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2015年汞污染防治与履行国际汞公约研讨会

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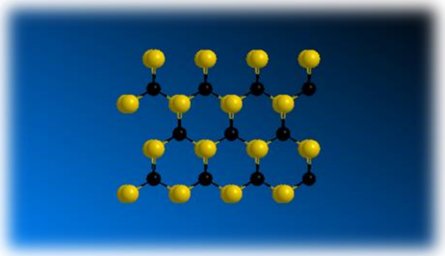

具有MoS_2纳米层状结构的新型汞吸附剂

MoS_2 nanosheets containing materials for mercury adsorption

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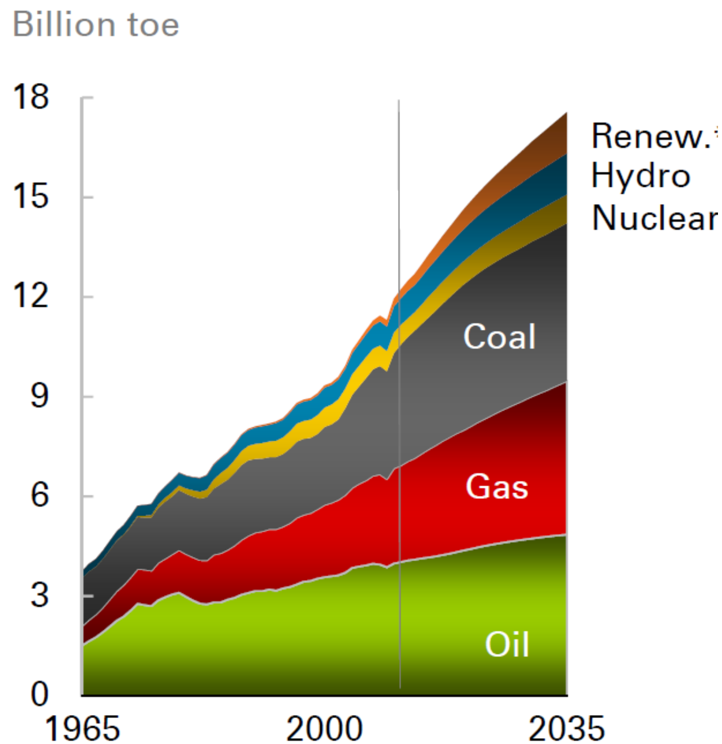
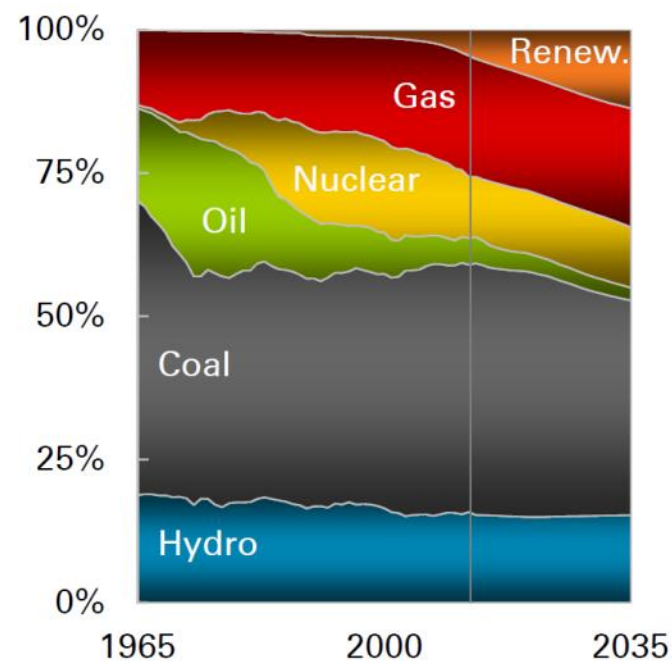
Introduction
研究背景

One of the main sources of clean energy in the next few decades will still be the “dirty” fossil fuels

(a) World primary energy consumption



(b) World primary energy inputs to power



(toe: tonne of oil equivalent)

BP, Energy Outlook 2035 [Online] available from <http://www.bp.com> (accessed Jan, 2015), 2014.
IEA, World Energy Outlook 2014 [Online] available from <http://www.worldenergyoutlook.org> (accessed Jan, 2015). 2014.

