SUPPORTING INFORMATION

Thermo-Magneto-Responsive Dual Function Nanoparticles: An Approach for Magnetic Entrapable-Releasable Chitosan

Chutamart Pitakchatwong[†], Suwabun Chirachanchai[*,§,†]

[†]*The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*

[§]*Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand*

[*]Corresponding author

Chirachanchai, Suwabun, Professor,

The Petroleum and Petrochemical College

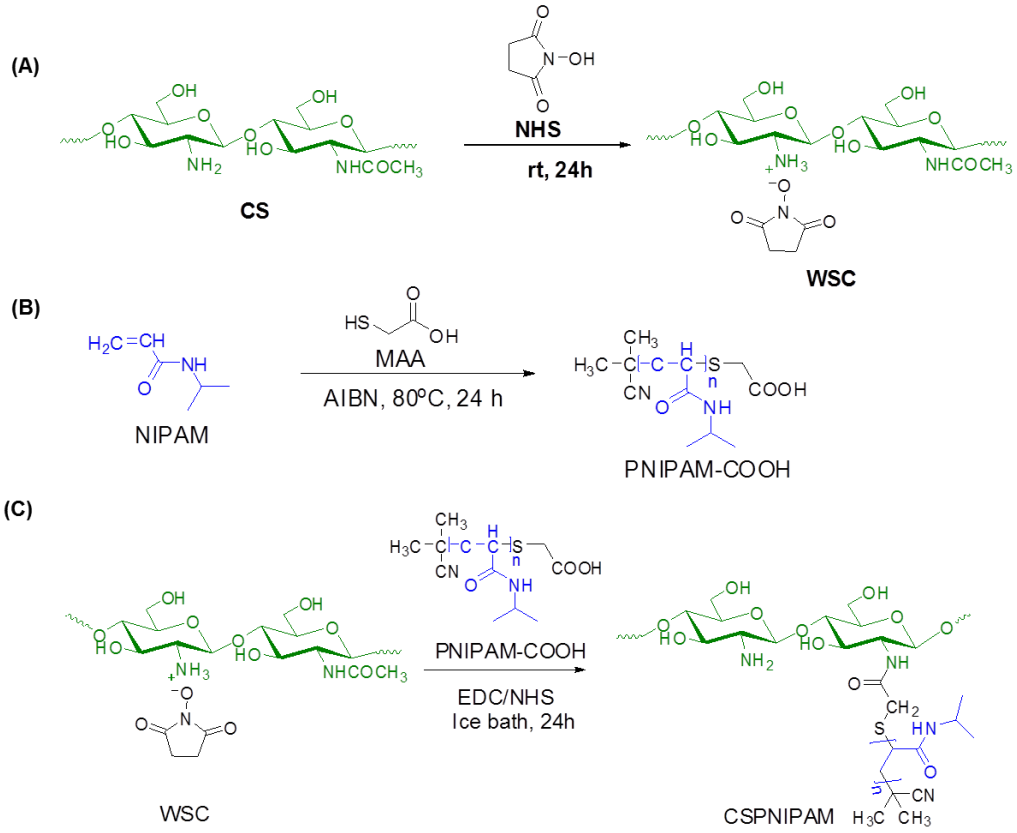
Chulalongkorn University

E-mail address: csuwabun@chula.ac.th.

Tel: (+66) 02-218-4134

Fax: (+66) 02-218-4134

Scheme S1. Schematic representation for synthesis of (A) water soluble chitosan (WCS), (B) PNIPAM-COOH, and (C) CSPNIPAM



