Supporting information

Magnetic Polymer Bowl for Enhanced Reduction of Toxic Organic Dyes in Wastewater

Determination of MPS grafting density on silica-coated magnetic clusters

For the silica-coated magnetic cluster seeds with a mass of m_{seed}, the grafting density of MPS on their surfaces (Q_{MPS}, μmol/m^2) is calculated as follows:

$$Q_{MPS} = (C_0 - C_e)\cdot V_{solution}\cdot \rho_{MPS} / (M_{MPS}\cdot m_{seed}\cdot S_{spec})$$

, where C_0 (mL/mL) is the concentration of MPS initially fed for the grafting of MPS, C_e (mL/mL) is the concentration of MPS not grafted on the seeds, which is determined from the UV-Vis absorbance spectra at 210 nm using a calibration curve obtained from a series of known concentrations of MPS solutions in ethanol, and $V_{solution}$ is the total volume of the solution. ρ_{MPS} and M_{MPS} are the density (1.045 g/mL) and molecular weight (248.35 g/mol) for MPS, respectively.

The specific surface area of the seeds (S_{spec}) = $4\pi R_{seed}^2$ / $\{\rho_{seed} \cdot (4/3)\pi R_{seed}^3\}$, where R_{seed} is the radius of the seeds, which was measured from their TEM images, and the value is 200.5 nm.

The density of the seed (ρ_{seed}) = (mass of Fe_3O_4 cluster + mass of silica coating) / volume of seed = $\{\rho_{mag} \cdot (4/3)\pi R_{mag}^3 + \rho_{silica} \cdot (4/3)\pi(R_{seed}^3 - R_{mag}^3)\}$ / $\{(4/3)\pi R_{seed}^3\}$, where R_{mag} is the radius of the magnetic cluster (~127 nm), which was measured from their TEM images. ρ_{silica} and ρ_{mag} are 2.2 and 5.1 g/cm^3, respectively, which are the bulk densities for silica and Fe_3O_4.

Calculation of the number of the AgNPs immobilized on a magnetic polymer particle

For the AgNP-immobilized, magnetic polymer particles with a mass of $m_{Ag\text{-}polymer}$, the mass of the polymer component encapsulated with the silica-coated magnetic seed ($m_{polymer}$) is calculated as follows:

$$m_{polymer} = m_{Ag\text{-}polymer} - m_{Ag}$$

, where m_{Ag} is the mass of the AgNPs, which is obtained by ICP-MS characterization.

The number of the magnetic polymer particles ($N_{polymer}$) = $m_{polymer}$ /mass of one magnetic polymer particle = $m_{polymer}$ / [ρ_{PS} · {V – (4/3)πR_{seed}^3} + ρ_{seed} · (4/3)πR_{seed}^3], where V is the volume of one magnetic polymer particle and ρ_{PS} is the density of bulk PS (1.04 g/cm^3).

The number of the immobilized AgNPs (N_{Ag}) = m_{Ag} / mass of one AgNP = m_{Ag} / {(4/3)πR_{Ag}^3 · ρ_{Ag}}, where R_{Ag} is the mean radius of the AgNPs (~3 nm) and ρ_{Ag} is 10.49 g/cm^3.

The number of AgNPs immobilized on one polymer particle (X_{Ag}) is determined by dividing N_{Ag} by $N_{polymer}$.

Calculation of turnover frequency (TOF) for AgNP-immobilized magnetic polymer particle

Turnover frequency (TOF), which can quantify the specific activity of a catalytic system or center for a reaction under defined conditions, is calculated as follows:

Turnover number (TON) = mol of transformed substrate / mol of catalytic center

TOF = TON / time

Assuming that each magnetic polymer particle with immobilized AgNPs worked as each catalytic center, the number of the AgNP-immobilized magnetic polymer particles used for the 4-NP reaction was 6.3 × 10^7, which corresponds to 1.04 × 10^{-16} mol. Based on 90% conversion of the initial 4NP (4 × 10^{-4} mol) at 25 ^oC, the TOF values for the magnetic polymer bowl, magnetic polymer flower, and magnetic polymer sphere were calculated to be 3.01 × 10^{11}, 1.61 × 10^{11}, and 9.11 × 10^{10} min^{-1}, respectively.

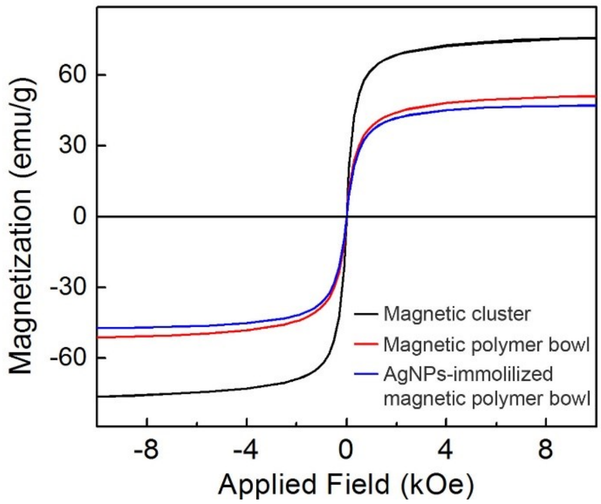

Figure S1. Field-dependent magnetization of magnetic clusters, magnetic polymer bowls, and AgNP-immobilized, magnetic polymer bowls.

