Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Title: Adsorptive Catalysis of Hierarchical Porous Heteroatoms-Doped Biomass: From Recovered Heavy Metal to Efficient Pollutant Decontamination

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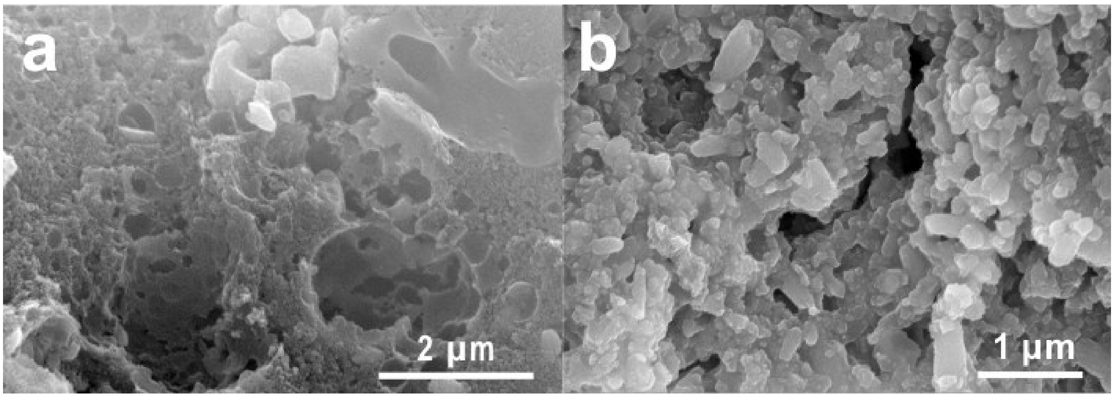

Figure S1. SEM image of the prepared a) CK and b) CS.

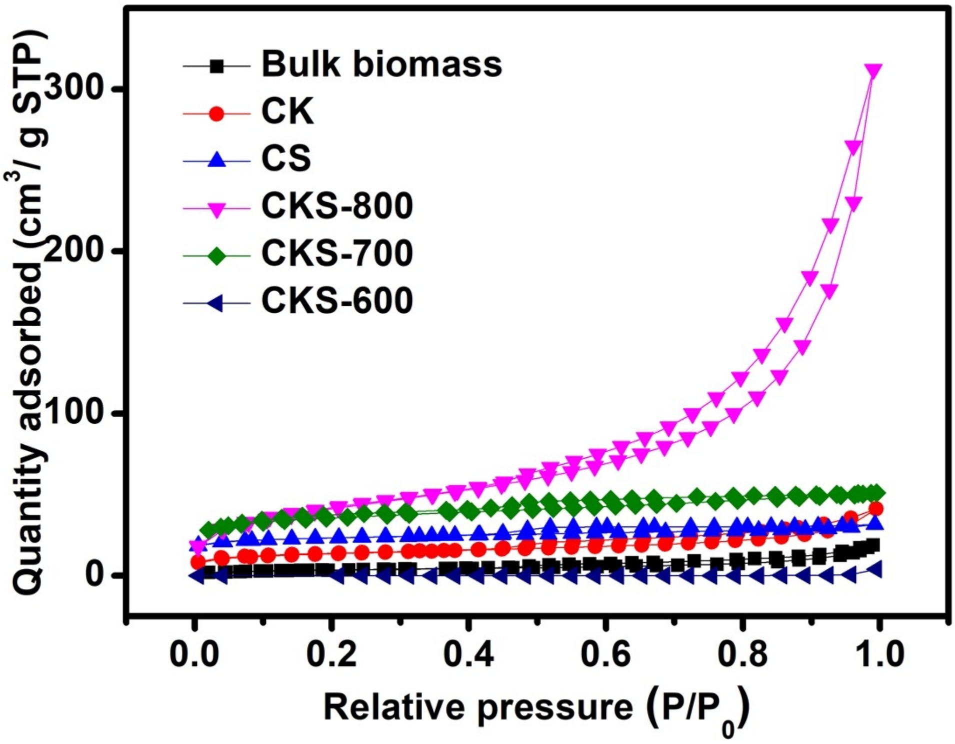

Figure S2. N_2 sorption isotherms of different biomass composites.