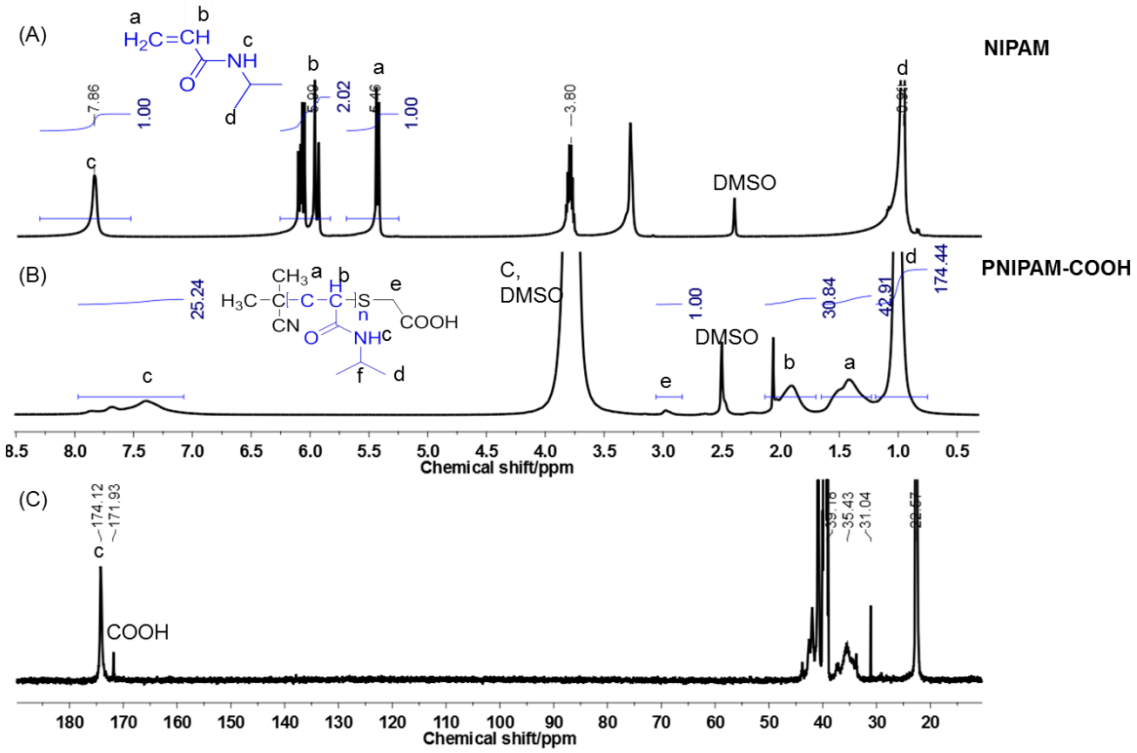


Figure S1. ^{1}H-NMR spectra of (A) NIPAM, (B) PNIPAM-COOH, and (C) ^{13}C-NMR spectrum of PNIPAM-COOH (500 MHz, DMSO).

