Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

A general autocatalytic route toward silica nanospheres with ultrasmall sized and well-dispersed metal oxides nanoparticles

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Experimental

Materials

(3-Aminopropyl) triethoxysilane (APTES, ≥99%), bromoacetic acid (HBA, ≥99%) and polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich corporation (shanghai, China). Zinc oxide (ZnO, 99.9%), basic cupric carbonate ($Cu_2(OH)_2CO_3$, 99.9%) and cadmium oxide (CdO, 99.99%) were purchased from Aladdin company (shanghai, China). absolute ethanol (EtOH, ≥99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd (shanghai, China). The water used in experiments was deionized with the resistivity of 18 $M\Omega \cdot cm^{-1}$. All the reagents were used as obtained without further purification.

Preparation of metal bromoacetate (MBA)

Take the synthesis of ZnBA as an example, typically, ZnO (4.07g, 0.05mol) and HBA (13.89g, 0.1mol) were mixed in 150 mL deionized water under magnetic stirring at 60°C. After stirring for 4 h, the mixture was filtered and the filter liquor was applied vacuum-rotary evaporation at room temperature to remove water and then collected the white powder. The other metal bromoacetate, including CuBA, CdBA, were prepared by the same process as that of ZnBA.

Preparation of mNPs@SiO_2 nanocomposites

PVP (0.5 g, M_w=1300000) were dissolved in 18 mL absolute ethyl alcohol, and then APTES (1.2 mL, 5mmol) was injected into the above mixture solution under vigorous stirring. Metal bromoacetate (1.25 mmol) were dissolved in the mixture solution of water (0.5 mL) and absolute ethyl alcohol (17 mL), and then added to the ethanol solution containing APTES and PVP. The mole ration of metal bromoacetate, APTES, water and ethanol is 1: 4: 22.4: 480. The whole process was carried out under magnetic stirring at 60℃ in water bath. After the mixture was continuously stirred for 4 h, the resultant solution was kept statically at room temperature for 14 h to age. Then the generated deposits were collected after centrifugation and washed with absolute ethanol for several times and put it in oven at 60℃ to dry. Finally, the powder was calcined at 600℃ for 4h to obtain the mNPs@SiO_2 composites.

Characterization

Fourier-transform infrared (FT-IR) spectra were recorded with KBr carrier containing the powder sample employing a Nicolet AVATAR 360 FT-IR spectrometer. ^{1}H-NMR spectrum was obtained with the metal bromoacetate powder dissolved in D_2O with a Bruker AVANCE500 liquid NMR spectrometer. A JEOL JSM-6700F scanning electron microscope (SEM) with primary electron energy of 15 kV was employed to examine the surface morphologies of products. TEM images were obtained by applying a FEI Tecnai G2F30 transmission electron microscope with the accelerating voltage of 300 kV. X-ray diffraction (XRD) data was tested by Rigaku D/Max-2500 X-ray diffractometer using a Cu target radiation source. X-ray photoelectron spectra (XPS) were collected by using a VG ESCALAB MKII with Al Kα excitation (1361 eV), Binding energy calibration was based on C 1s at 284.8 eV. TGA measurements were performed using a Netzsch STA 449C thermogravimetric analyzer. Nitrogen adsorption-desorption isotherms were measured with a ASAP 2000 analyzer at 77 K. Before the measurements, the samples were degassed under vacuum at 180℃ for 12 h. The BET method was used to calculate the surface areas. The pore volumes and pore size distributions were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method. All the optical properties were measured on a F-7000 FL spectrophotometer.