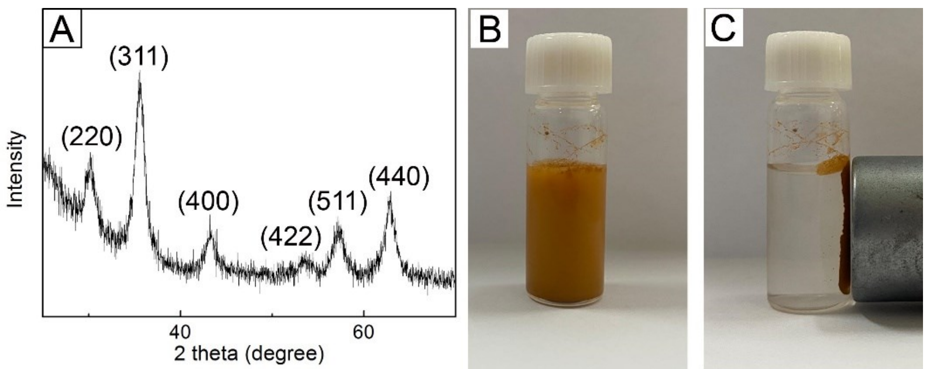

Figure S2. A) XRD pattern of the silica-coated Fe_3O_4 magnetic clusters. B,C) Photographs of the silica-coated Fe_3O_4 magnetic clusters dispersed in DI water: (B) without and (C) with application of a magnet.

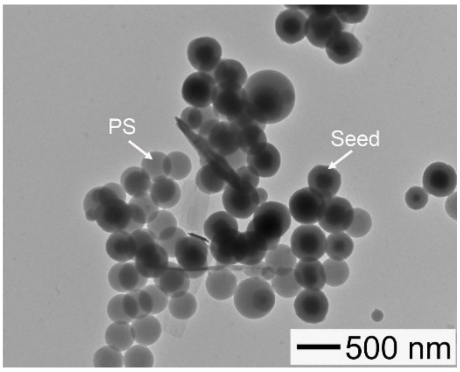

Figure S3. TEM image of the resultant sample after the polymerization at 70 °C for 6 h in the presence of silica-coated magnetic clusters.

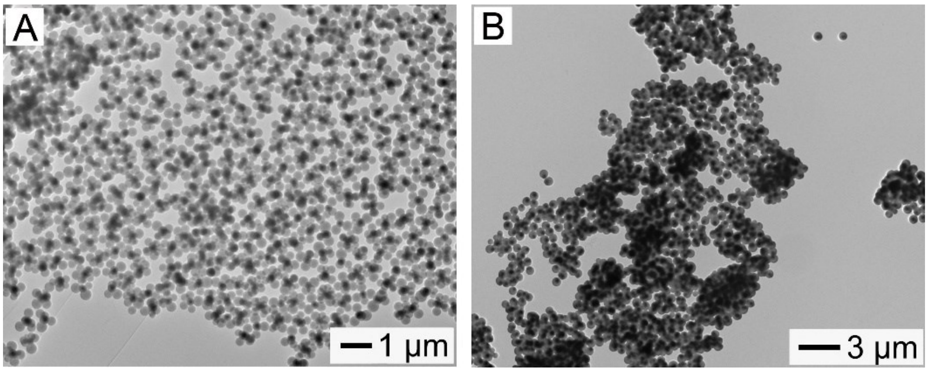

Figure S4. TEM images with low magnification for: A) flower-like particles and B) core-shell spheres.

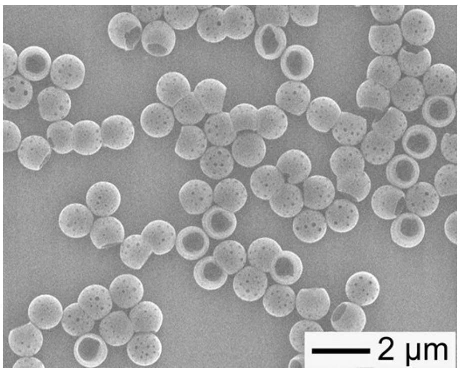

Figure S5. SEM image of the resultant sample after thermally treating the magnetic seed-encapsulated spheres at 70 °C for 2 h in the presence of decane, EHMA, and AIBN.