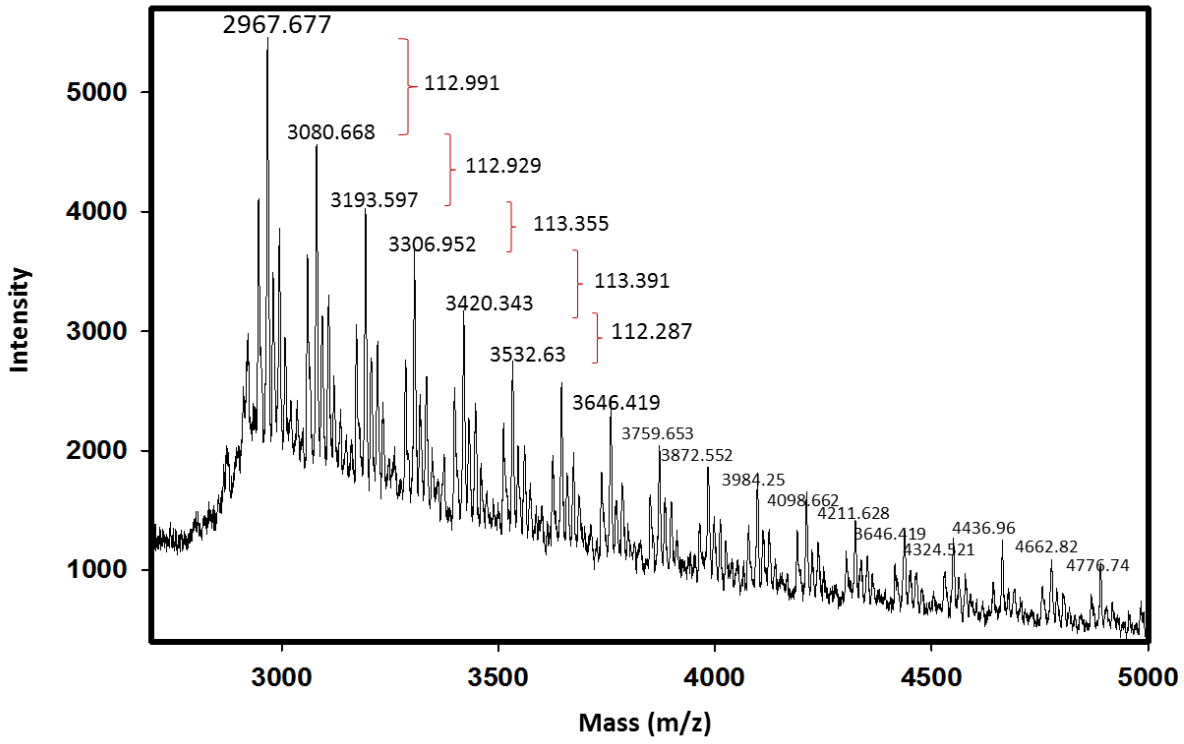


Figure S2. Degradation of PNIPAM-COOH evaluated by MALDI-TOF mass spectrometry.

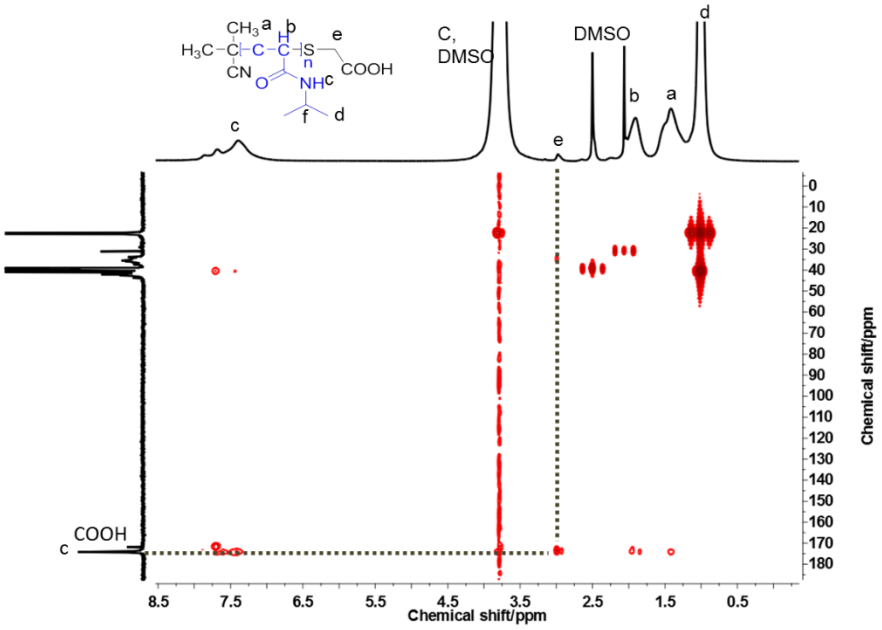


Figure S3. HMBC-2D NMR spectrum of PNIPAM-COOH.