Table S1. Physico-chemical properties of the hierarchical porous carbons.

materials	textural properties			element composition (wt %)			
	S_{BET} (m^2 g^{-1})	pore volume (cm^3 g^{-1})	pore size distribution (nm)	C	N	O	S
Bulk biomass	12.62	0.031	1.152	63.43	1.53	27.46	-
CK	47.78	0.062	5.15	64.15	1.68	26.03	-
CS	79.77	0.049	2.44	66.97	1.72	12.65	5.04
CKS-600	66.49	0.059	4.08	63.44	2.62	12.17	4.62
CKS-700	111.76	0.079	2.83	72.11	1.17	8.52	7.13
CKS-800	152.08	0.481	12.54	78.18	1.05	5.89	9.42
CKS-Cu	154.64	0.431	11.37	-	-	-	-
Regenerated CKS	137.47	0.293	8.36	-	-	-	-
CKS-Cu after	147.15	0.395	8.23	-	-	-	-

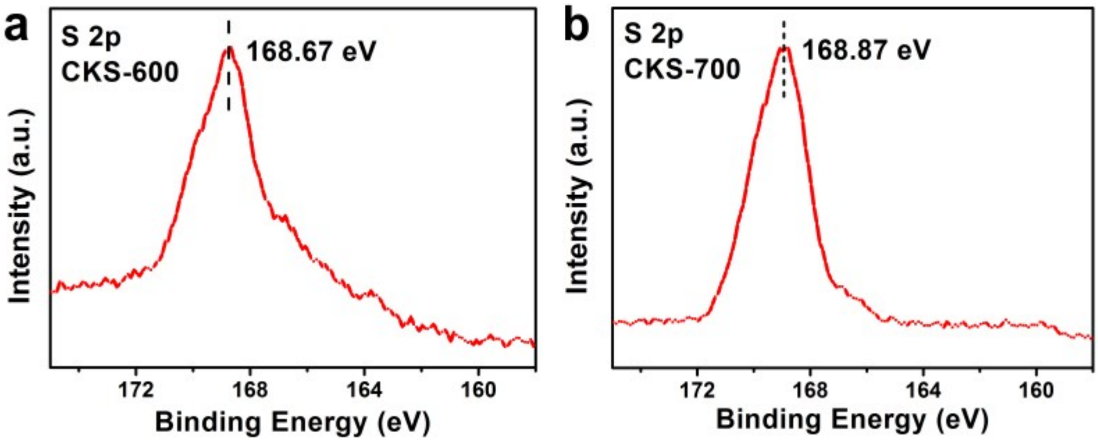

Figure S3. XPS spectra S 2p signal deconvolution of CKS-600 and CKS-700.

Results

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	8.24	**Peak 1:**	8.24	100.0	3.87
Zeta Deviation (mV):	3.87	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/c...	1.35	**Peak 3:**	0.00	0.0	0.00
Result quality	**Good**				

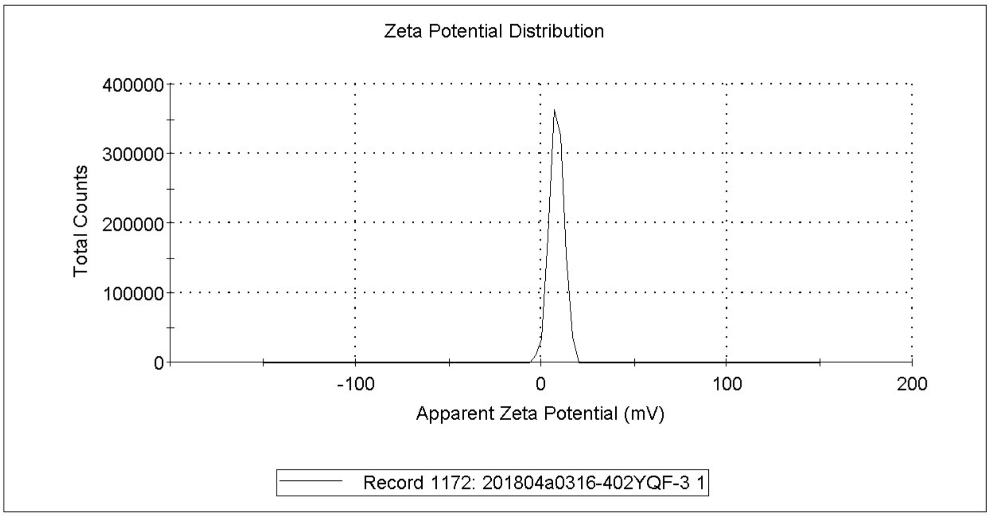

Figure S4. Zeta potential of hierarchical porous CKS biomass.