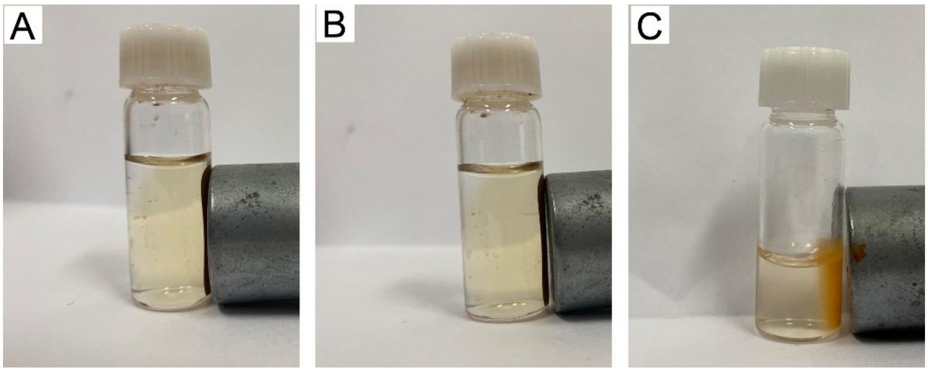

Figure S6. Photographs showing the magnetic response of each type of particles under application of magnet: A) flower-like particles, B) spherical particles, and C) bowl-like particles.

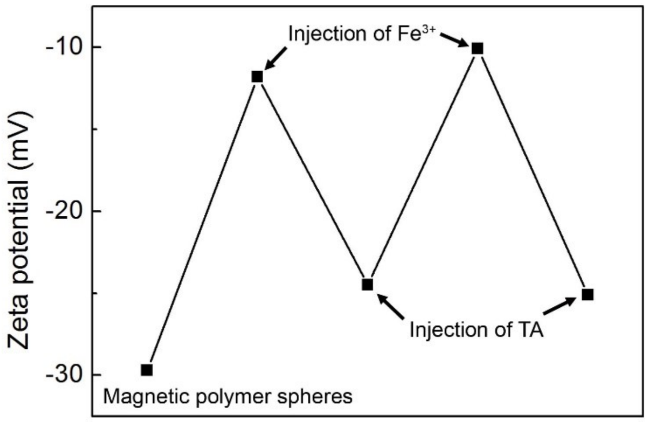

Figure S7. Zeta potential values for the magnetic polymer spheres after layer-by-layer deposition of Fe^{3+} and TA.

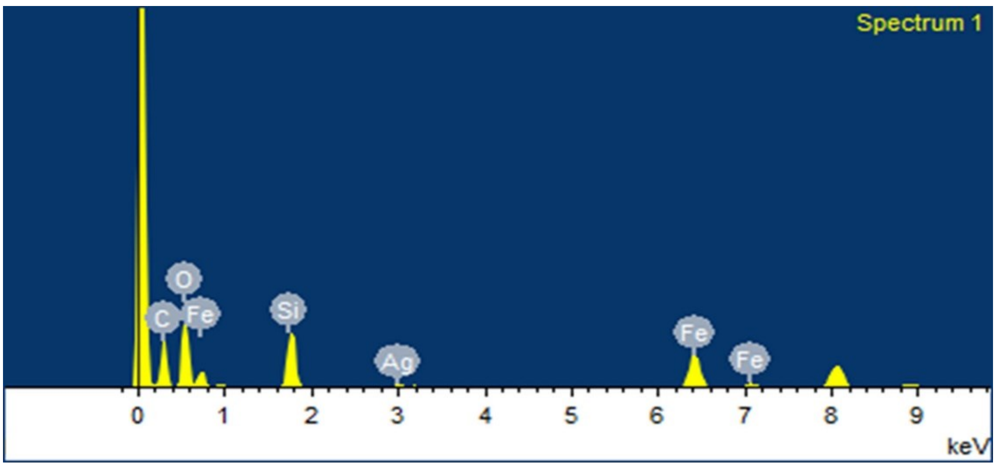

Figure S8. EDS spectrum for the magnetic polymer bowls with immobilized AgNPs.

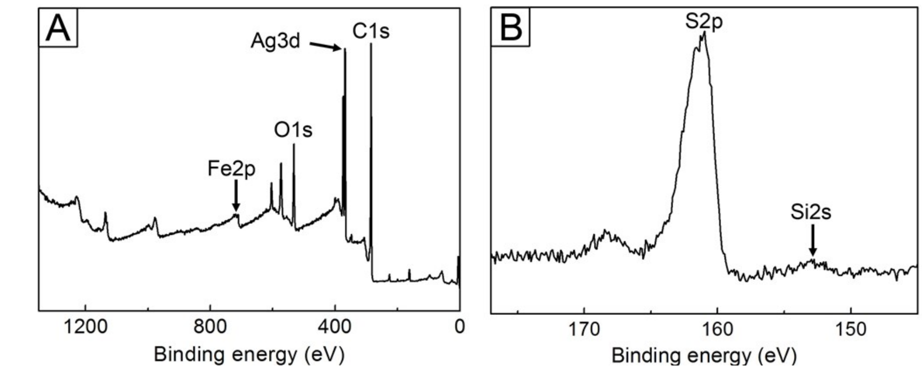

Figure S9. XPS spectra of the magnetic polymer bowls with immobilized AgNPs in the binding energy range: A) 0-1350 eV and B) 145-175 eV.