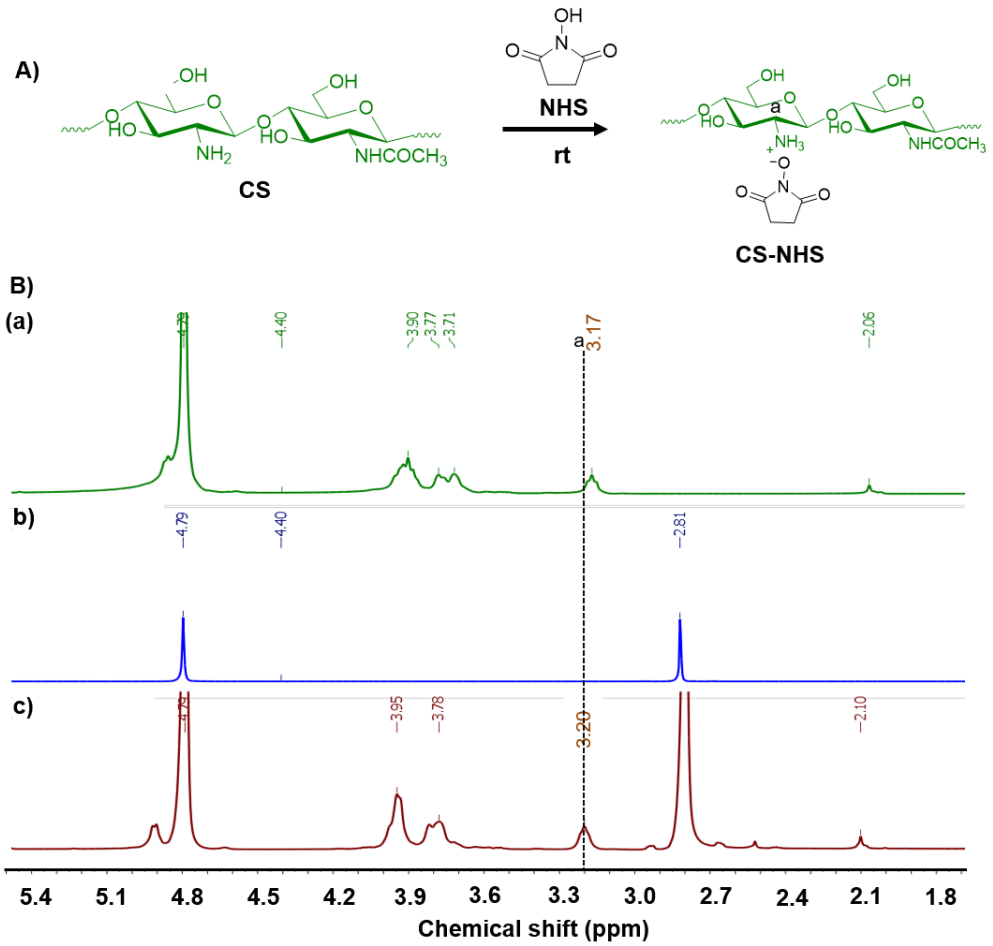


Figure S4. A) Complexation between CS and pristine NHS, and B) ^{1}H-NMR spectra of (a) CS, (b) pristine NHS, and (c) CS-NHS (1:3 molar ratio) (500 MHz, D_2O).