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Background
研究背景

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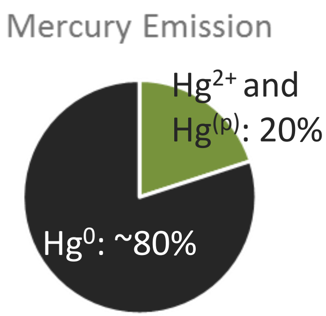
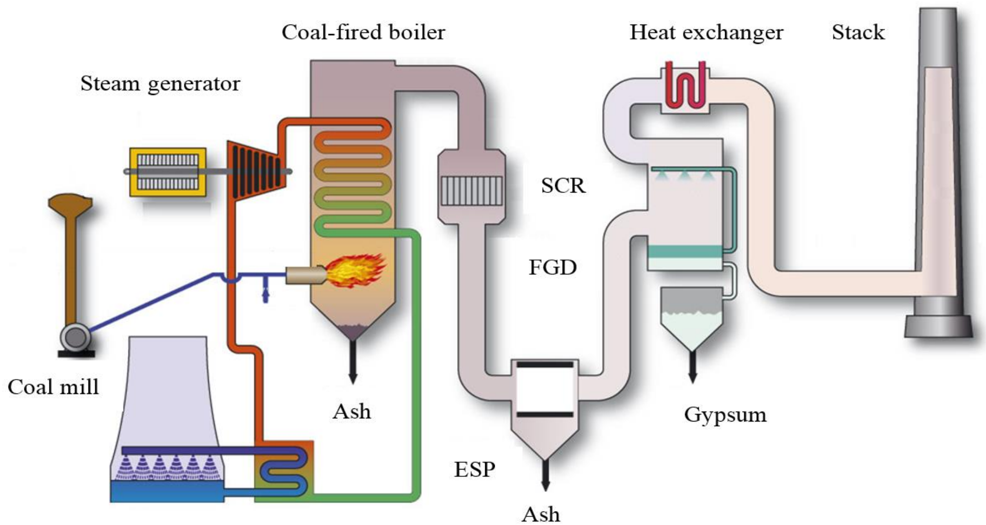
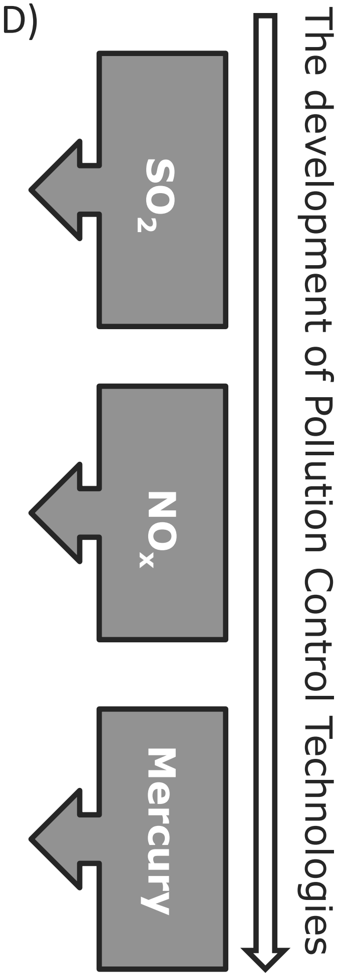
Current Pollution Control Technologies in Practice

•Post-combustion: Wet (lime-scrubbing) flue gas desulfurization (wet-FGD)
Selective catalytic reduction (SCR) of NO_x

•Combustion process: Low NO_x Combustion Technologies







- Hg^{2+} and $Hg^{(p)}$ could be removed by the **existing** air pollution control devices (APCDs), such as wet-FGD and ESP
- Hg^0 is extremely difficult to be removed because it is highly volatile, insoluble in water.
- The injection of powdered activated carbon (PAC) has been commercially introduced in the US for Hg^0 capture. However, it is of several drawbacks: additional capital investment, relative high operating costs and secondary environmental pollutions, etc.

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Objectives
研究目的

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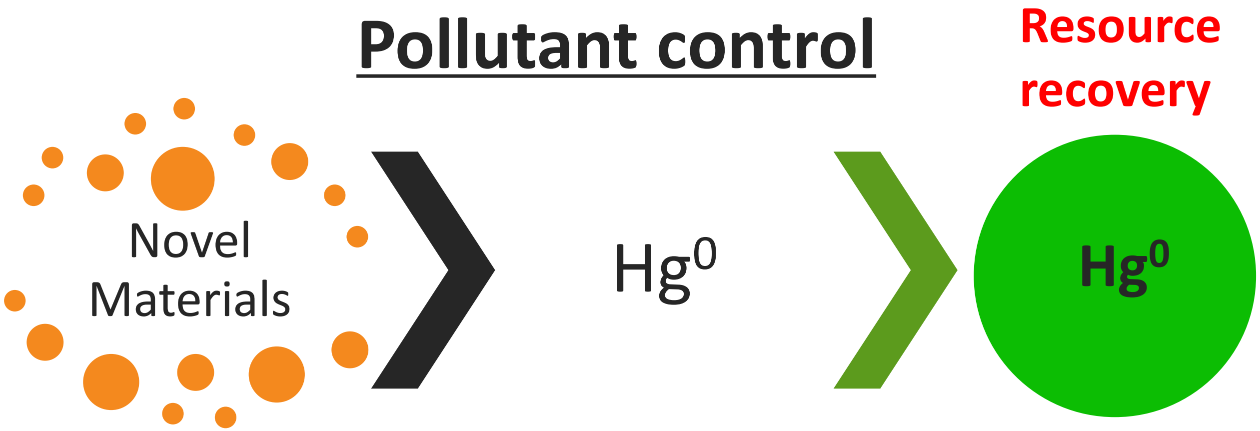

- **Mercury removal in flue gas/process gas 化石能源烟气废气脱汞：**
  - Coal-fired power stations 燃煤电厂
  - Coal-fired boilers燃煤供热锅炉
  - Petrochemical plants石油炼化厂等行业
- **Fuel gas cleaning化石能源燃气脱汞净化**
  - Coking gas焦炉煤气
  - natural gas天然气
  - Shale gas页岩气等燃气净化行业
- **Mercury recovery 废气燃气汞资源化回收**
  - **Recovery of mercury as resource during the regeneration of mercury capture materials**研发汞吸附材料再生的同时实现汞资源化回收