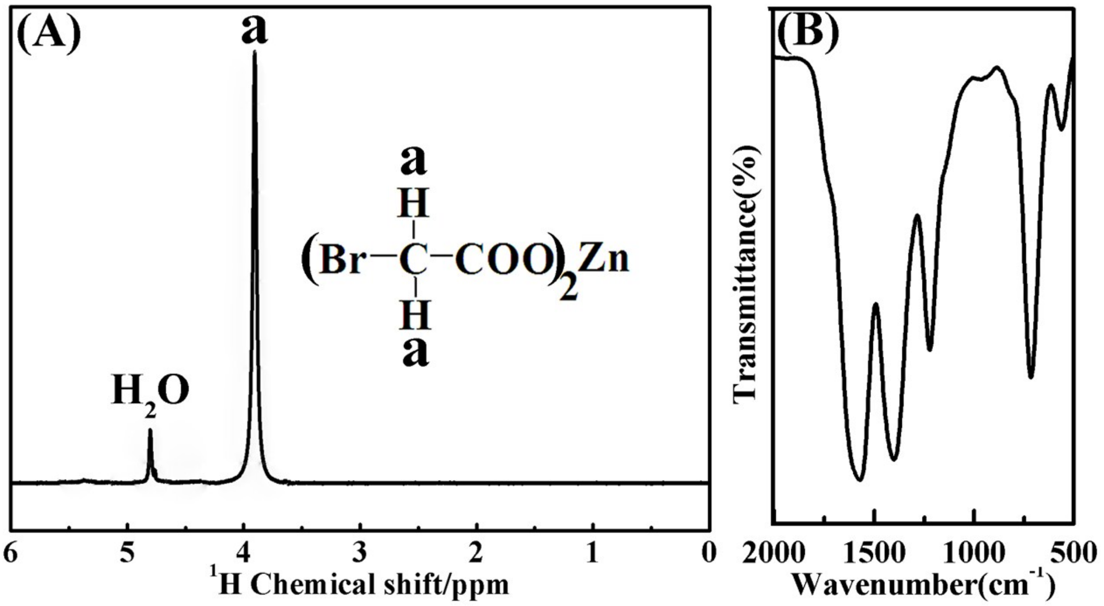

Figure S1. ^{1}H-NMR spectrum (A) and FT-IR spectrum (B) of ZnBA

In the ^{1}H-NMR spectrum (Figure S1A), the chemical shift at 3.38 ppm is corresponding to the methylene hydrion of ZnBA. The FT-IR spectrum illustrates three strong absorption peaks at 1568, 1400 and 715 cm^{-1} can be assigned to the antisymmetric stretching vibration, symmetric stretching vibration and deformation vibration of the carboxylate groups, respectively. The two bands appear at 1219 and 560cm^{-1} are the out-of-plane vibration of methylene and the stretching vibration of C-Br groups respectively.

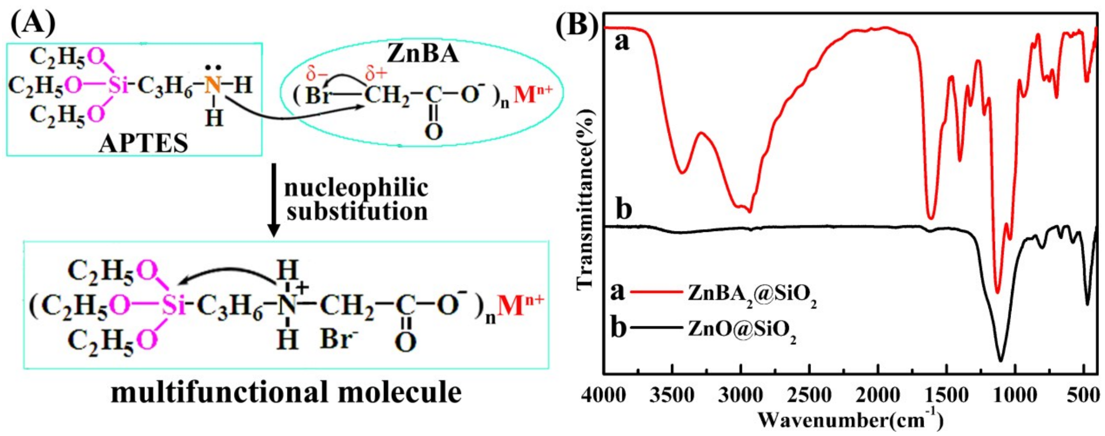

Figure S2. The multifunctional molecule (A) and FT-IR spectra of ZnBA@SiO$_2$ (curve a) and ZnO@SiO$_2$ nanocomposites (curve b) (B)