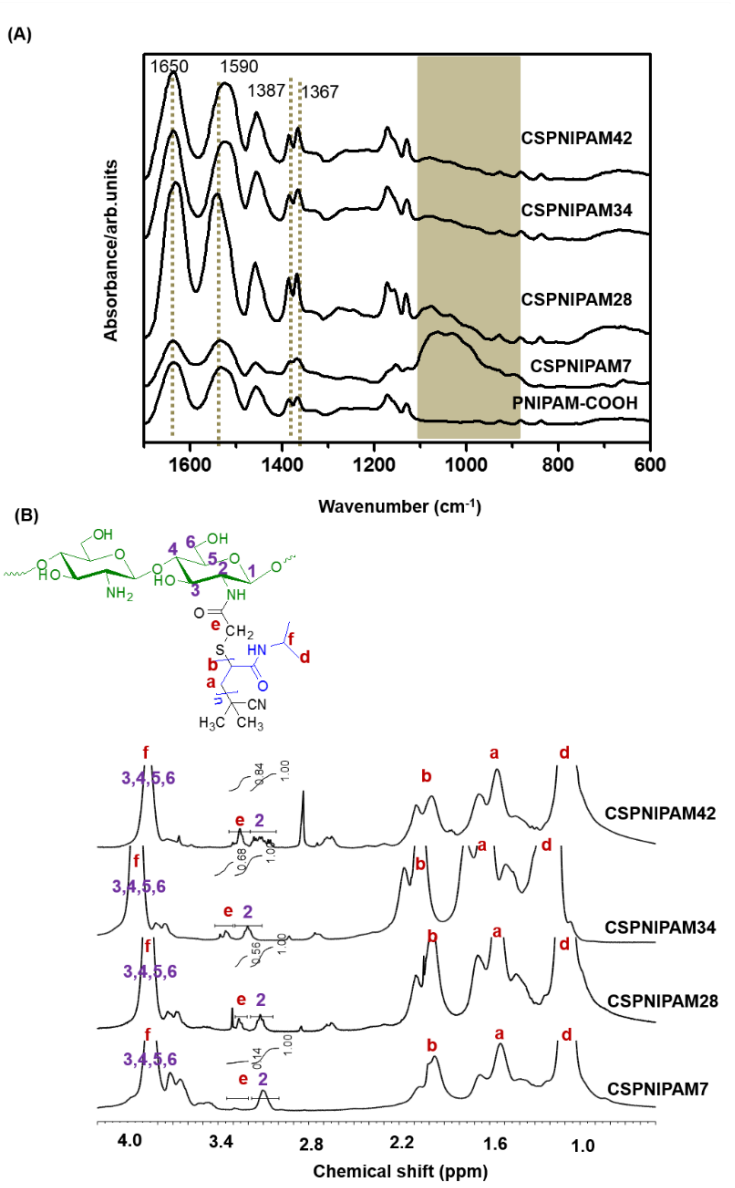


Figure S5. (A) FTIR analysis of CSPNIPAM in different %DS (M_n of PNIPAM 1000-2000). The shaded region represent the pyranose ring of chitosan, and dotted lines represent the methyl group of PNIPAM, N-H bending of chitosan, and carbonyl of amide, respectively, and (B) ^{1}H-NMR spectra of the synthesized CSPNIPAM.

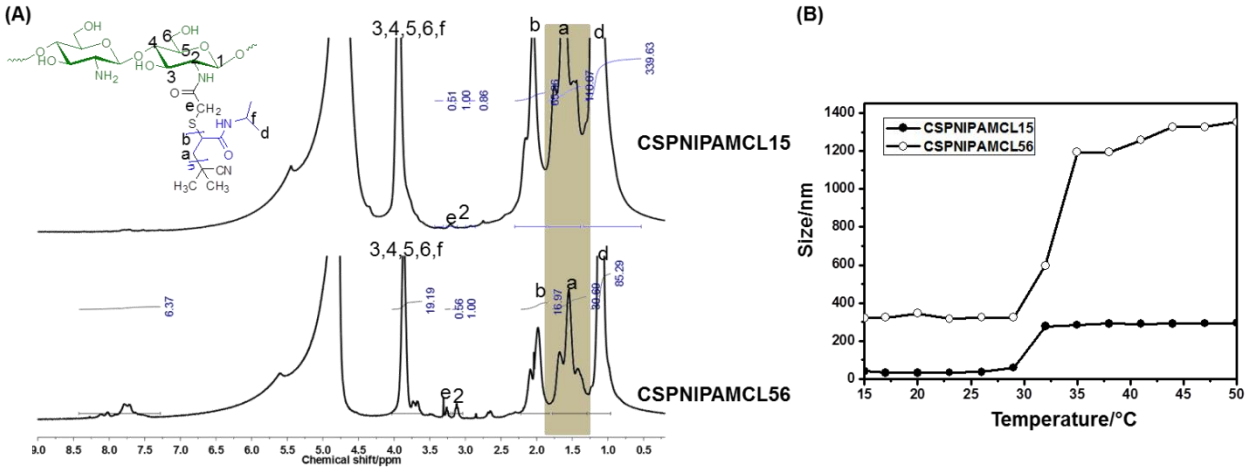


Figure S6. A) ^{1}H-NMR spectra of the synthesized CSPNIPAM25 CL15 and CSPNIPAM25 CL56, and B) Temperature dependence of size of various chain lengths of CSPNIPAM25 by DLS: CSPNIPAM25 CL15 and CSPNIPAM25 CL56. The concentration of all samples were 6 mg/mL^{-1}.