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Experimental system
实验系统

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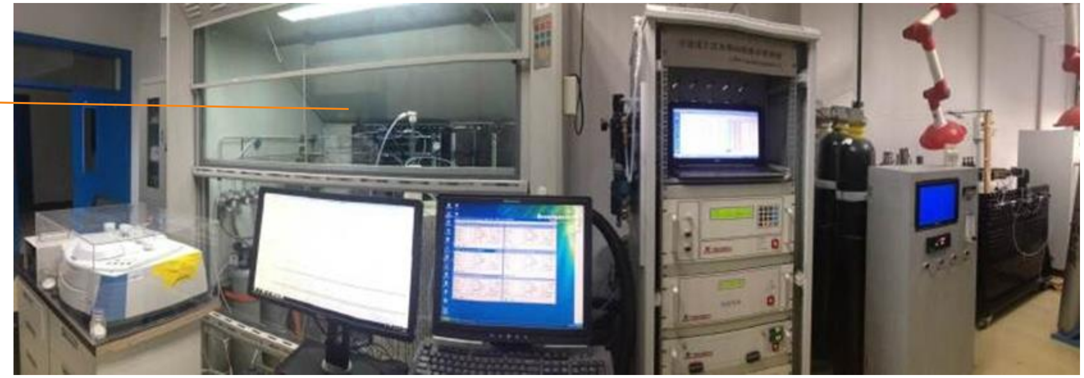
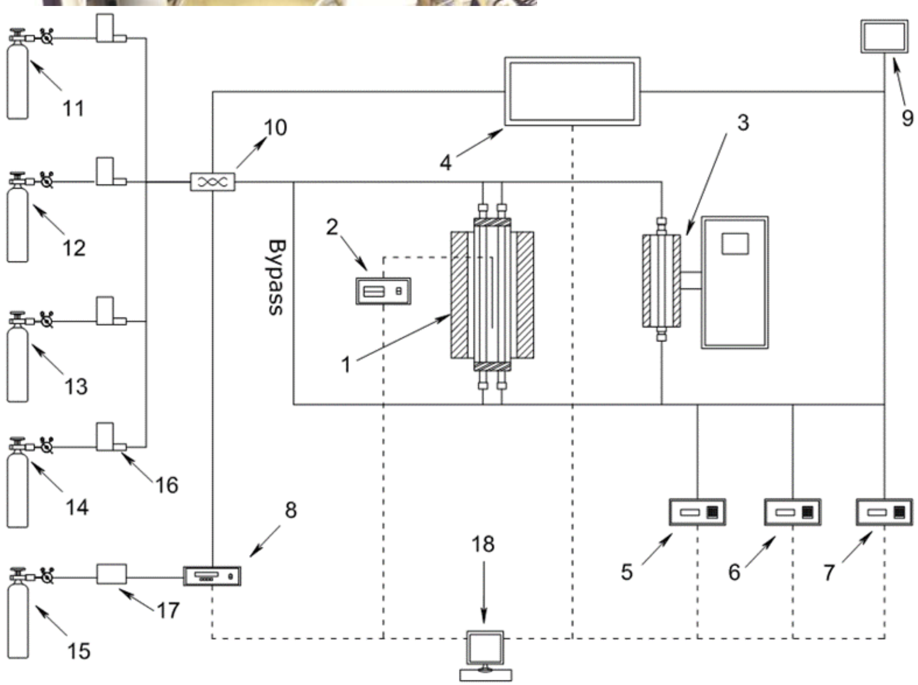




1. **Conventional reactor**; 2.Temperature controller; 3. **Single mode microwave reactor**; 4. **In-situ DRIFT**;

5. Hg^0 analyser; 6 Flue gas analyser;

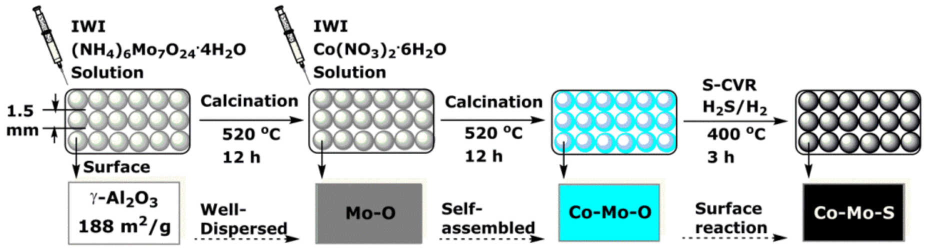
8. Hg^0 generator; 9. Exhaust gas treatment; 10. Blender; 11. Other gases cylinder; 14. N_2 gas cylinder; 15 N_2 gas cylinder; 16. Flowmeters; 17. AC filter;

18. Computer with data analysis software.

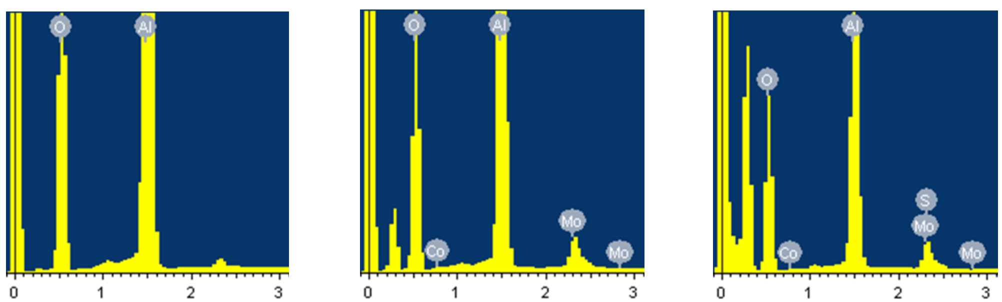
Schematic diagram of the experimental system
脱汞材料筛选和活性测试系统