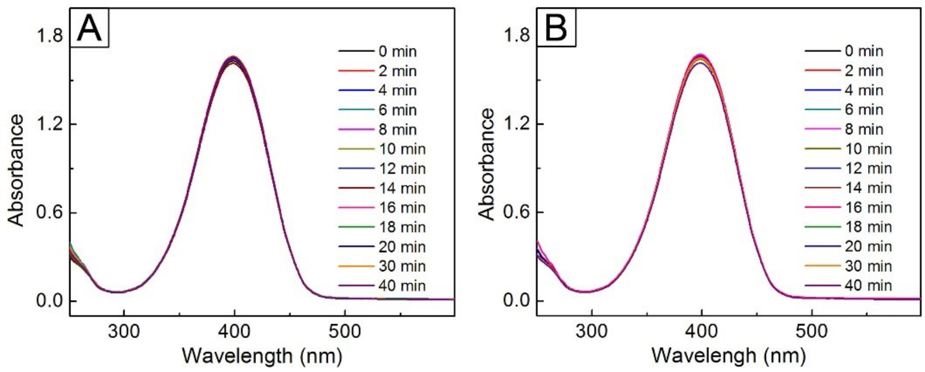

Figure S10. UV–Vis absorbance spectra at 25 ^{o}C for 4-NP as a function of time in the presence of: A) only $NaBH_4$ and B) the magnetic polymer spheres without immobilized AgNPs together with $NaBH_4$.

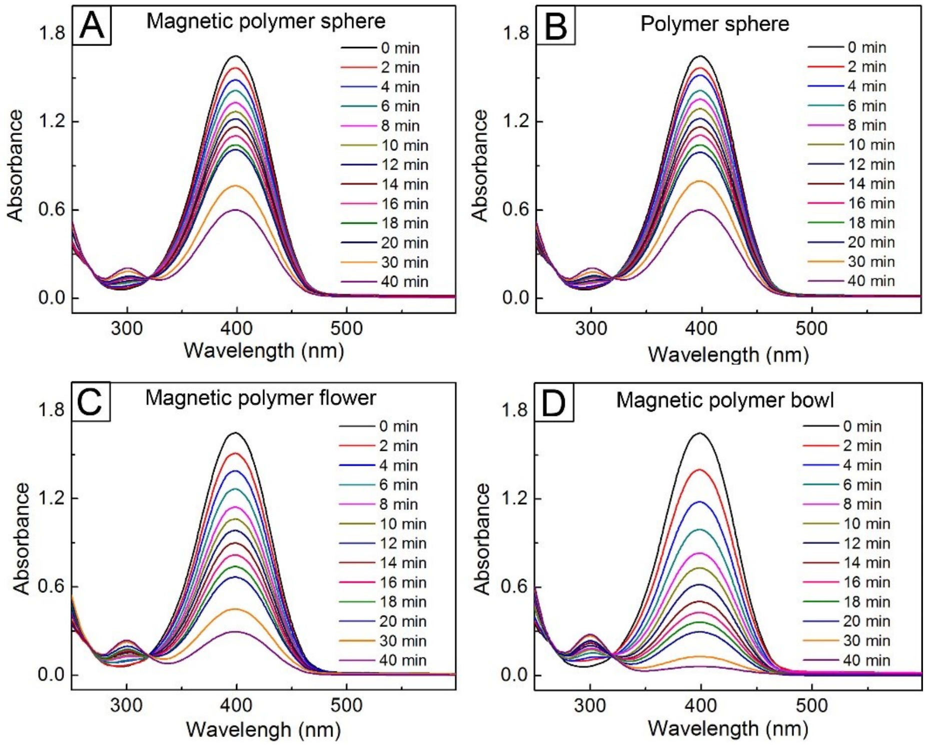

Figure S11. UV–vis absorbance spectra at 4 °C for 4-NP as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

