Electronic Supplementary Information

Preparation of silver-tungsten nanostructure materials for selective oxidation of toluene to benzaldehyde with hydrogen peroxide†

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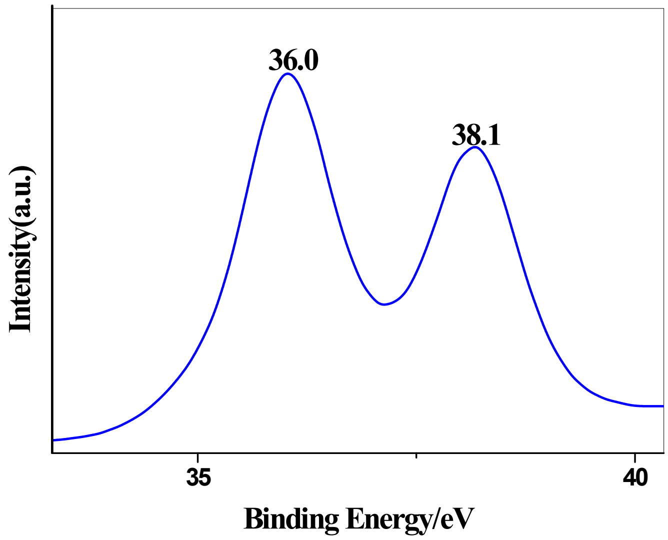


Fig. S1 W $2p_{3/2}$ core level spectra of AgW-N catalyst.

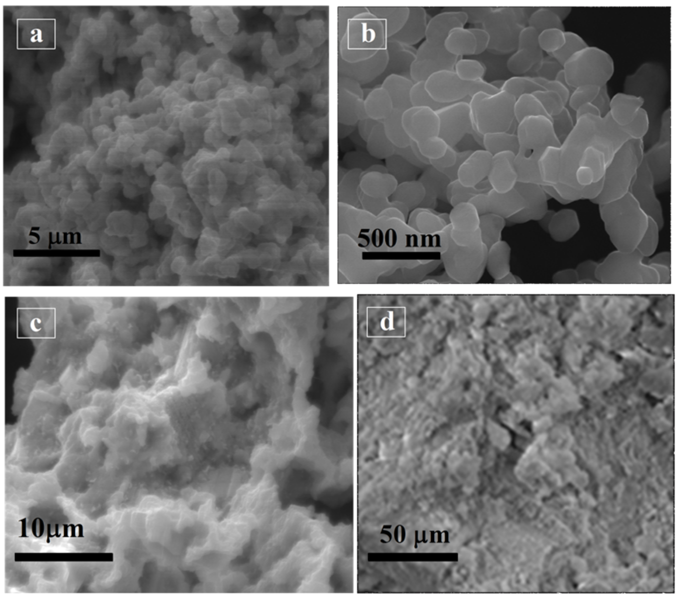


Fig. S2 SEM images of Ag/WO_3 catalyst a) without addition of CTAB, b) WO_3 catalyst, without addition of Ag, c) without addition of hydrazine and d) AgW^{imp} catalyst prepared by conventional impregnation method.

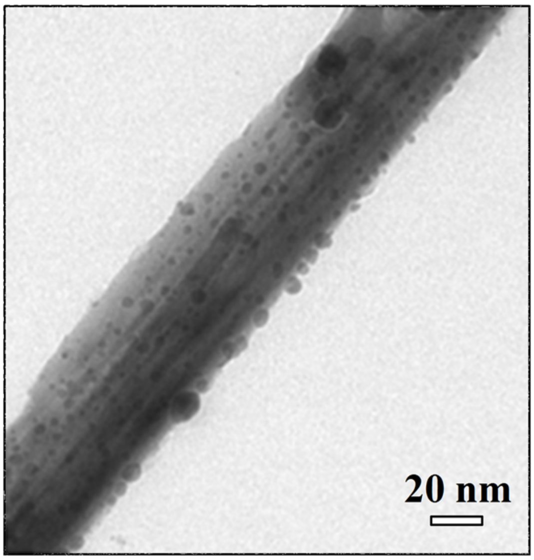
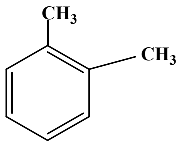
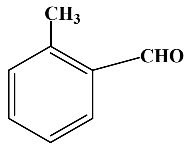
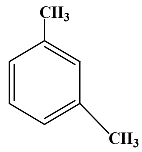
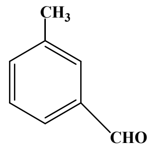
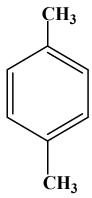
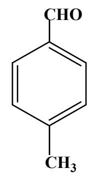
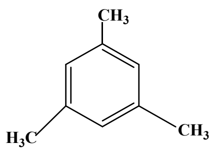
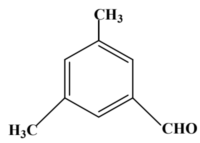
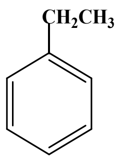
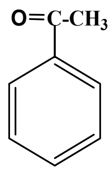
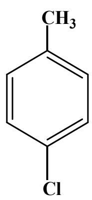
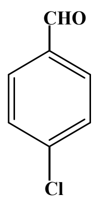