Preparation
材料制备

活性物质自组装

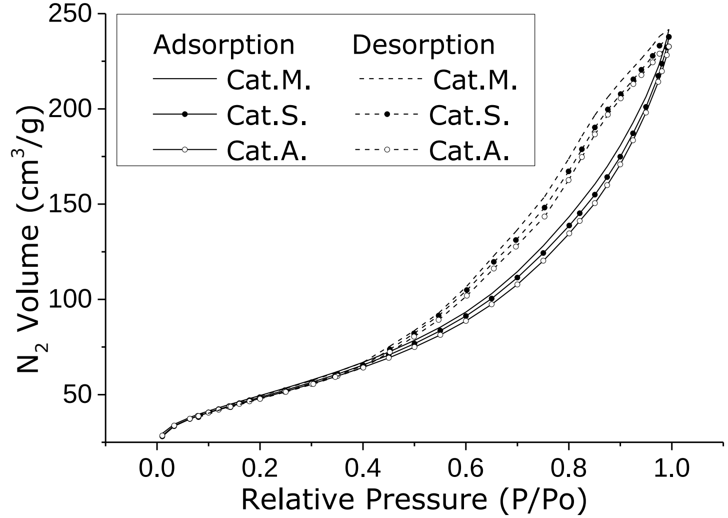


EDS spectrum



Phases transformation

Type IV isotherms:
Capillary condensation



N_2-adsorption-desorption isotherms plots

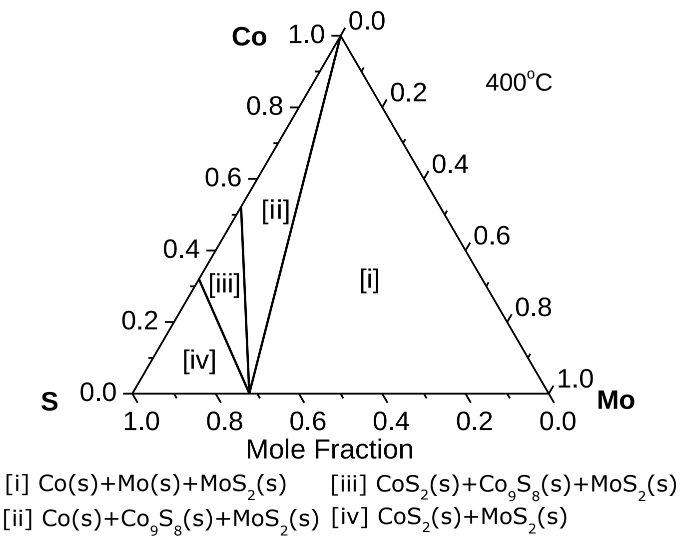
Textual properties & BJH pore distribution

Sample	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Width (nm)	Macropores (%)	Mesopores (%)	Micropores (%)
γ-Al_2O_3	188	0.49	10.3	6	88	6
CoMoO/γ-Al_2O_3	181	0.39	8.2	6	83	11
CoMoS/γ-Al_2O_3	177	0.37	8.2	6	83	11

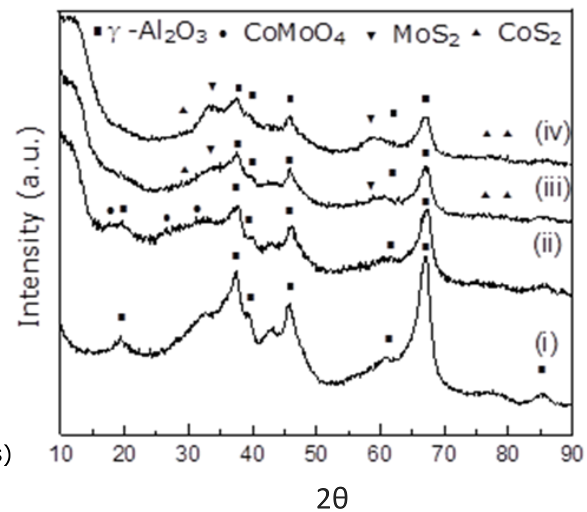
(Cat.M. - γ-Al2O3 supported metal oxide catalysts; Cat.S. – The catalysts with sulfurization; Cat.A.- the catalysts after around 7 h testing.)