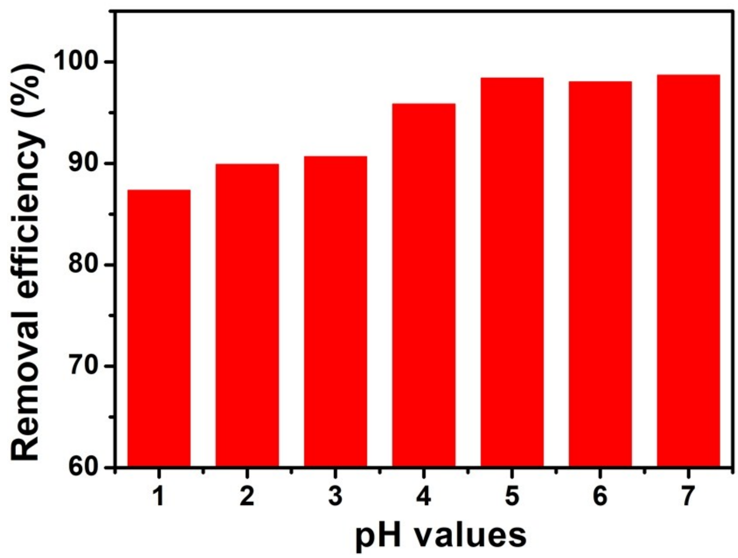

Figure S5. Removal efficiency of CKS toward Cu(II) under different pH values.

Table S2. Initial (before adsorption) and finial (after adsorption) pH values

	pH values					
initial	1.21	2.32	3.07	4.01	5.20	6.14
final	1.18	2.24	2.94	3.89	5.01	5.87

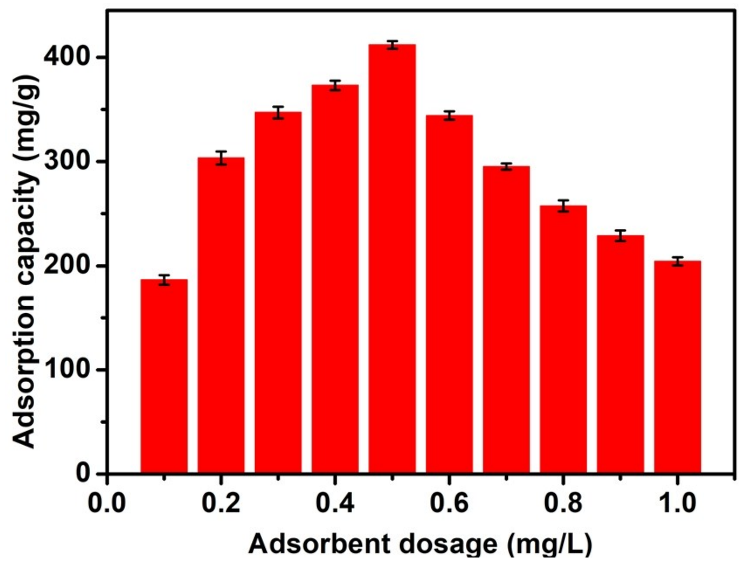

Figure S6. Adsorption capacities of CKS toward 300 ppm of Cu(II) under different adsorbent dosage.

Table S3. Kinetic parameters of metal ions adsorption on CKS

Single ions	pesudo-second-order				
	$q_{e,\ exp}$ (mg/g)	k_2 (g/mg min)	$q_{e,\ cal}$ (mg/g)	R^2	Fitting equation
Cu^{2+}	412.10	0.0002	414.14	0.997	t/q=0.029+0.002t
Ni^{2+}	312.88	0.0009	322.58	0.996	t/q=0.011+0.003t
Pb^{2+}	267.53	0.0003	264.12	0.998	t/q=0.047+0.004t