Table S1. Calculation of HLB of CSPNIPAM

Molar ratio of CS:PNIPAM-COOH	DS	CL	*Mh* of PNIPAM	*Mh* of CS	Total *Mh*	M of PNIPAM	*M* of CS	Total *M*	HLB[a]
1:1	7	8	2,408	1,789	4,197	7,435.96	15,988	23,423.96	3.58
1:3	28	17	20,468	2,356	22,824	58,260.16	15,652	73,912.16	6.16
1:5	34	28	40,936	2,518	43,454	113,066.32	15,556	128,622.32	6.76
1:7	42	11	19,866	2,734	22,600	58,873.92	15,428	74,301.92	6.08
1:3	25	15	16,125	2,275	18,400	46,360	15,700	62,060	5.93
1:3	25	56	60,200	2,275	62,475	162,349	15,700	178,049	7.02

[a] Calculation of HLB based on Griffen equation[1] (Eq 1.)

$$\frac{20 \times Mh}{M} = \frac{wt\%\ hydrophile}{5} \quad (1)$$

(where *Mh* is molecular mass of the hydrophilic portion of the molecule, and *M* is molecular mass of the whole molecule).

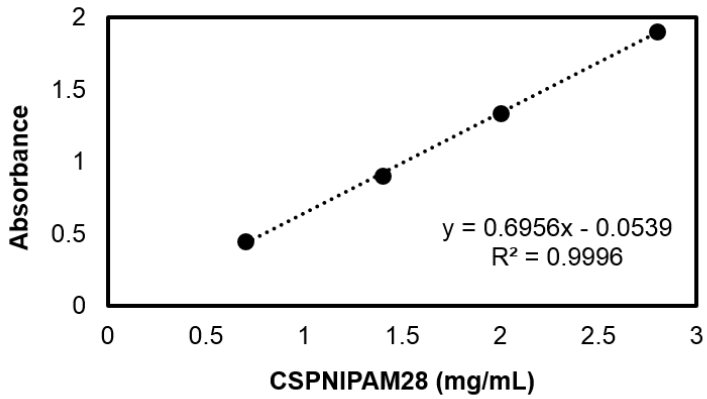


Figure S7. Calibration curve of the turbidity of CSPNIPAM28 at 40 °C 650 nm by UV-Vis spectroscopy. The calibration curve was obtained from CSPNIPAM28 aqueous solutions at different concentrations and shifting the temperature above LCST.

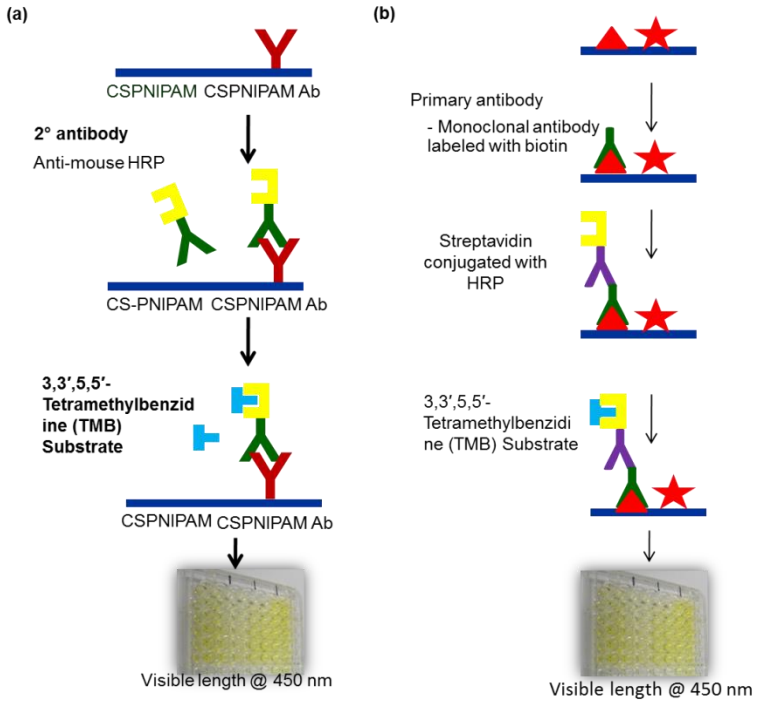


Figure S8. Method applied to qualify/quantify of (a) Ab, and (b) Ag.