Fig.S3 TEM image of the spent AgW-N nanostructure catalyst.

Table S1 XPS analysis of Ag/WO_3 catalyst with various morphologies.

Catalysts	**Ag3d Binding Energy (eV)**	
	Ag3d5/2	**Ag3d7/2**
AgW-N	368.5	374.5
AgW-A	368.3	374.4
AgW-H	368.2	374.2

Table S2. Activities of the AgW-N nanostructure catalyst on different substituted aromatic alkanes[a]

Entry	**Substrate**	**Conversion (%)**	**Main Product**	**Selectivity (%)**
1.		63		95
2.		52		92
3.		69		96
4.		57		94
5.		73		97
6.		25		91

[a]Reaction conditions: solvent (acetonitrile) = 10ml, substrate (Toluene) = 1g, weight of the AgW-N nanostructure catalyst = 0.10 g, silver loading= 4.6 wt%, reaction temperature = 90 °C; time = 16 h; toluene: H_2O_2 mole ratio = 1:3.

Table S3. Catalytic activities of different reported catalysts for toluene to benzaldehyde reaction.

Entry	Catalyst	Temperature (°C)	Oxidant	Condition	Toluene Conversion (%)	Benzaldehyde Selectivity (%)	References
1.	$CNB_{0.15}$	150	H_2O_2	In autoclave	12.4	99	1
2.	TiO_2 supported Au-Pd	80	TBHP	Atmospheric pressure	4.4	32	2
3.	V-substituted polyoxometalate	70	TBHP	Atmospheric pressure	76	83	3
4.	CrS-1 molecular sieve	80	TBHP	6	18.4	23.3	4
5.	g-C_3N_4	160	O_2	2	2.6	99	5
6.	CeO_2	150	O_2	4	11	99	6
7.	Fe-Cu	190	O_2 in presence of pyridine, 10 bar pressure	2	7	86	7
8.	Ag/WO_3	90	H_2O_2	Atmospheric pressure			Our work

1. Y. Wang, H. R. Li, J. Yao, X. C. Wang and M. Antonietti, *Chem. Sci.,* 2011, **2**, 446.

2. M. I. bin Saiman, G. L. Brett, R. Tiruvalam, M. M. Forde, K. Sharples, A. Thetford, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, D. M. Murphy, D. Bethell, D. J. Willock, S. H. Taylor, D. W. Knight, C. J. Kiely and G. J. Hutchings, *Angew. Chem. Int. Ed.,* 2012, **51**, 5981.
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6. J. Lv, Y. Shen, L. Peng, X. Guo and W. Ding, *Chem. Commun*., 2010, **46**, 5909.
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The detail kinetic calculation is provided :

$t_{(1/2)} = 0.03r^2/D_p$ (a)

$t_{(1/2)} = 0.23r\delta/D_f \, x(C_0/C_e)$ (b)

Where

r = Radius of adsorbent in cm

δ = Thickness of water film adhered to the adsorbent in cm (assume = 0.001cm)

D_p = Pore diffusion coefficient in cm^2/s

D_f = Film diffusion coefficient in cm^2/s

C_0 = Concentration of metals on adsorbent in mg/gm

C_e = Concentration of metals in solution at equilibrium in mg/l

$t_{(1/2)}$ = time required to bring down the metals concentration to half of initial concentration in seconds.

$t_{(1/2)}$ has been calculated from equation no. (c)

$$t_{(1/2)} = -\frac{[ln(0.5)]}{K1} \quad (c)$$

To findout the rate limiting step of the overall adsorption the value of first order rate constant (K_1) obtained from the slopes of the straight lines of first order model.