Characterisation
材料表征

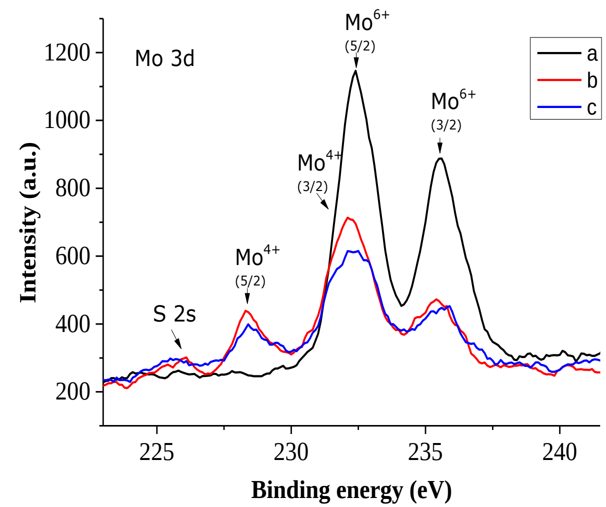
活性组分
MoS_2



Phase diagram



XRD analyses



XPS spectra

Surface chemistry

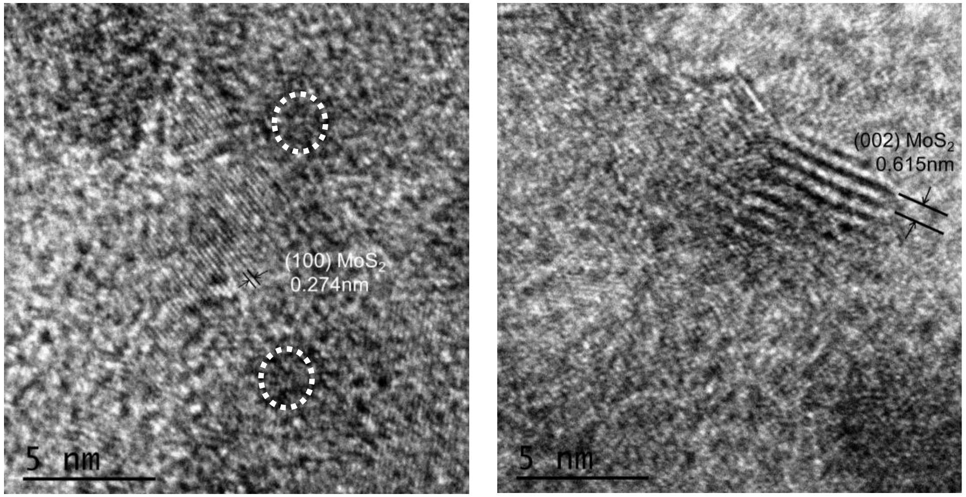
Sample/Product	Element concentration wt%				
	Al 2p	O 1s	Mo 3d	Co 2p	S 2p
γ-Al_2O_3	48.0	52.0	-	-	-
(a) CoMoO/γ-Al_2O_3	43.1	46.2	9.7	1.0	-
(b)CoMoS/γ-Al_2O_3	42.2	42.0	9.6	1.2	5.0
(c) CoMoS#/γ-Al_2O_3	43.7	43.0	8.6	1.2	3.5

XRD analyses of (i) γ-Al2O3, (ii) Cat.M., (iii) Cat.S. and (iv) Cat.A.
XPS spectra (Mo 3d) of (a) CoMoO/γ-Al2O3, (b) CoMoS/γ-Al2O3, and (c) CoMoS#/γ-Al2O3

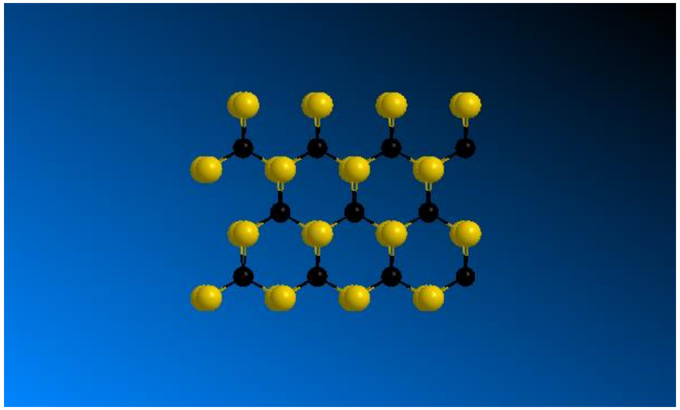
Characterisation
材料表征

具有类石墨烯结构的二维过渡金属二硫属化物

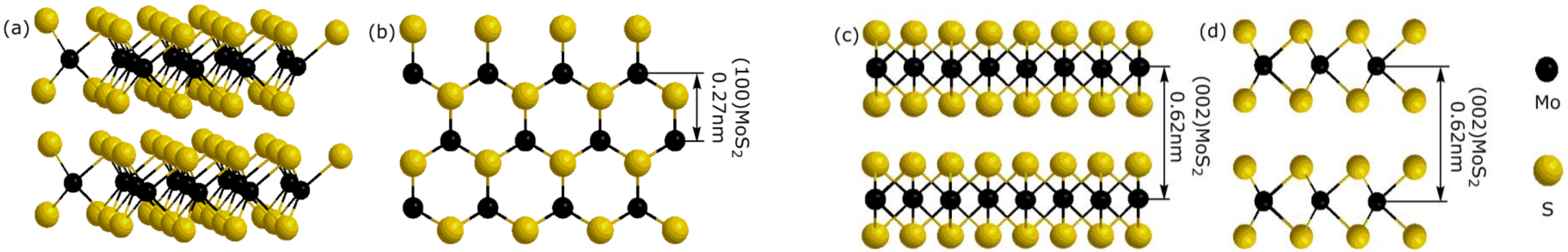
MoS_2超薄纳米层状结构



HREM images



Dynamic video



The layered MoS_2 nanosheets

(a) overall schematic structure, (b) (001) plane, (c) (100) plane, (d) (110) plane