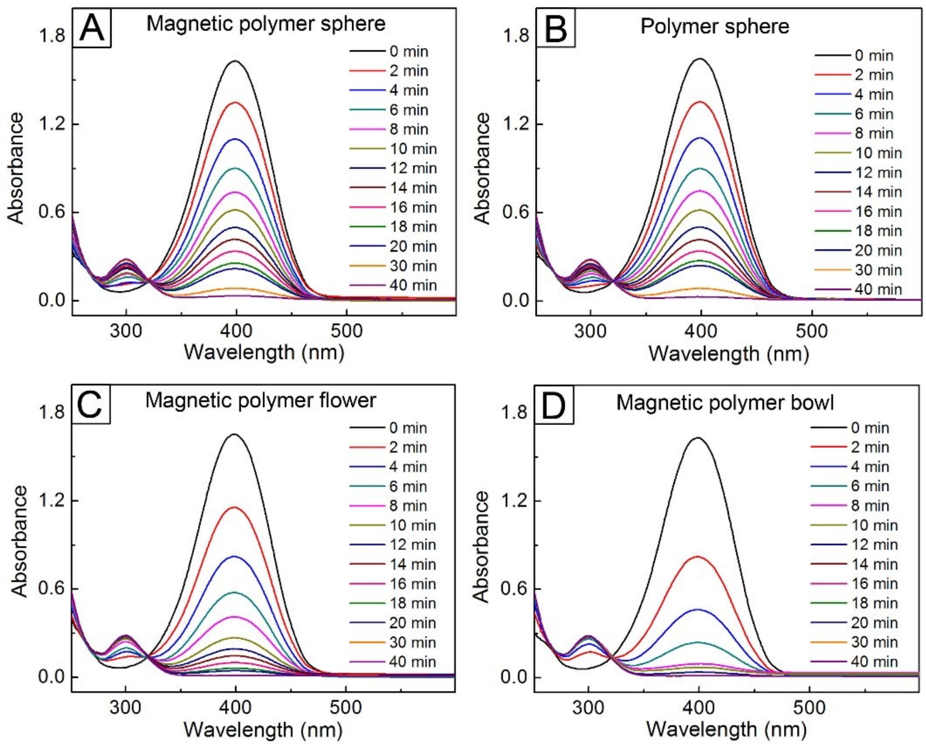

Figure S12. UV–vis absorbance spectra at 37 °C for 4-NP as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

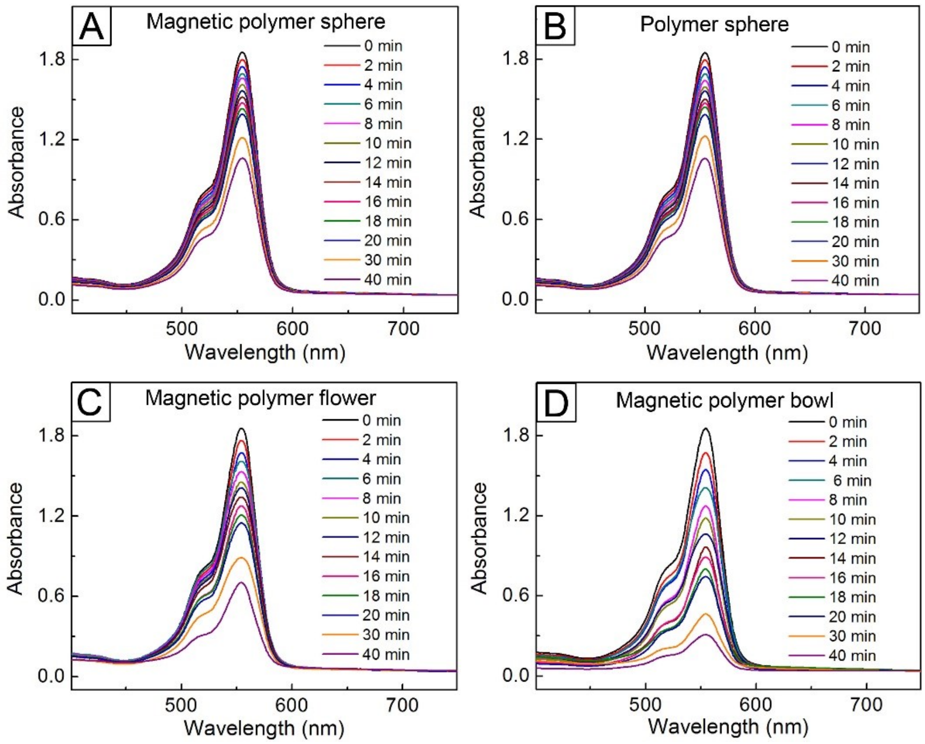

Figure S13. UV–vis absorbance spectra at 4 °C for rhodamine B as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

