

Self-assembly of nanoparticles onto the surfaces of polystyrene spheres with a tunable composition and loading

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Abstract. Functional colloidal materials were prepared by design through the self-assembly of nanoparticles on the surfaces of polystyrene spheres with control over nanoparticle surface coverage, nanoparticle-to-nanoparticle spacing, and nanoparticle composition. The ability to control and fine tune the coating was extended to the first demonstration of the co-assembly of nanoparticles (NPs) of dissimilar composition onto the same polystyrene (PS) sphere, forming a multi-component coating. A broad range of NP decorated PS spheres were prepared with uniform coatings attributed to electrostatic and hydrogen bonding interactions between stabilizing groups on the NPs and the functionalized surfaces of the PS spheres. This versatile two-step method provides more fine control than methods previously demonstrated in the literature. These decorated PS spheres are of interest for a number of applications, such as catalytic reactions where the PS spheres provide a support for the dispersion, stabilization, and recovery of nanoparticle catalysts. The catalytic properties of these NP decorated PS spheres were assessed by studying the catalytic degradation of azo dyes, an environmental contaminant detrimental to eye health. The NP decorated PS spheres were used in multiple, sequential catalytic reactions while largely retaining the NP coating.

1. Introduction

A versatile method for the preparation of nanoparticle (NP) decorated polystyrene (PS) spheres (PS@NPs) has been sought by a number of researchers due to the broad applicability of these materials in areas such as environmental catalysis, and contrast agents in biological imaging [1-19]. Coating the PS sphere with NPs imparts unique properties to the PS sphere. In addition, colloidal stability of NPs can be enhanced through their assembly onto the PS, improving their capacity for a variety of applications. The preparation of multi-component PS@NPs, consisting of two or more different types of NPs decorated onto each PS sphere, is of particular interest for applications such as multimodal sensing [20]. Currently reported methods have, however, had limited success in preparing PS@NPs from NPs of a diverse range of compositions, and in controlling the uniformity and loading of the NPs over the surfaces of the PS sphere [4-19].

Herein, we describe a method for the preparation of PS@NPs from NPs with a diverse range of compositions, sizes and shapes. Nanoparticles are first synthesized with desired specifications (e.g., size and shape) and subsequently decorated onto the PS spheres, allowing fine control over the PS@NPs material properties. Through this method we are able to control the quantity of NPs, spacing between NPs within the coatings, and relative ratios of NPs of different compositions within a multi-

component NP coating. This report demonstrates the preparation and fine tuning of multi-component PS@NPs for the first time. The NP decorated PS spheres retain their colloidal stability over the course of multiple solution based catalytic reactions. The ease in tuning this method to prepare a wide range of PS@NPs is attributed to the versatility of our approach, using polyvinylpyrrolidone (PVP) stabilized NPs that have favorable interactions with the functionalized PS spheres.

2. Experimental

Synthesis of Platinum Nanoparticles. Platinum nanoparticles were synthesized by an ethanol based reduction [21]. Polyvinylpyrrolidone (PVP) (55k MW, 98%) and hexachloroplatinic acid (H_2PtCl_6 , ACS grade) were purchased from Sigma-Aldrich. Anhydrous ethyl alcohol (EtOH) was purchased from Commercial Alcohols. All chemicals were used as received, without any further purification. All glassware and stir bars were treated with aqua regia and piranha prior to use. The aqua regia solution was prepared from a 3:1 (v/v) solution of hydrochloric acid (36.5 – 38.0% in water; Anachemia Inc.) and nitric acid (68 – 70% in water; Anachemia Inc.). The piranha solution was prepared from a 5:2 (v/v) solution of concentrated sulfuric acid (90 – 100% in water; Anachemia Inc.) and hydrogen peroxide (30% in water; Caledon Laboratories Ltd.). CAUTION: Aqua regia and piranha solutions should be handled with extreme care. Briefly, 5.0 mL of 6 mM H_2PtCl_6 was prepared one day in advance in demineralized water (18 M Ω -cm, produced using a Barnstead NANOpure DIAMOND water filtration system). A solution of 40 mL EtOH, 5 mL demineralized water, and 1.65 g 55k MW PVP was prepared and stirred for 10 min in a 100 mL round bottom flask equipped with a reflux condenser and stir bar. The 6 mM H_2PtCl_6 solution was then added to the EtOH mixture and the resulting solution was heated to reflux under continuous stirring. After 3 h at reflux under continuous stirring, the mixture was removed from heat and slowly cooled to room temperature. The resulting solution of Pt NPs was directly used for coating onto the PS spheres without any purification.