Mercury adsorption
吸附活性

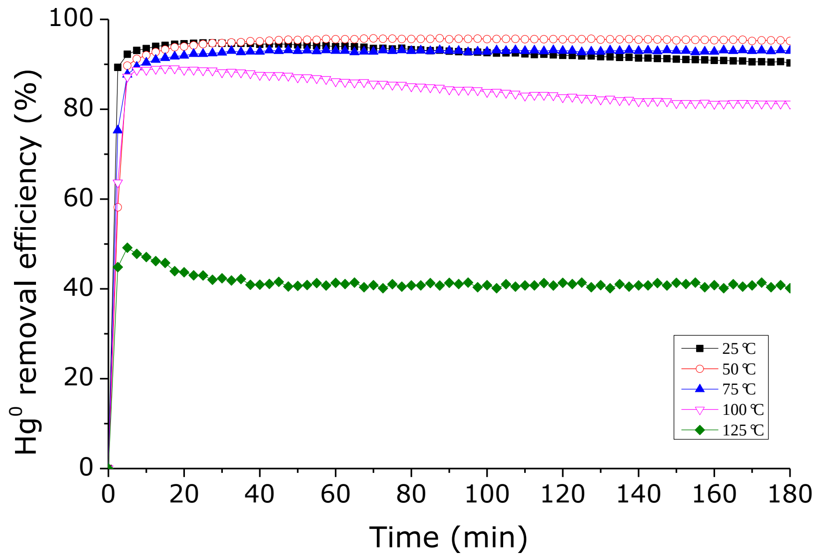


图 吸附剂不同温度下的吸附活性测试

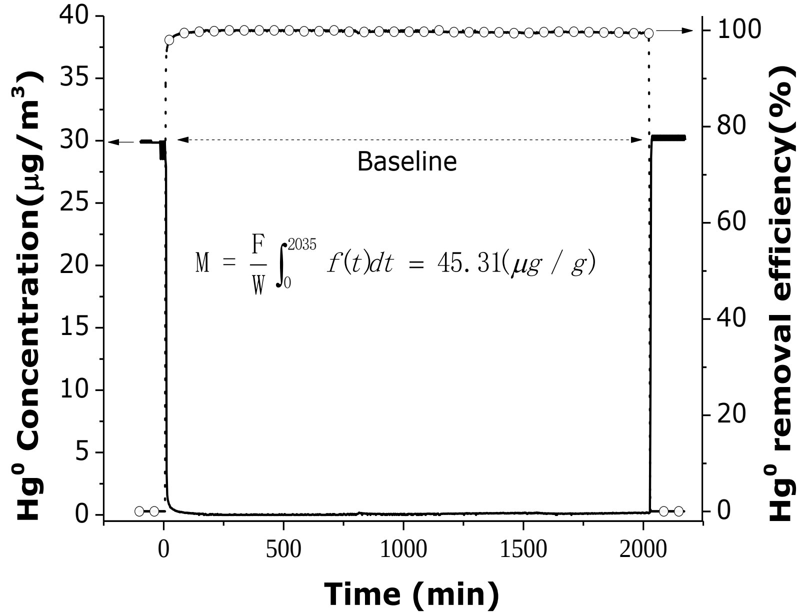


图 吸附剂长时间测试

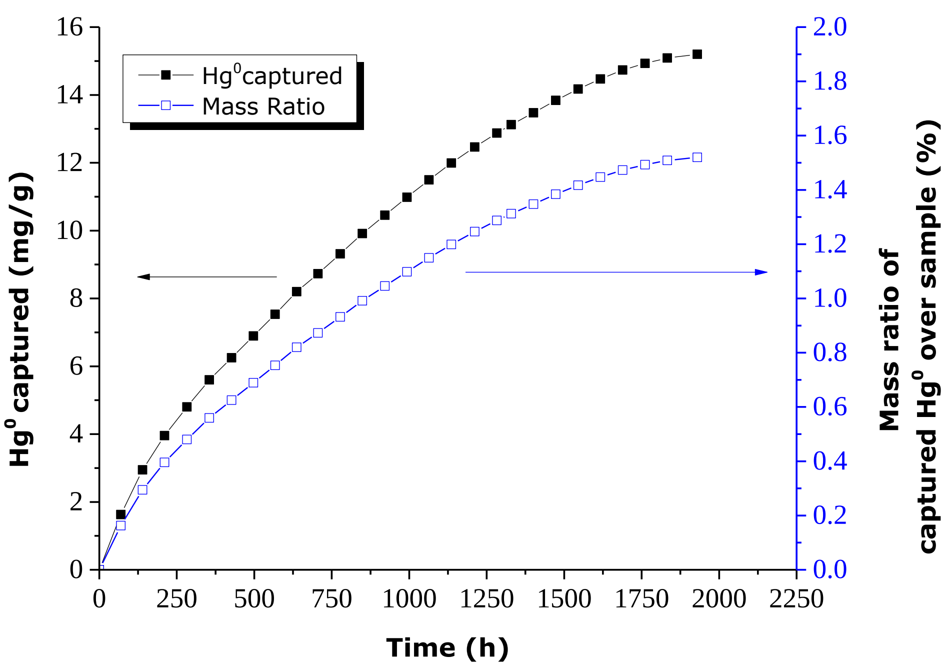
It is shown that 吸附活性测试结果表明：

❖The Co-Mo-S sorbent exhibited excellent performance in the removal of Hg^0 at lower temperatures. 此吸附剂具有低温超高活性；