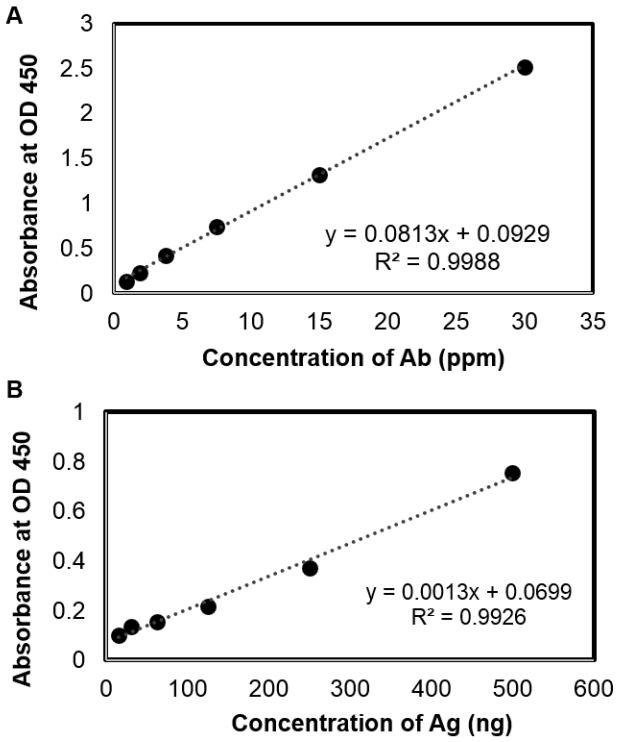


Figure S9. Calibration curve for the concentration of (A) antibody, and (B) antigen in aqueous solution.

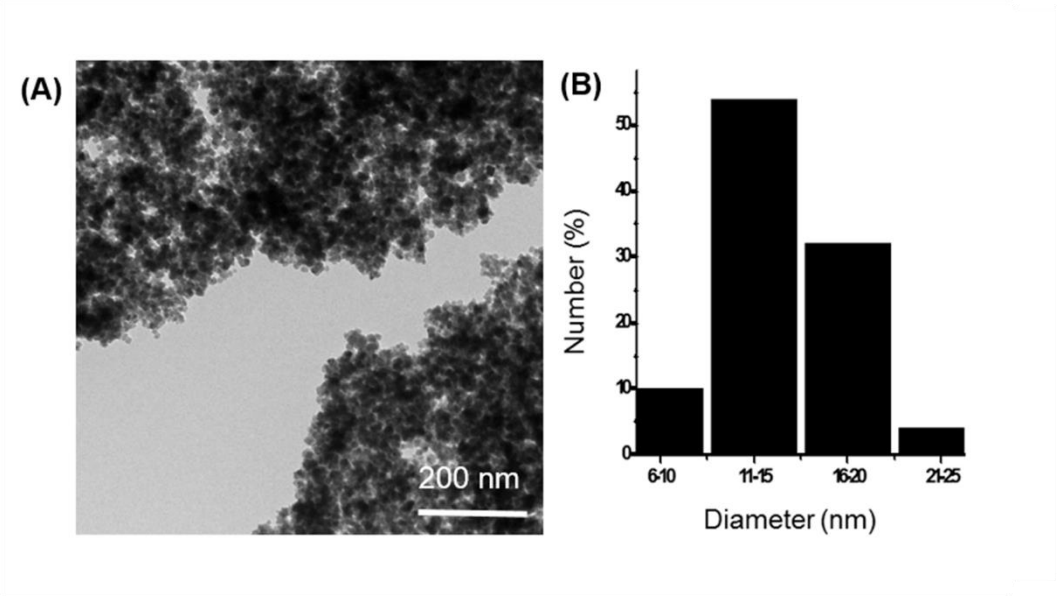


Figure S10. (A) Representative TEM images of pristine magnetic nanoparticles. The scale bars is 200 nm, and (B) Histogram of particles size distribution of pristine magnetic nanoparticles as obtained from TEM image.

Movie S1: The entrapment of MAG by using CSPNPAM-Ab-Ag at 40 °C

Movie S2: The release of MAG by using CSPNPAM-Ab-Ag at 6 °C

REFERENCE

1. Szymanowski, J.; Cox, M.; Hirons, C. G. The Determination of Hydrophilic Lipophilic Balance Values for Some Hydroxyoximes and Their Correlation with Rates of Copper Extraction. *J Chem Technol Biotechnol.* **1984,** *34* (5), 218-226.