Table S4. Isotherm parameters of metal ions adsorption on CKS

single ions	$q_{m,exp}$ (mg/g)	Langmuir isotherm model				Freundlich isotherm model		
		k_L	$q_{m,\ cal}$ (mg/g)	R^2	Fitting equation	K_F (mg/g)	n	R^2
Cu^{2+}	1356.62	0.0071	1366.67	0.991	C_e/q_e=0.1+0.0007C_e	110.58	2.4888	0.9209
Ni^{2+}	1122.63	0.0104	1250.21	0.994	C_e/q_e=0.08+0.0008C_e	228.40	4.0766	0.9432
Pb^{2+}	612.31	0.0072	619.23	0.996	C_e/q_e=0.22+0.0016C_e	65.75	2.8353	0.9723

Table S5. XPS analysis of Surface Functionality

content/functionality (at.%)	CKS	CKS-Pb	CKS-Cu
total oxygen content	43.02	19.58	15.37
total sulfur content	10.73	1.63	1.41
O-M	7.18	9.02	9.17
O=C-O	4.45	3.82	2.38

Table S6. Estimated total cost for preparing 1 g of nanoadsorbents and corresponding adsorption capacities.

classfication	adsorbent	material	amount used	unit cost (dollar)	Cost (dollar)	total cost (dollar)	Cu^{2+} adsorption capacity	k_2 (g/mg min)	ref
metal oxide-based nanoadsorbent	Hematite (α-Fe_2O_3)	$FeCl_3$	2.7	6.52	17.60	**21.75**	84.46	0.0025 ($C_{Cu^{2+}, initial}$= 3.79 mg L^{-1})	1
		DI water	500	0.0226	11.3				
	γ-Fe_2O_3	HCl	0.05	0.549	0.027	**19.01**	26.8	-	2
		DI water	200	0.0226	4.52				
		$FeCl_3$	5.2	6.52	33.90				
		$FeCl_2$	2	3.18	6.36				
		NH_4OH	1.5	0.0826	0.1239				
		Tetramethylammonium hydroxide	1	0.2264	0.2264				
		99% Octyl ether	N/A	N/A					
	α-MnO_2 (OMS-1)	$NaSO_4$	0.15 M, 250 mL	0.1042	0.56	**1.84**	57.6	-	3
		$MnSO_4$	C_{Mn2+}=0.6 M, 400 mL	0.273	11.07				
		NaOH	5 M, 400 mL	0.1886	15.09				
	α-MnO_2 (OMS-2)	$MgCl_2$	1M	0.537	12.24	**10.35**	83.2	-	4
		DI water	250	0.0226	5.65				
		65% HNO_3	11.5	0.41	2.46				
		$KMnO_4$	2.1	1.592	3.34				
	TiO_2 monolith	TiO_2	4.6	8.68	39.93	**18.68**	398.72	-	5
		HCl	1M, 1000	0.046	46				
		5 M, tetrabutylammonium	N/A	8.08	N/A				
carbonhydrate	TEMPO	CNC	1 g	0.3	0.3	**2.72**	268.2	-	6

	oxided CNC								
		TEMPO	0.059	0.57	0.33				
		NaBr	0.325 g	0.112	0.04				
		NaClO	7.1 mL	0.19	1.35				
		Methanol	11 mL	0.063	0.7				
		NaOH	N/A	0.008	N/A				
		HCl	N/A	0.01	N/A				
based-adsorbent	Succinic anhydride/CNC	CNC	1 g	0.3	0.3	**0.78**	121.6	-	6
		Succinic anhydride	0.6 g	0.26	0.16				
		Sodium hydrogencarbonate	N/A	0.018	N/A				
		N,N-dimethylacetamide	5 mL	0.063	0.32				
	MWCNT					**42.35**	24.49	-	7
	SWCNT					**676**	24.29	-	8
carbon-based nanoadsorbent	MWCNT, carboxylic acid functionalized					**116.5**	77	-	9
	Graphene oxide					**2215**	294	0.016 ($C_{Cu^{2+}, initial}$= 5 mg L^{-1})	10
	Soy protein-based PEI hydrogel	soy protein isolate	1 g	0.06	0.06	**1.78**	136.2	0.0046 ($C_{Cu^{2+}, initial}$= 100 mg L^{-1})	11
		PEI (Mw % ca. 25000)	1 g	1.72	1.72				
biomass-based adsorbent		epichlorohydrin	N/A						
	soybean dregs-PAA	Soybean dregs	0.60 g	N/A		**0.11**	75.4	0.0333 ($C_{Cu^{2+}, initial}$= 150 mg L^{-1})	12
	tea waste					**N/A**	48	0.0133 ($C_{Cu^{2+}, initial}$= 200 mg L^{-1})	13
	Activated slag					**N/A**	30	-	14