Figure S2(B) shows the FT-IR spectra of the silica material before and after calcination. The information shown in curve (a) makes we believe that we successfully synthesized ZnBA@SiO_2 nanocomposites. Firstly, the expected C-N strength of the secondary amine group appears at 1135 cm^{-1} gives the information of the occurrence of nucleophilic substitution reaction, the characteristic peak at 2970 cm^{-1} is assigned to protonated amine group, further confirming the nucleophilic substitution reaction. Secondly, the peaks at 1041 and 936 cm^{-1} are the antisymmetric stretching vibration and symmetric stretching vibration of Si-O-Si, which demonstrate the Si-O-Si networks of the hybrid material, the typical Si-C stretching peaks at 792 and 750 cm^{-1} confirm the organic chains are covalently bounded on Si-O-Si networks. Thirdly, three strong peaks appear at 1613, 1404 and 697 cm^{-1} are assigned to the antisymmetric stretching vibration, symmetric stretching vibration and deformation vibration of the carboxylate group respectively, which clearly demonstrate zinc bromoacetate was under well protection in the sol-gel process due to the mild reaction condition. After calcination, all organic parts were disappeared and the Si-O-Si networks transformed into amorphous with the characteristic peaks appear at 1110 and 802 cm^{-1} shown in curve (b).

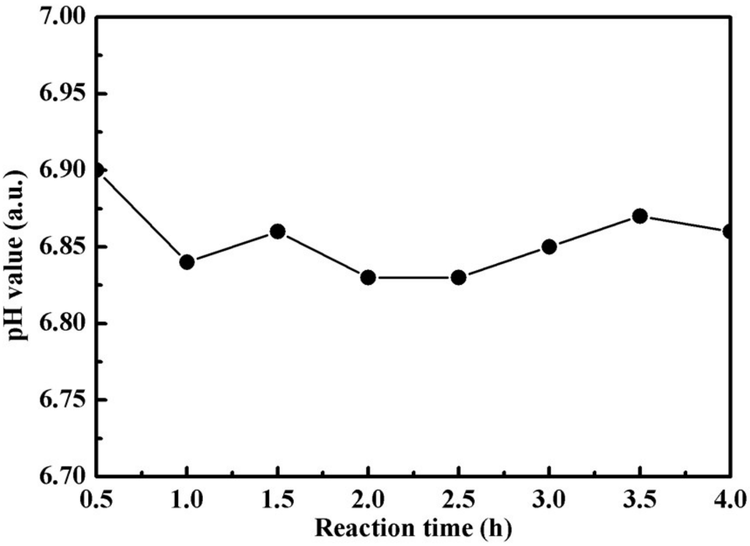

Figure S3. The pH change in the whole process of intramolecular autocatalytic route for fabricating ZnBA@SiO_2 nanocomposites

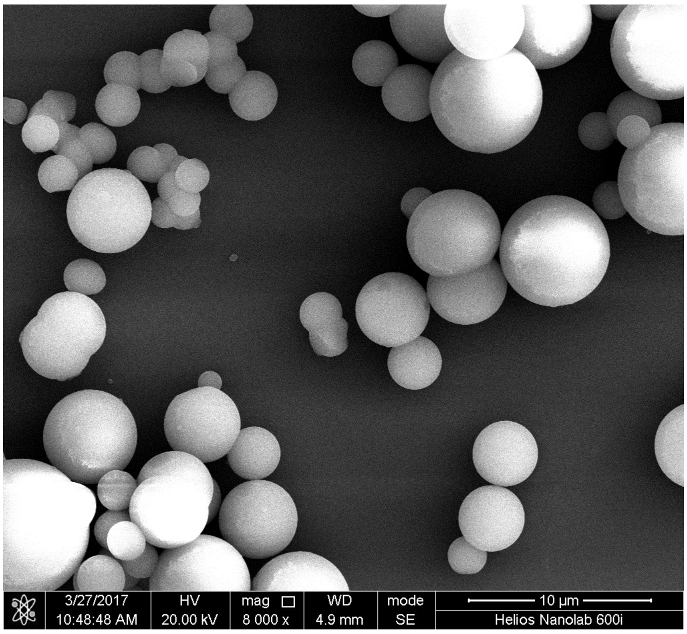

Figure S4. SEM image of hybrid ZnBA@SiO_2 nanocomposites synthesized without using PVP surfactant

The hybrid ZnBA@SiO_2 material synthesized without using PVP surfactant is shown in Figure S4, the obtained silica material has spherical morphology with a very wide particle size distribution.