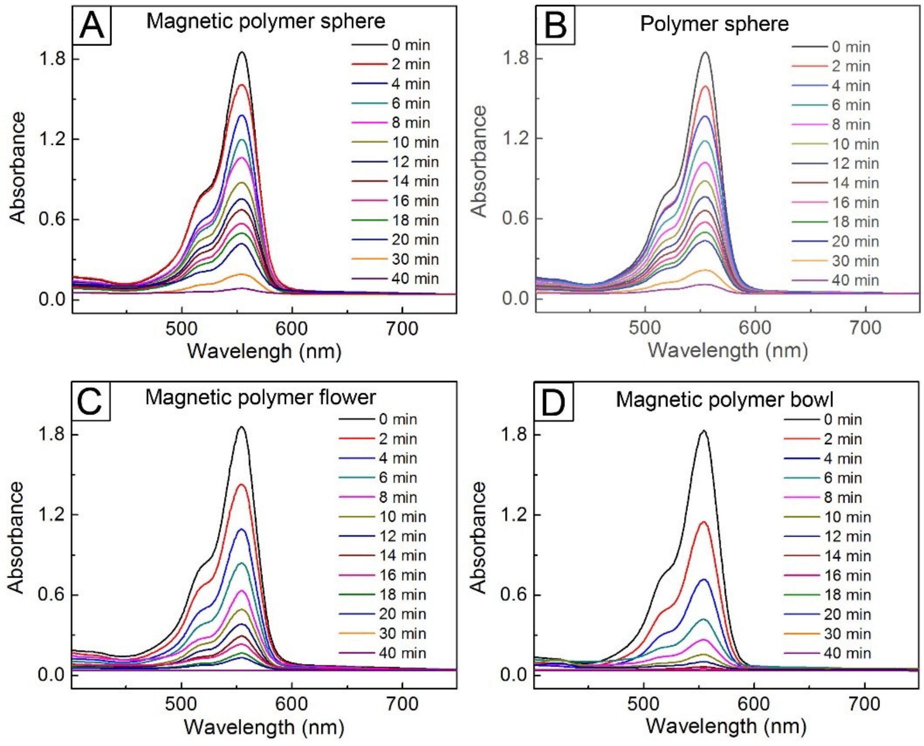

Figure S14. UV–vis absorbance spectra at 37 ^{o}C for rhodamine B as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

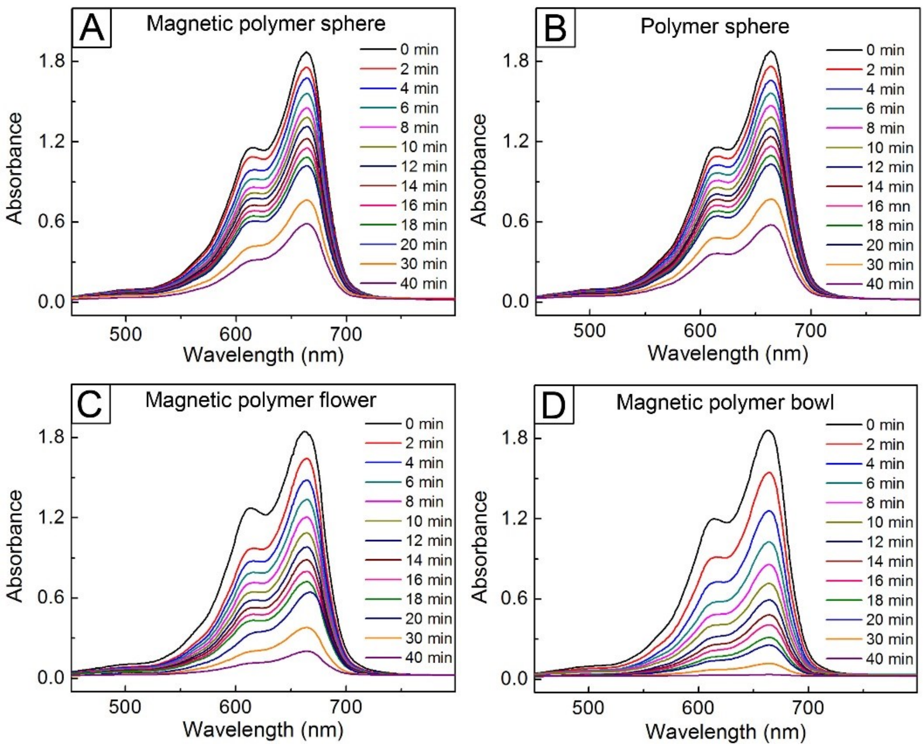

Figure S15. UV–vis absorbance spectra at 4 ^{o}C for MB as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