	Sewage sludge					**N/A**	83	-	15
	CKS	soybean dregs	1 g	8.3×10^{-7}	8.3×10^{-7}	**0.041**	1366.67	0.0002 ($C_{Cu^{2+}, initial}$= 100 mg L^{-1})	This work
		$CaSO_4$	1 g	0.022	0.022				
		oxalate	1 g	0.019	0.019				

Detailed information: CNC, cellulose nanocrystals; DNPH, 2,4-Dinitrophenylhydrazine; PEI, polyethylenimine; PAA, poly(acrylic acid)

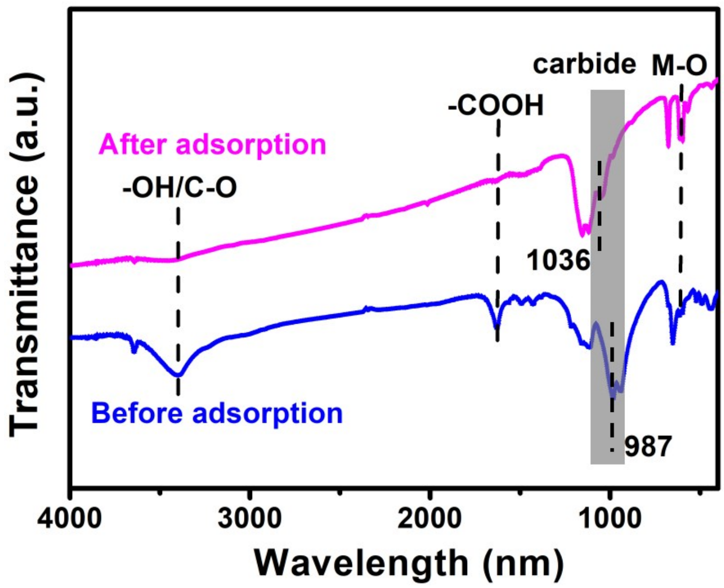

Figure S7. FT-IR spectra of CKS before and after Cu(II) adsorption.

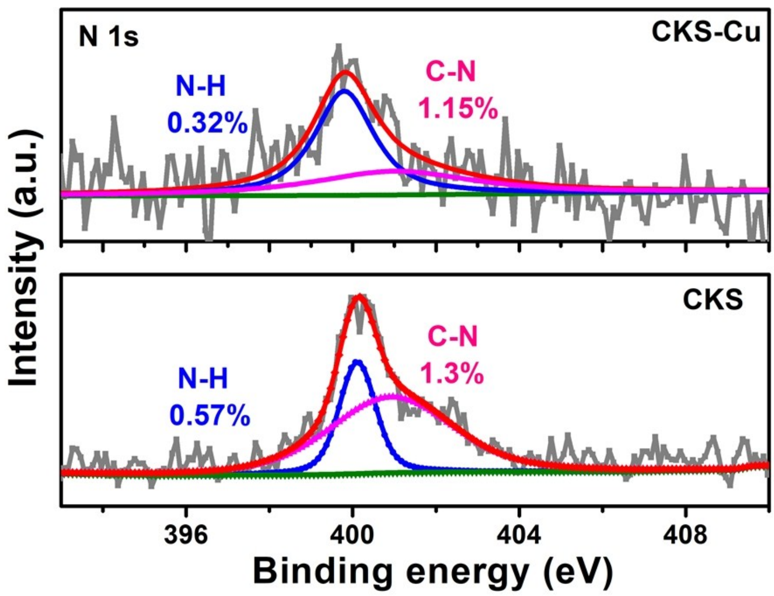

Figure S8. XPS detailed studies of N 1s signal deconvolution of CKS biosorbent before and after Cu^{2+} adsorption.