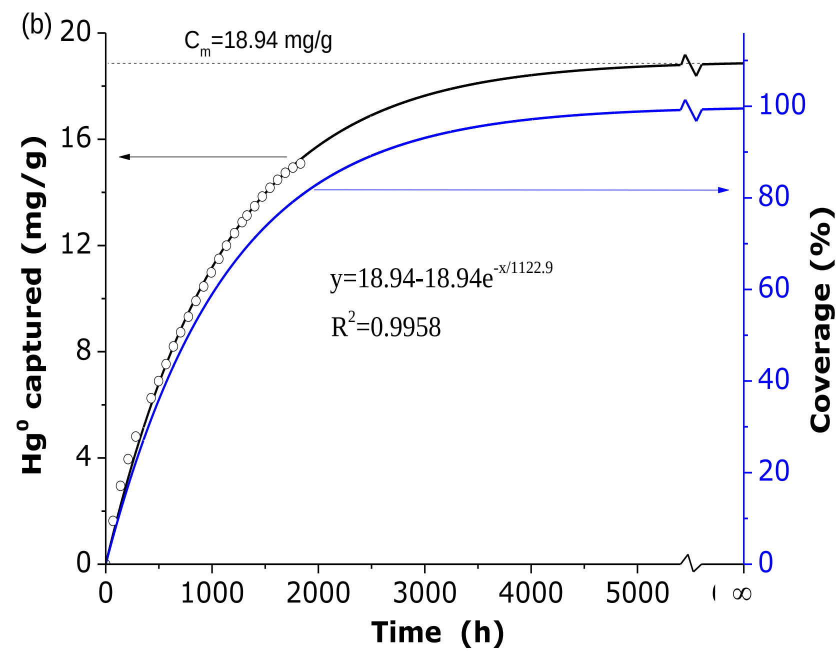
❖For 2000 min test, the removal efficiency remained at almost 100% with a calculated Hg^0 capture capacity of 45.31 μg/g. 30μg/m³的汞能够全部去除并且能维持活性2000分钟以上。

Long-period evaluation

- During the 2000 h test, the amount of Hg^0 captured was 15 mg/g.
- **To further understand the kinetics, the experimental data was analyzed by using the Elovich model.**
- **The non-linear mathematical function fitted well with the experimental data.**



2000 h test



2000 h test with kinetics study

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Regeneration of materials
脱附活性

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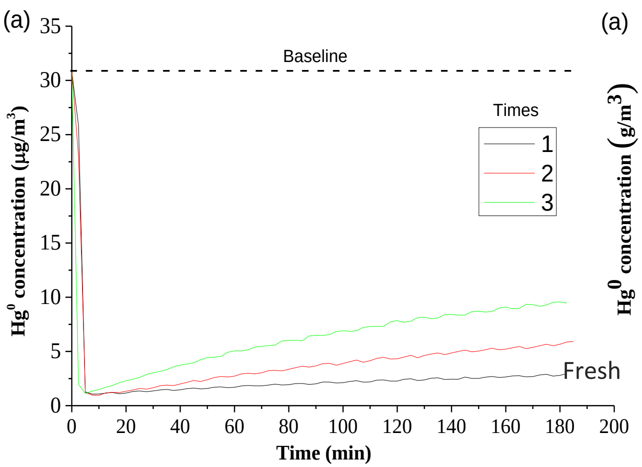
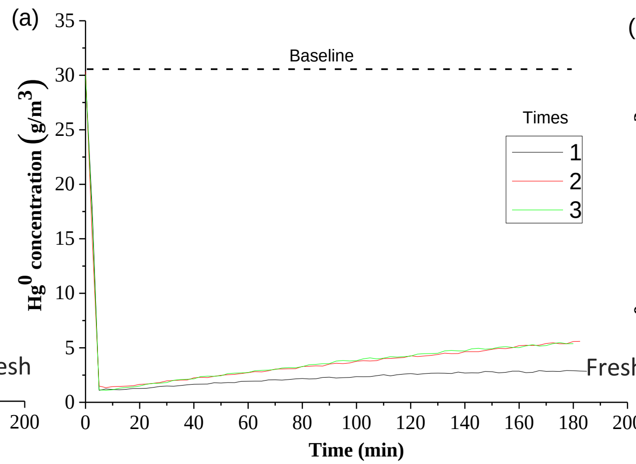
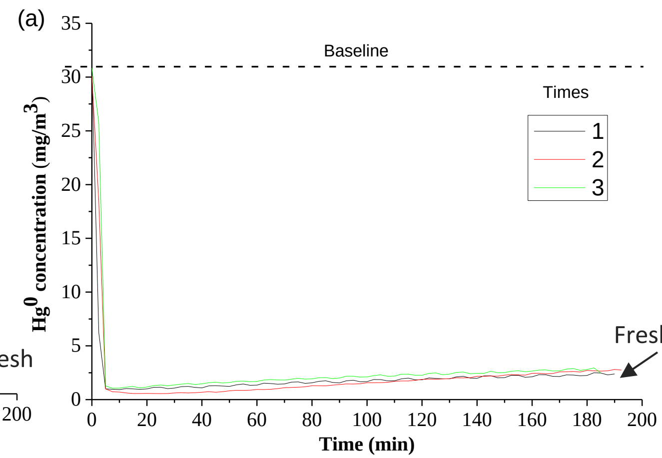


