Supporting Information

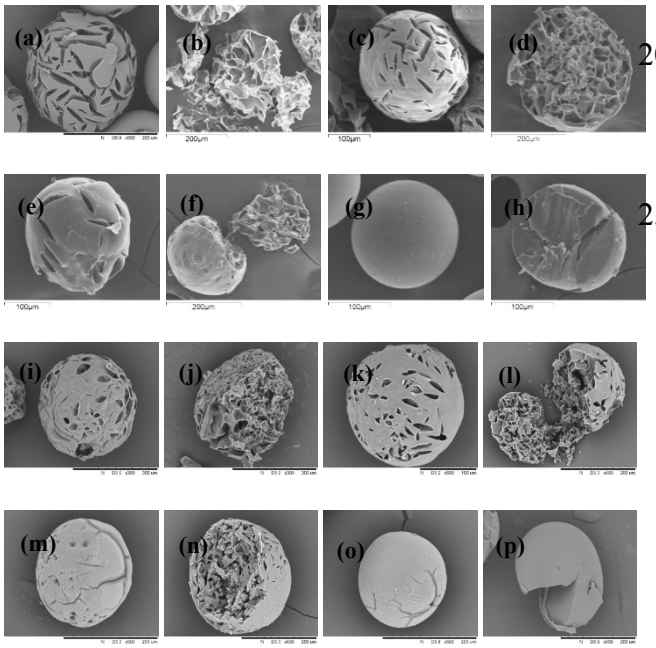


Fig.S1 SEM images of microspheres; (a)-(h) microspheres gelated for 12h, pre-solidification time for (a)(b), (c)(d), (e)(f) and (g)(h) was 10min, 20min, 30min and 40min, respectively; (i)-(p) gelated for 17h, pre-solidification time for (i)(j), (k)(l), (m)(n) and (o)(p) was 10min, 20min, 30min and 40min, respectively.

By comparing with the published work, the porous chitosan/silica core-shell hybrid microspheres have advantages in its adsorption performance of metal ion, like Cu(II) and Pd(II), as shown in Table S1 and S2. The chitosan/silica core-shell composite showed better adsorption property than chitosan-silica composite with uniform component distribution because the silica shell could provide effective protection for the chitosan from reacting with glutaraldehyde.

Table S1 Adsorption of Cu(II)

Adsorbents	Maximum adsorption capacity(mg/g)	Adsorption time/min
SBA-15 grafted with aminopropy and then calcination (1)	15(C_0=100ppm)	120
Chitosan-cellulose (non-crosslinked) (2)	51(C_0=100ppm)	700
Chitosan-cellulose (crosslinked) (2)	37(C_0=100ppm)	500
Chitosan-silica composite (3)	53(C_0=100ppm)	360
Chitosan/silica composite (present work)	89(C_0=100ppm)	600

(1) *A. Shahbazi, H. Younesi and A. Badiei, Chemical Engineering Journal, 2011, 168, 505-518.*
(2) *N. Li and R. Bai, Separation and Purification Technology, 2005, 42, 237-247.*
(3) *H. Zhao, J. Xu, W. Lan, T. Wang and G. Luo, Chemical Engineering Journal, 2013, 229, 82-89.*

Table S2 Adsorption of Pb(II)

Adsorbents	Maximum adsorption capacity(mg/g)	Adsorption time/min
Pb(II) ion-imprinted polymer (1)	26(C_0=100 ppm)	40
Pb(II)-IIP on nano-TiO_2 matrix (2)	120(C_0=80 ppm)	370
Chitosan/silica composite (present work)	31(C_0=100 ppm)	180

(1) Y. Liu, Z. Liu, J. Gao, J. Dai, J. Han, Y. Wang, J. Xie and Y. Yan, *J Hazard Mater*, 2011, **186**, 197-205.
(2) S. Jayakumar, T. Gomathi and P. N. Sudha, *Int J Biol Macromol*, 2013, **59**, 165-169.

Fig. S2 is the measurement equipment of mechanical property. Three uniform-sized microspheres forming an equilateral triangle were put between two glass sides. Then weights were added onto the center of the glass slide one by one until at least one of the microspheres was broken. The process was operating under the microscope to observe whether the sphere was broken or not. Mechanical intensity was calculated by dividing the spheres' weight bearing with the whole sectional area of the three spheres.

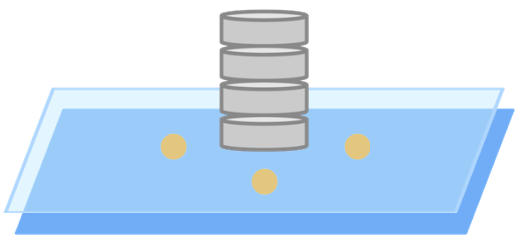


Fig. S2 The measurement equipment of mechanical property

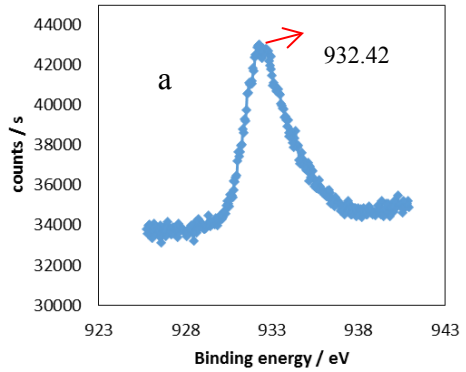
Table 1 shows the lost ratio of Cu during the catalysis. After every cycle of use, a certain amount of water from reaction solution would be taken out to determine how much Cu was lost during the process using Raman atomic absorption spectrophotometer (Type Z-5000, Hitachi, Japan).

Table S3 Lost ratio of Cu

No of cycles	Cu lost ratio%
1	0.210
2	0.093

3	0.039

Fig. S3 shows the XPS results of Cu before and after inactivation. Analysed by the software of XPSpeak41, it can be found that when the catalyst loses part of activity, there are more than half of the Cu(I) becoming Cu(II).



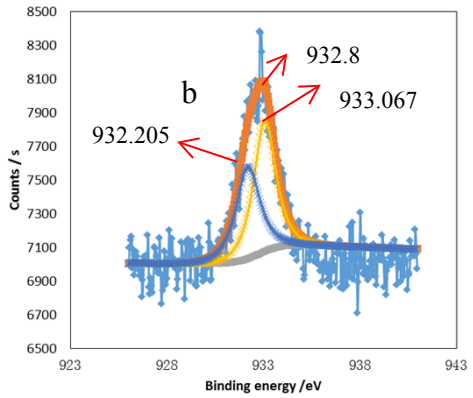
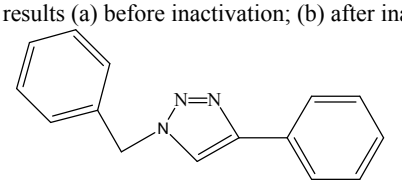


Fig. S3 XPS results (a) before inactivation; (b) after inactivation.



IR(KBr, cm^{-1}): 3121, 3096, 3063, 3031, 2927, 2654, 2363, 1654, 1606, 1496, 1483, 1466, 1455, 1442, 1427, 1357, 1333, 1224, 1205, 1156, 1140, 1075, 1049, 1028, 1002, 975, 913, 859, 827, 805, 766, 729, 693, 617, 579, 509.

MS (ESI) m/z: 236.2 [M+H]+; [M+NH_4-2H^+]: 250.10.