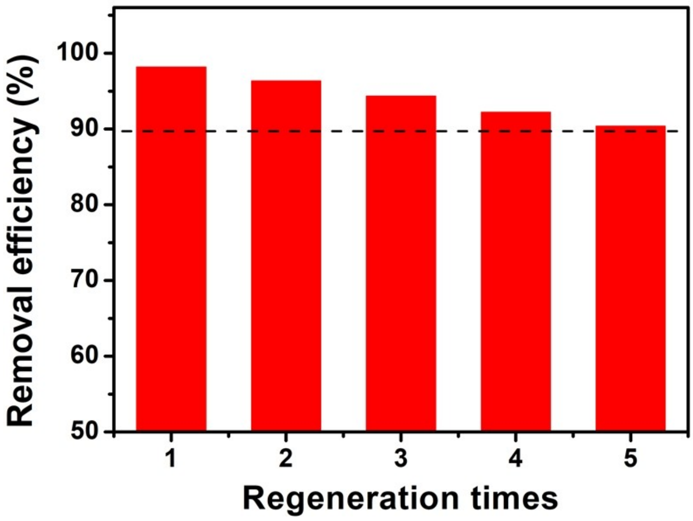

Figure S9. Cu(II) removal efficiency and recycling of CKS biomass adsorbents. The initial concentration of Cu(II) is 10 mg L^{-1}.

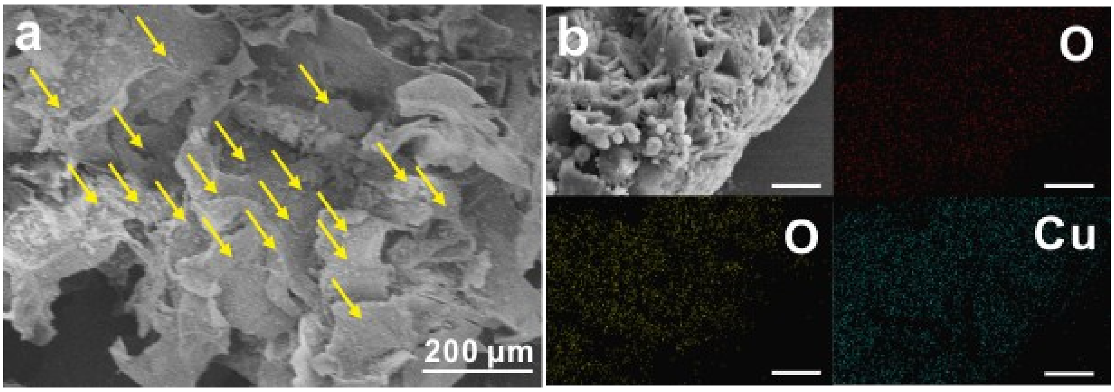

Figure S10. a) SEM image of CKS, the arrows label the Cu nanoparticles on the surface of CKS. b) Mapping images of CKS-Cu, the scale bar is 2 μm.

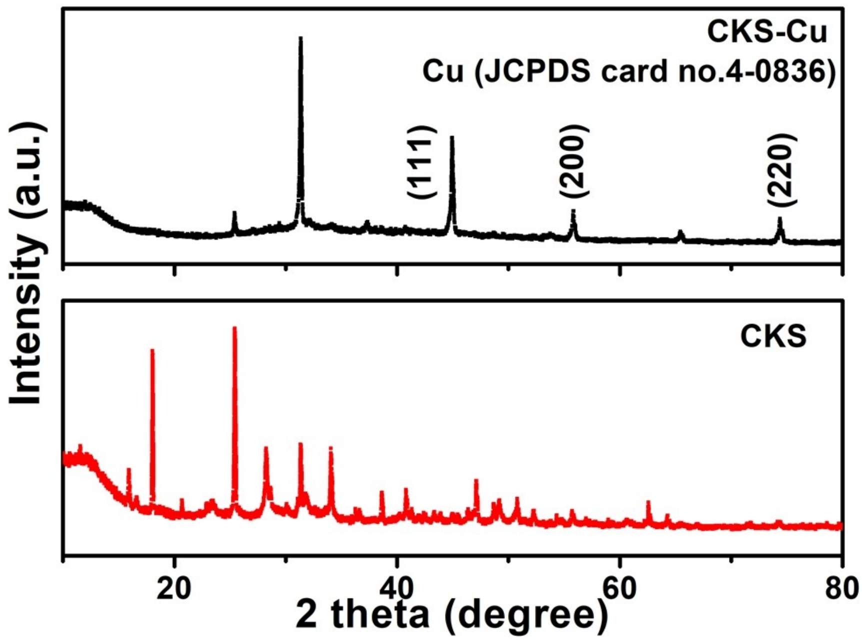

Figure. S11 XRD patterns of CKS before and after Cu^{2+} adsorption.