300°C 再生



250°C 再生



200°C 再生

It is shown that 脱附活性测试结果表明：

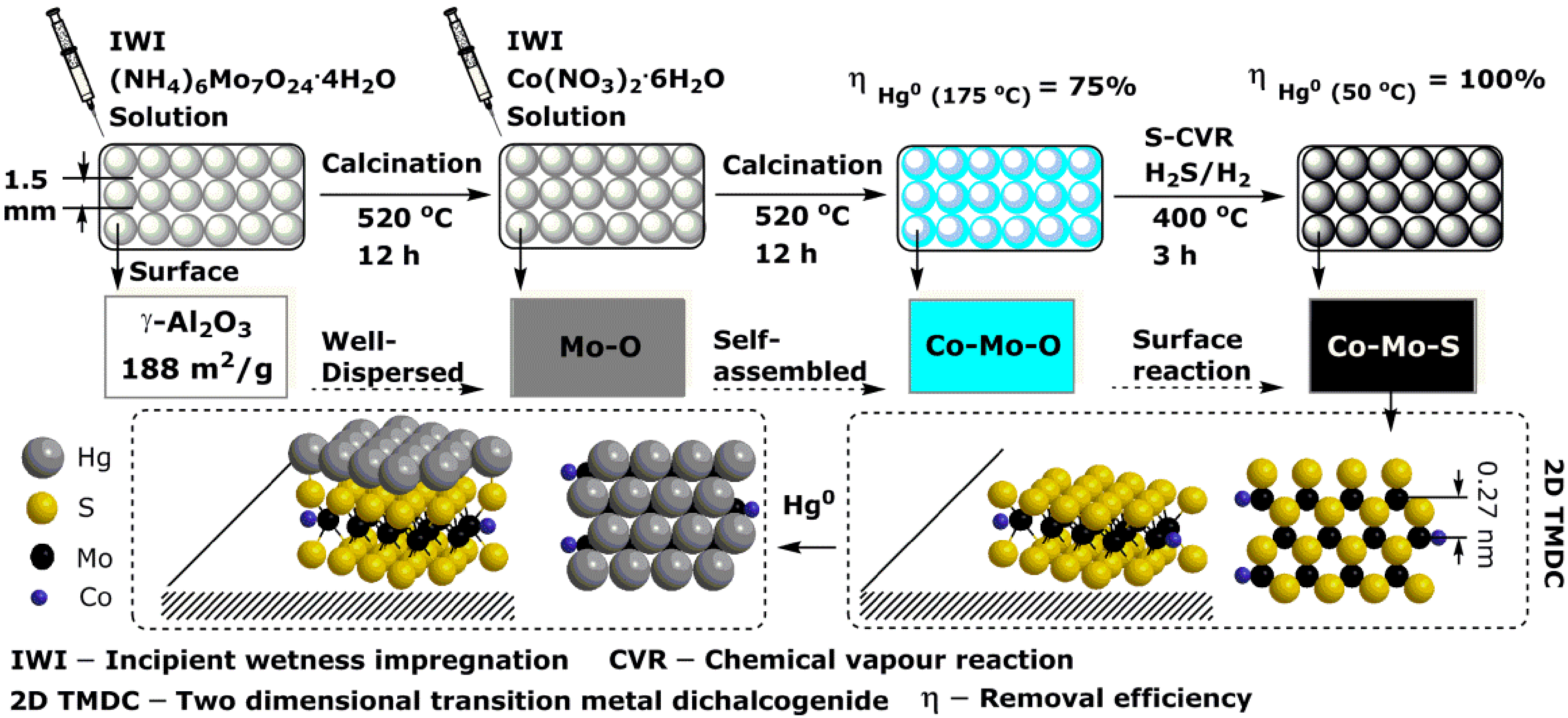
❖The regeneration temperature was found to be 200 ° C

此吸附剂在200 ° C的可再生性能最佳

❖Elemental mercury can be recovered as a resource

再生的同时有回收汞资源的巨大潜力。

Understanding of the Process
过程研究



Graphical abstract: Haitao Zhao et al., Environmental Science & Technology, under review.

专利：具有纳米层状结构的脱汞吸附剂及其制备方法（201510870489.02）

Conclusions
结论

- Graphene-like MoS_2 nanosheets containing materials were prepared and characterised. 本研究制备并表征了具有类石墨烯结构的二维过渡金属二硫属化物MoS_2超薄纳米层状结构；

- These materials showed excellent mercury removal capability at low temperatures. 吸附活性测试结果表明，此吸附剂具有低温超高脱汞活性；

- These materials can be regenerated at 200° C with the potential to recover mercury as a resource. 脱附活性测试结果表明，此吸附剂在200° C的可再生性能最佳，再生吸附剂的同时有回收汞资源的巨大潜力；

- Further study is need to explore the potential of these materials for commercial uses in the cleaning of a variety of gases. 具有纳米层状MoS_2结构的吸附剂可作为高效废气和燃气净化汞脱除材料进行进一步开发。

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Acknowledgement
致谢

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宁波市重大科技项目“燃煤电厂多种污染物联合脱除技术的研究与开发”(20012B10042)

宁波市电子废弃物资源化技术科技创新团队(2012B82011)

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