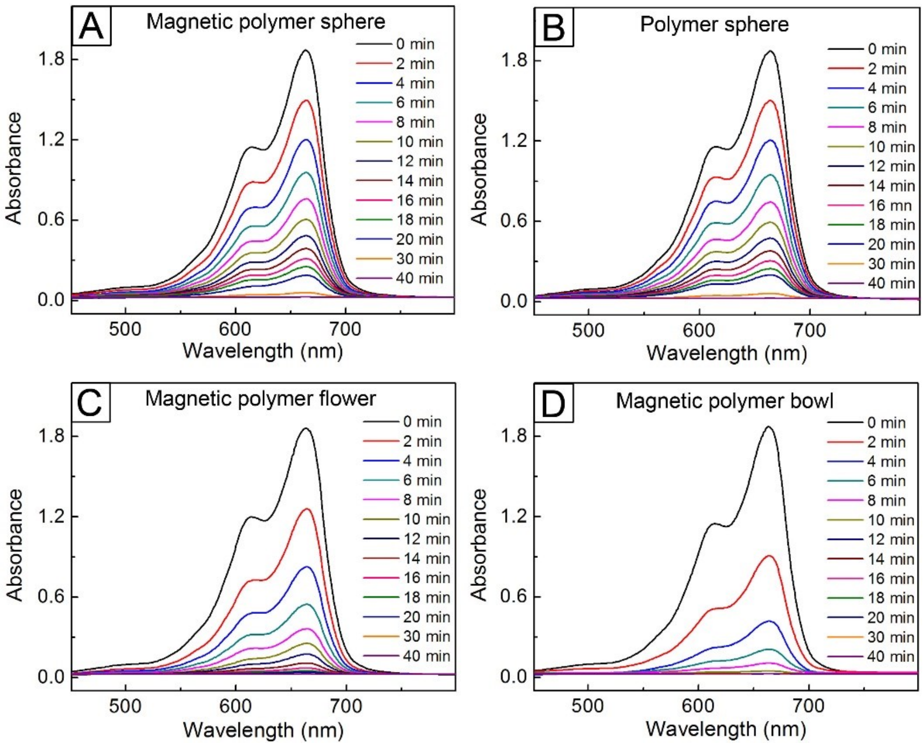

Figure S16. UV–vis absorbance spectra at 37 ^{o}C for MB as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

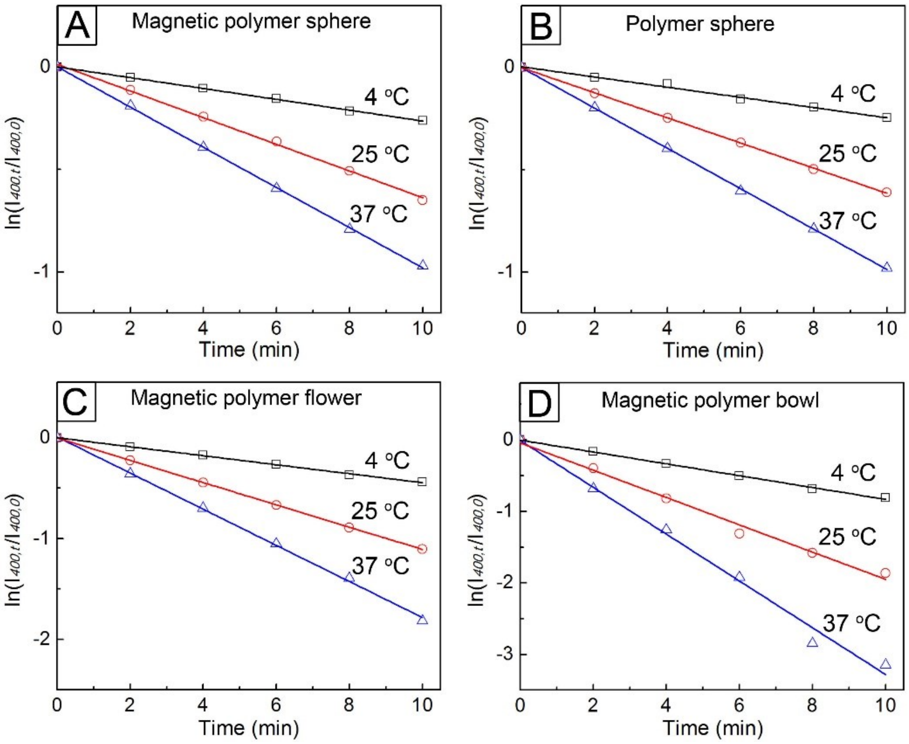

Figure S17. Plots of ln($I_{400,t}/I_{400,0}$) for 4-NP as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