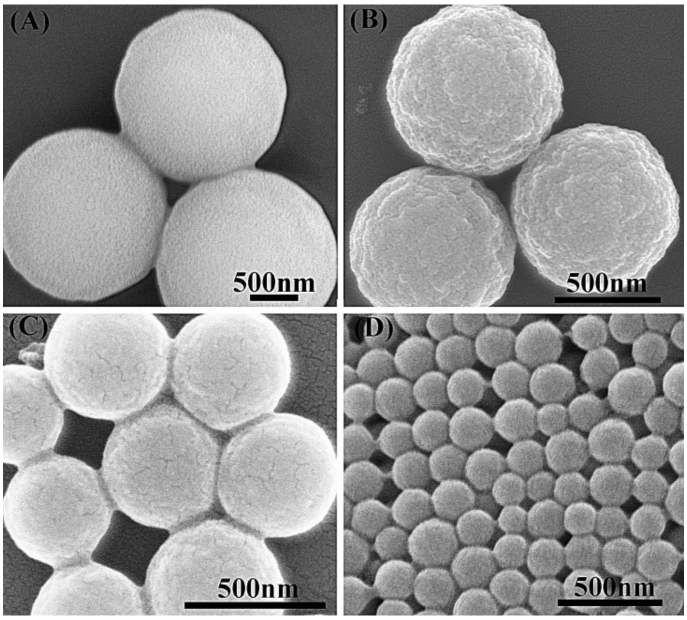

Figure S5 .SEM images of hybrid ZnBA@SiO_2 nanocomposites synthesized by using PVP with different molecular weight: average M_w=10000 (A); average M_w= 58000 (B); average M_w=360000 (C) and average M_w=1300000 (D)

ZnBA@SiO_2 nanocomposites with different size could be obtained by using PVP surfactant with different molecular weight. As shown in Figure S5, ZnBA@SiO_2 material with average size of ~1.8 µm, 800nm, 475nm and 200nm were obtained under the same condition, which are in agreement with the reported work [1]

