.-L.; Cai, X.-X., Sorption performance and mechanisms of arsenic(V) removal by magnetic gelatin-modified biochar. *Chem. Eng. J.* **2017**, 314, 223-231.
4. Cao, C.-Y.; Qu, J.; Yan, W.-S.; Zhu, J.-F.; Wu, Z.-Y.; Song, W.-G., Low-Cost Synthesis

- of Flowerlike α -Fe₂O₃ Nanostructures for Heavy Metal Ion Removal: Adsorption Property and Mechanism. *Langmuir*, **2012**, 28(9), 4573-4579.
5. Yu, X.-Y.; Xu, R.-X.; Gao, C.; Luo, T.; Jia, Y.; Liu, J.-H.; Huang, X.-J., Novel 3D Hierarchical Cotton-Candy-Like CuO: Surfactant-Free Solvothermal Synthesis and Application in As(III) Removal. *ACS Appl. Mater. Inter.* **2012**, 4(4), 1954-1962.
 6. Wei, Z.-H.; Xing, R.-G.; Zhang, X.; Liu, S.; Yu, H.-H.; Li, P.-C., Facile Template-Free Fabrication of Hollow Nestlike α -Fe₂O₃ Nanostructures for Water Treatment. *ACS Appl. Mater. Inter.* **2013**, 5(3), 598-604.
 7. Cao, C.-Y.; Qu, J.; Wei, F.; Liu, H.; Song, W.-G., Superb Adsorption Capacity and Mechanism of Flowerlike Magnesium Oxide Nanostructures for Lead and Cadmium Ions. *ACS Appl. Mater. Inter.*, **2012**, 4(8), 483-4287.
 8. Cao, C.-Y.; Li, P.; Qu, J.; Dou, Z.-F.; Yan, W.-S.; Zhu, J.-F.; Wu, Z.-Y.; Song, W.-G., High adsorption capacity and the key role of carbonate groups for heavy metal ion removal by basic aluminum carbonate porous nanospheres. *J. Mater. Chem.*, **2012**, 22(37), 19898-19903.
 9. Zhang, Y.-X.; Yu, X.-Y.; Jin, Z.; Jia, Y.; Xu, W.-H.; Luo, T.; Zhu, B.-J.; Liu, J.-H.; Huang, X.-J., Ultra high adsorption capacity of fried egg jellyfish-like gamma-AlOOH(Boehmite)@SiO₂/Fe₃O₄ porous magnetic microspheres for aqueous Pb(II) removal. *J. Mater. Chem.*, **2011**, 21(41), 16550-16557.
 10. Sun, T.-Y.; Zhao, Z.-W.; Liang, Z.-J.; Liu, J.; Shi, W.-X.; Cui, F.-Y., Efficient As(III) removal by magnetic CuO-Fe₃O₄ nanoparticles through photo-oxidation and adsorption under light irradiation. *J. Colloid Inter. Sci.*, **2017**, 495, 168-177.
 11. Dhobleb, R.-M.; Lungea, S.; Bholec, A.-G.; Rayalua, S., Magnetic binary oxide particles (MBOP): A promising adsorbent for removal of As (III) in water. *Water Research*, **2011**, 45(16), 4769-4781.
 12. Nata, I.-F.; Salim, G. -W.; Lee, C.-K., Facile preparation of magnetic carbonaceous nanoparticles for Pb²⁺ ions removal. *Journal of Hazardous Materials*, **2010**, 183, 853-858.
 13. Kampalanonwat, P.; Supaphol, P., Preparation and Adsorption Behavior of Aminated Electrospun Polyacrylonitrile Nanofiber Mats for Heavy Metal Ion Removal. *ACS Applied Materials & Interfaces*, **2010**, 2(12), 3619-3627.

14. Huang, R.-Y.; Wu, M.-J.; Zhang, T.; Li, D.-Q.; Tang, P.-G.; Feng, Y.-J., Template-free Synthesis of Large-Pore-Size Porous Magnesium Silicate Hierarchical Nanostructures for High-Efficiency Removal of Heavy Metal Ions. *ACS Sustainable Chem. Eng.* **2017**, *5*, 2774-2780.
15. Nagarajah, R.; Jang, M.; Pichiah, S.; Cho, J.; Snyder, S.-A., Nano-Structured Magnesium Oxide Coated Iron Ore: Its Application to the Remediation of Wastewater Containing Lead. *J. Nanosci. Nanotech.*, **2015**, *15*(12), 9603-9611.