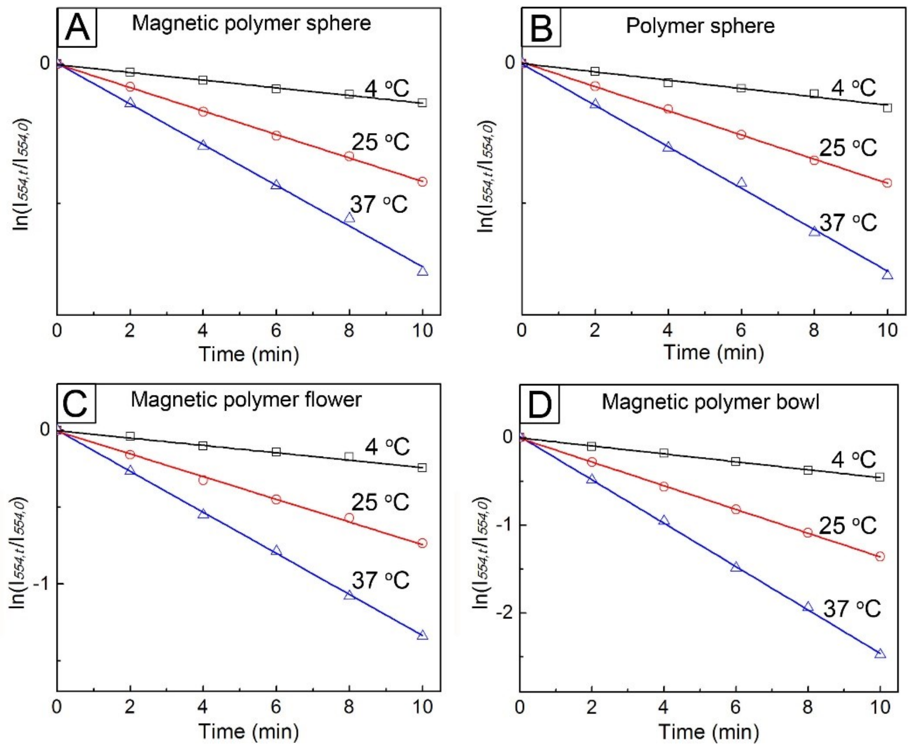

Figure S18. Plots of ln($I_{554,t}/I_{554,0}$) for rhodamine B as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

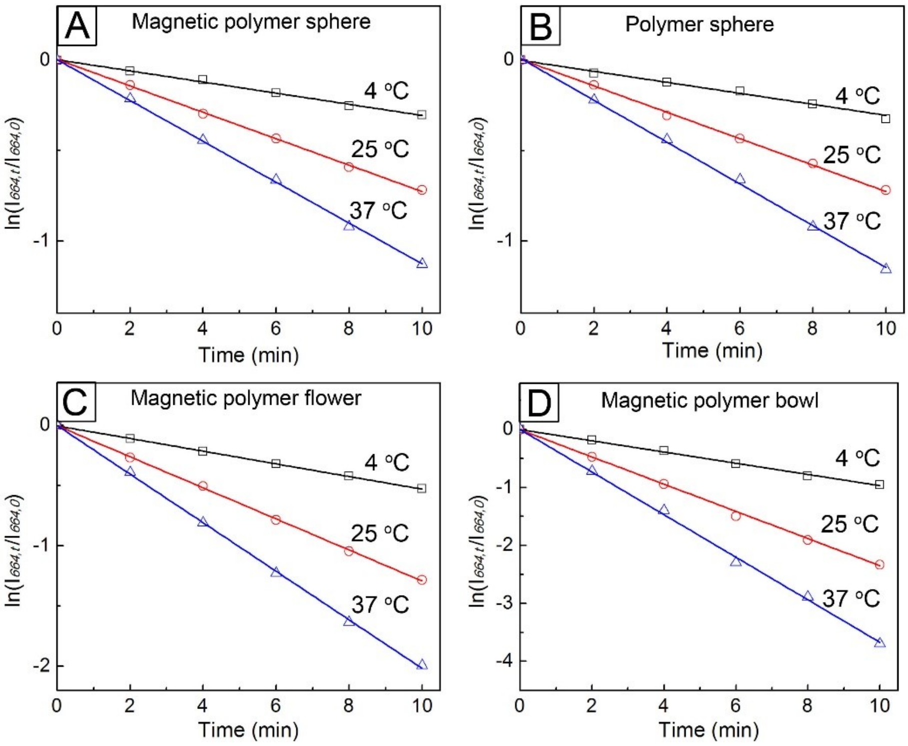

Figure S19. Plots of ln($I_{664,t}/I_{664,0}$) for MB as a function of time under the use of various particles with immobilized AgNPs: A) magnetic polymer spheres, B) polymer spheres without the magnetic cluster seeds, C) magnetic polymer flowers, and D) magnetic polymer bowls.

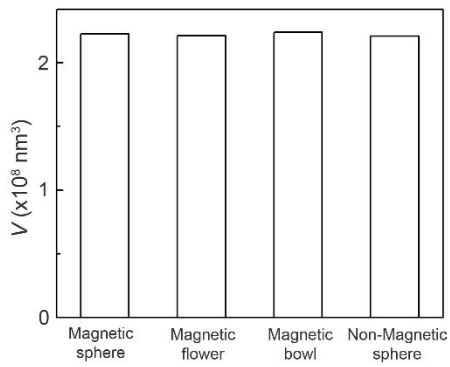

Figure S20. Volume (V) of each type of magnetic polymer particle.

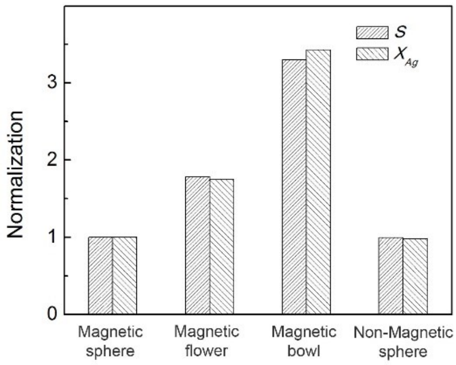

Figure S21. Normalized surface areas for the magnetic polymer particles with different structures and normalized numbers of immobilized AgNPs per magnetic polymer particle, which are obtained by dividing the surface area (S) or number of immobilized AgNPs (X_{Ag}) for each type of magnetic polymer particle by that of the nonmagnetic polymer sphere.