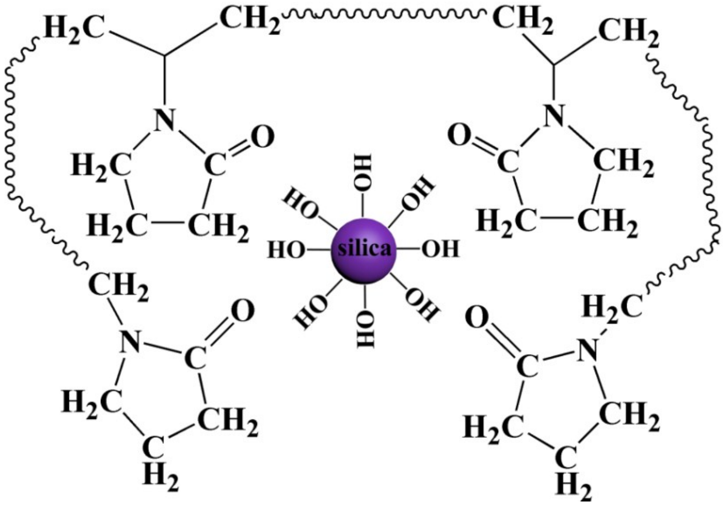

Figure S6 Scheme of silica nuclei enclosed by PVP molecules

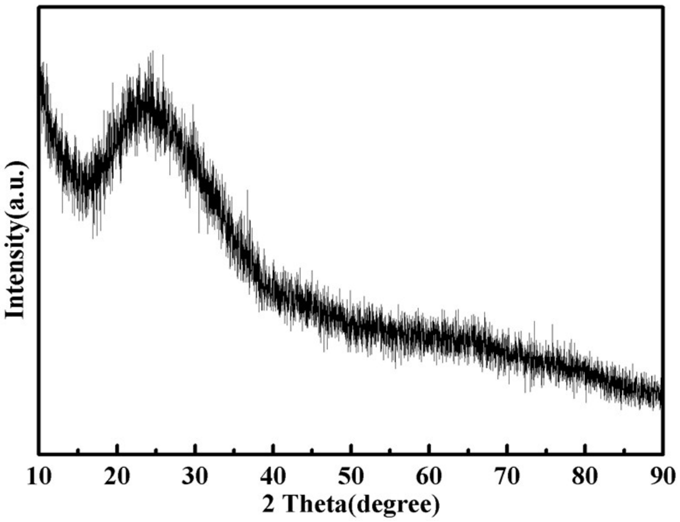

Figure S7. Power XRD pattern of ZnO@SiO_2 nanocomposites

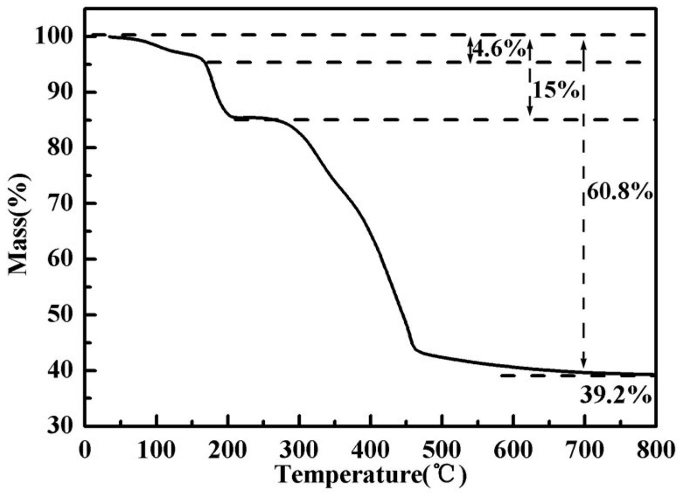

Figure S8. TGA curve of ZnBA@SiO$_2$ nanocomposites

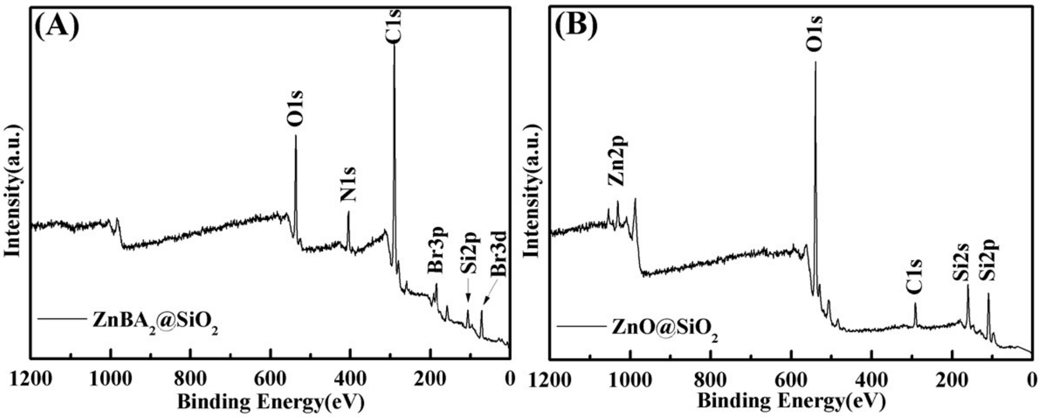

Figure S9. XPS spectra of the ZnBA@SiO$_2$ (A) and ZnO@SiO$_2$ (B) nanocomposites