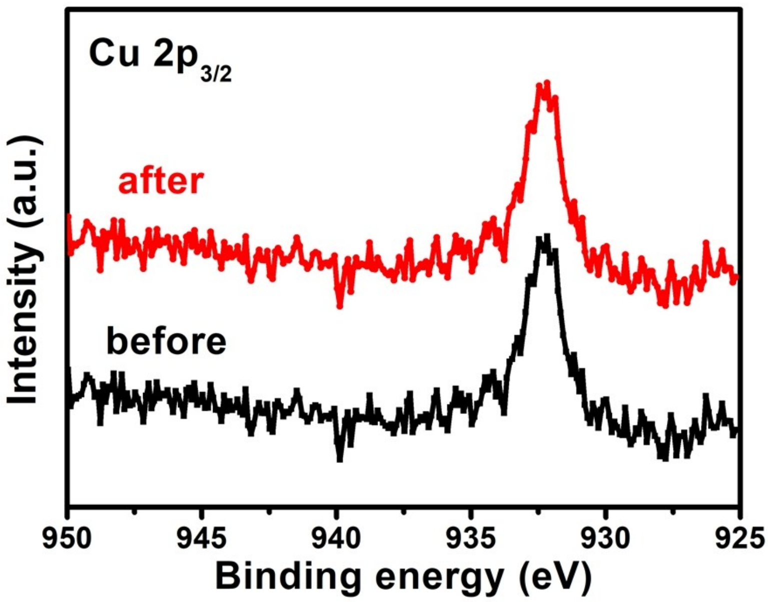

Figure. S12 XPS patterns of Cu 2p of CKS-Cu before and after Cr^{VI} reduction.

Reference:

[1] Y.-H. Chen, F.-A. Li, *J. Colloid Interface Sci.,* 2010, **347**, 277-281.

[2] J. Hu, G. H. Chen, I. M. C. Lo, *Water Res.,* 2005, **39**, 4528-4536.

[3] J. Pakarinen, R. Koivula, M. Laatikainen, K. Laatikainen, E. Paatero, R. Harjula, *J. Hazard. Mater.,* 2010, **180**, 234-240.

[4] R. Koivulaa, J. Pakarinenb, M. Siveniusb, K. Sirolab, R. Harjulaa, E. Paaterob, *Sep. Purif. Technol*. 2009, **70**, 53-57.

[5] W. Zhao, I. W. Chen, F. Xu, F. Huang, *J. Mater. Chem. A*, 2017, **5**, 15724-15729.

[6] S. Hokkanen, A. Bhatnagar, M. Sillanpää, *Water Res.* 2016, **91**, 156-173.

[7] Y. H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, B. Wei, *Carbon*, 2003, **41**, 2787-2792.

[8] O. Moradi, K. Zare, M. Monajjemi, M. Yari, H. Aghaie, *Fullerenes, Nanotubes, and Carbon Nanostructures*, 2010, **18**, 285-302.

[9] J. Liu, D. Su, J. Yao, Y. Huang, Z. Shao, X. Chen, *J. Mater. Chem. A*, 2017, 5, 4163-4171.

[10] R. Sitko, E. Turek, B. Zawisza, E. Malicka, E. Talik, J. Heimann, R. Wrzalik, *Dalton Trans.*, 2013, **42**, 5682-5689.

[11] J. Liu, D. Su, J. Yao, Y. Huang, Z. Shao, X. Chen, *J. Mater. Chem. A*, 2017, **5**, 4163-4171.

[12] M. Zhang, L. Song, H. Jiang, S. Li, Y. Shao, J. Yang, J. Li, *J. Mater. Chem. A*, 2017, 5, 3434-3446.

[13] B. M. Amarasinghe, P. K., W., R. A.Williams, *Chem. Eng. J.*, 2007, **132**, 299-309.

[14] V. K. Gupta, *Ind. Eng. Chem. Res.*, 1998, **37**, 192-202.

[15] S. Rio, C. Faur-Brasquet, L. Le Coq, P. Courcoux, P. Le Cloirec, *Chemosphere*, 2005, **58**, 423-437.