$\ln(q_e - q_t) = \ln(q_e) - K_1 t$

K_1 is the slope of graph

Initial concentration of toluene

Density of toluene = 0.87 gm/ml

Density of 505 H2O2= 1.197 gm/ml

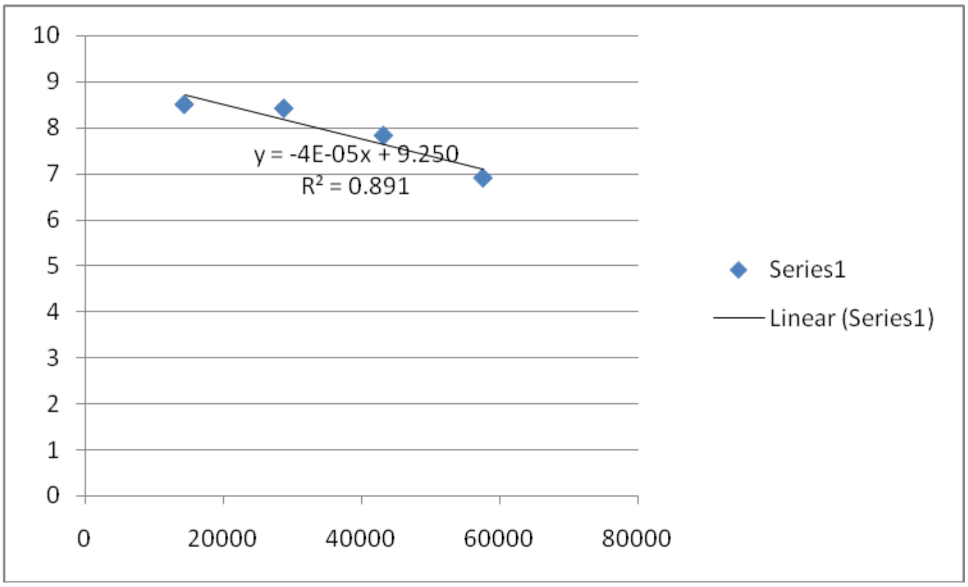
Total volume= 10ml AN + (1/0.87)ml of TOLUENE+(2.2/1.197) ml of H2O2

Total volume= 12.98ml

So toluene concentration= (1000*1000)/12.98

= 77000mg/l

t	ce		qe mg/gm	ln(qe-qt)
14400	3	74690	300.312	8.497947
28800	7	71610	700.728	8.412782
43200	27	56210	2702.808	7.824922
57600	42	44660	4204.368	6.908387
86400	52	36960	5205.408	#NUM!



Slope= -4*10^-5

$K_1 = 4x10^{-5}$

$$t_{(1/2)} = -\frac{[ln(0.5)]}{K1}$$

$t(1/2) = -ln(0.5)/\ 4*10^{-5}$

= 17328

r = 5Nm

= $5*10^{-7}$cm

$t_{(1/2)} = 0.03r^2/D_p$

$Dp = 0.03x(5x10^{-7})^2/17328$

$Dp = 4.328\ x\ 10^{-19}\ Cm^2/S$

$t_{(1/2)} = 0.23r\delta/D_f\, x(C_0/C_e)$

C_0 = Concentration of metals on adsorbent in mg/gm

C_e = Concentration of metals in solution at equilibrium in mg/l

Ce = 36960 mg/l

Co = (77000 – 36960)/7.692

= 5205.4

$D_f = 0.23r\delta/\, t_{(1/2)}\, x(C_0/C_e)$

Df= 0.23x $5x10^{-7}$x 0.001x 5204.4/(17328x 36960)

= $9.34x10^{-6}$ cm2/s

As the Df value is very small, we say that this is not a control reaction.

Table S4. Recyclability test of AgW-N nanostructure catalyst for the oxidation of toluene to benzaldehyde.

Recycling No.	Conversion of toluene (%)	Selectivity to benzaldehyde (%)	Yield(%)
1	42	93	39.0
2	42	92.5	38.8
3	42	92	37.7
4	42	92	38.6

Reaction Condition: solvent (acetonitrile) = 10 ml; Toluene =1g; weight of catalyst = 0.10 g; Toluene: H_2O_2 mole ratio =1:3; temperature = 90 °C, time= 16 h.