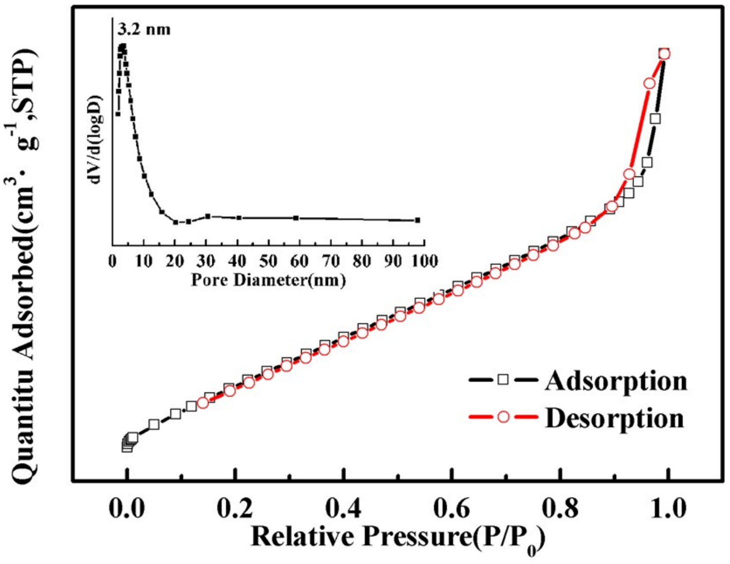

Figure S10. The N_2 adsorption-desorption isotherms and pore size distribution of ZnO@SiO$_2$ nanocomposites

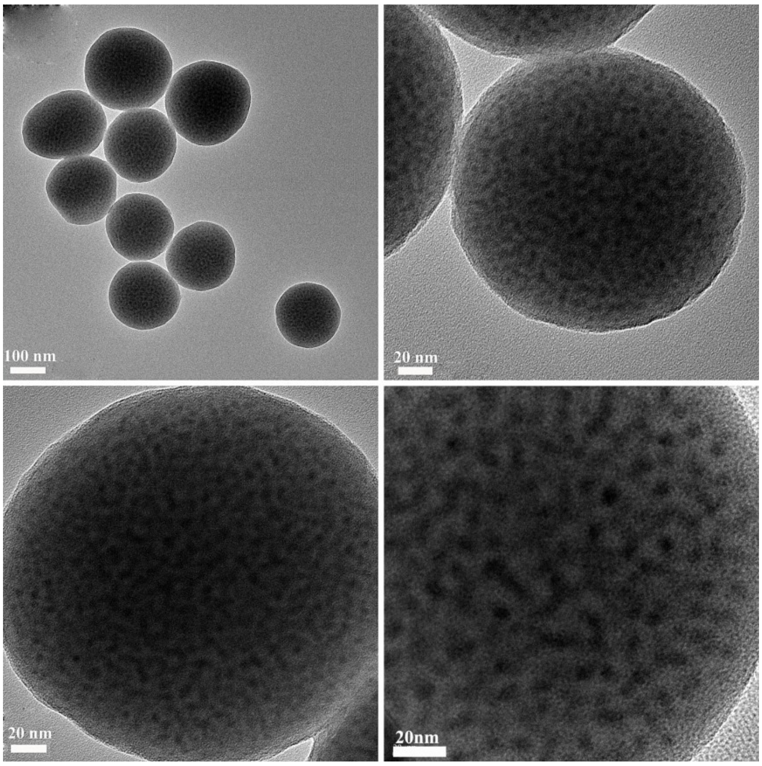

Figure S11. TEM images of ZnO@SiO_2 nanospheres (A-D) and the size distribution image of ZnO nanoparticles (inset in D)

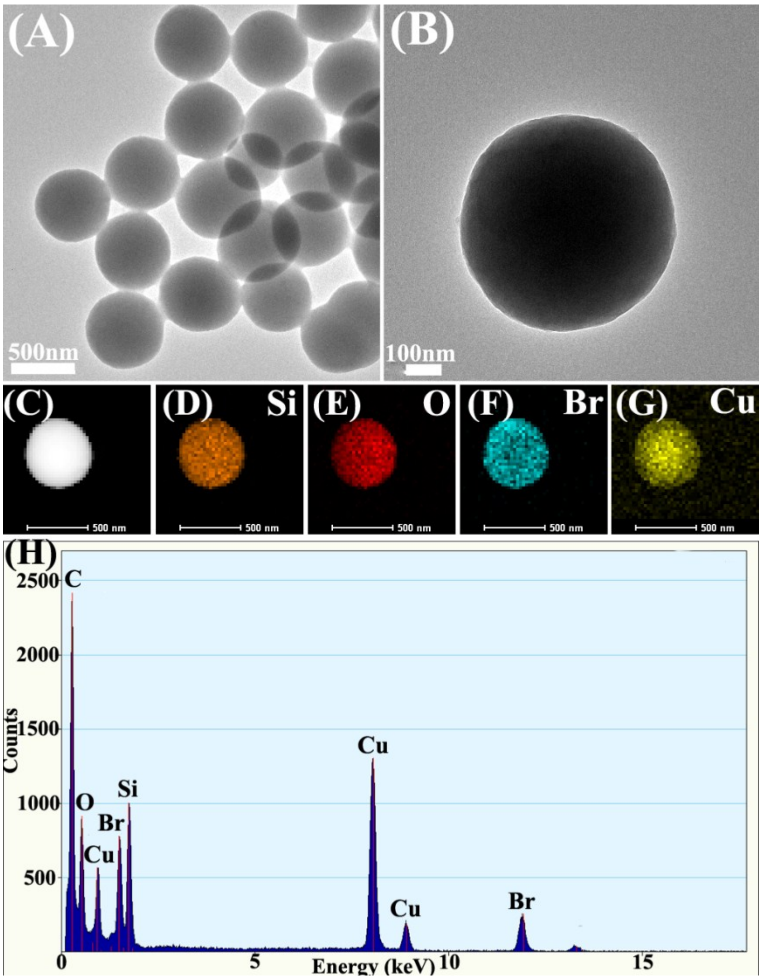

Figure S12 TEM images (A) and (B), HAADF image (C), EDX element mappings (D~G) and EDS spectrum of CuBA@SiO_2 nanocomposites.

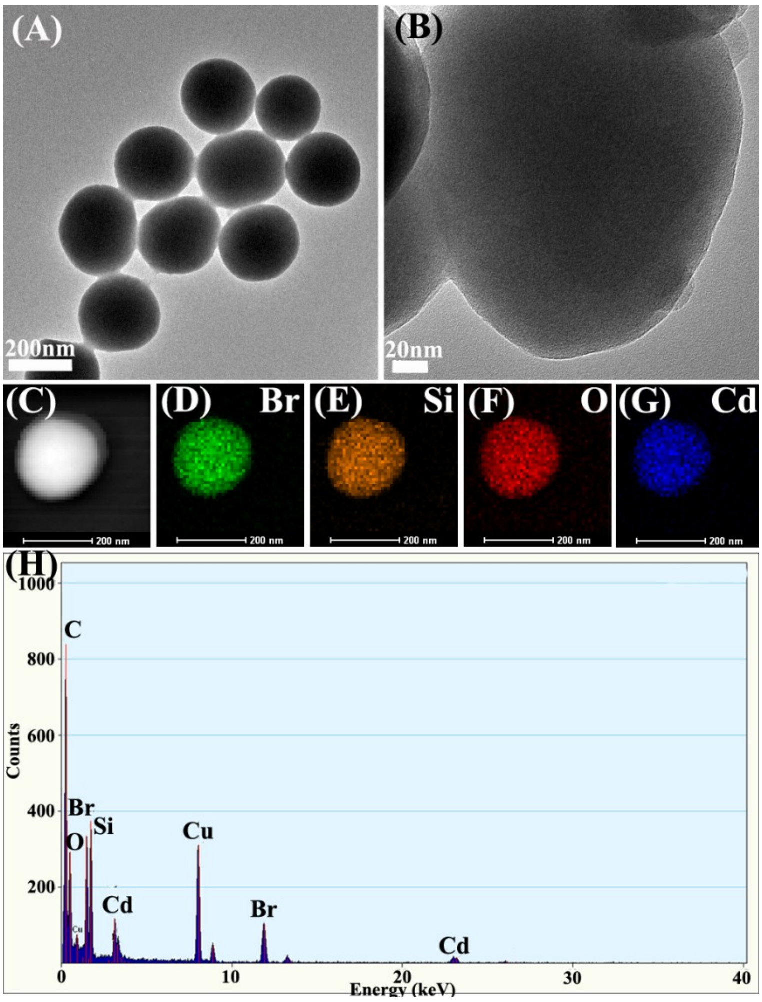

Figure S13 TEM images (A) and (B), HAADF image (C), EDX element mappings (D~G) and EDS spectrum of CdBA@SiO_2 nanocomposites.

References

(1) Cun, C. L.; Ryota, S.; Masayuki, K.; Hai, B. Z.; Yoshio, B.; Toshiharu, T. *Angew. Chem*, **2009**, 121, 7015