Synthesis of Palladium Nanoparticles. Nanoparticles of Pd were synthesized by reduction in ethylene glycol (EG) [22]. Glassware and stir bars were treated with aqua regia and piranha prior to use, as described above. Ethylene glycol (Caledon Laboratories Inc.), 55k MW PVP (98%; Sigma-Aldrich) and sodium tetrachloropalladate(II) (98%; Sigma-Aldrich) were purchased and used without further purification. Five milliliters of EG was added to a 25 mL round bottom flask equipped with a reflux condenser and stir bar, and heated to 110°C for 1 h with continuous stirring. Fresh solutions of 55k MW PVP (0.080 g) in EG (3 mL) and Na_2PdCl_4 (0.138 g) in EG (3 mL) were prepared during this time. After 1 h of heating, the two additional EG solutions were simultaneously injected into the hot EG at a rate of 45 mL/min. The reaction mixture was held at 110°C with continuous stirring for an additional 3 h before cooling slowly to room temperature. The resulting product was washed once with ~50 mL of acetone, isolated by centrifugation and redispersed in 50 mL of EtOH for use in coating of the PS spheres.

Synthesis of FePt Nanoparticles. The FePt NPs were prepared by polyol reduction in dioctyl ether, as per literature [23]. Platinum(II) acetylacetonate (acac) (97%, Sigma-Aldrich), iron pentacarbonyl (97%, Sigma-Aldrich), 1,2 hexadecanediol (>98%, TCI America), dioctyl ether (99%, Sigma-Aldrich), oleic acid (>98%, Sigma-Aldrich), oleylamine (70%, Sigma-Aldrich), toluene (Anachemia Inc.), 10k MW PVP (Sigma-Aldrich), dichloromethane (DCM) (Anachemia Inc.), dimethylformamide (DMF) (Anachemia Inc.), diethyl ether (Anachemia Inc.) and chloroform (Anachemia Inc.) were all purchased and used as-received without any further purification. All glassware and stir bars were treated with aqua regia and piranha prior to use, as described above. Briefly, a 20 mL solution of 0.5 mM Pt(acac) and 1.5 mM 1,2 hexadecanediol in dioctyl ether was heated to 100°C with continuous stirring under a N_2 atmosphere in a 100 mL round bottom flask equipped with a reflux condenser and

stir bar. Once all material appeared to be dissolved at 100°C (e.g., 5 min), 0.16 mL of 0.5 mM oleic acid in dioctyl ether and 0.17 mL of 1 mM oleylamine in dioctyl ether were added to the heated mixture. Finally, 0.13 mL of 1 mM Fe(CO)₅ was quickly injected. The reaction mixture was heated to 300°C and held at that temperature for 30 min while being continuously stirred. The resulting mixture was cooled to room temperature. The FePt NP product was washed 3 times by dispersing in hexanes, subsequently precipitating the NPs with ethanol and isolating the solid product by centrifugation. The purified FePt NPs were transferred to the aqueous phase as described below [24]. A dispersion of the purified FePt NPs in chloroform were added to a 50 mL round bottom flask equipped with a stir bar, followed by the addition of 5 mL each of DCM and DMF. This reaction mixture was stirred while adding 150 mg of 10k MW PVP. Once the PVP mixture dissolved (e.g., 15 min), the mixture was brought to reflux and held at reflux for 12 h with continuous stirring. The heated solution was subsequently cooled to room temperature, and the PVP-coated NPs selectively precipitated by addition to diethyl ether (90 mL) via Pasteur pipette. The NPs were isolated by a centrifugation process, and the resulting pellet of NPs redispersed in ethanol for use in coating the PS spheres.

Preparation of Nanoparticle Coatings. The NP coatings were prepared by combining the synthesized NPs with amine functionalized PS spheres (Polysciences, Inc. or Bangs Laboratories, Inc.). Before use, the PS spheres were washed once with a 1:1 (v/v) mixture of EtOH and water, and isolated via centrifugation. In a typical experiment, NP coatings were prepared by combining 1 to 10 mL of the synthesized NPs with 40 to 500 mg of the washed PS spheres. The reaction was adjusted to a pH of 3 by the addition of 1% HCl, prepared by dilution of concentrated HCl (Anachemia, ACS Reagent Grade) with demineralized water (18 MΩ·cm, produced using a Barnstead NANOpure DIAMOND water filtration system), for coating the FePt NPs onto the PS spheres. This step was not necessary for Pd or Pt NP coatings since the pH of these solutions was near pH 3 as a result of their synthetic methods. This mixture of particles was continuously stirred at 55°C for 3 h. After 3 h of heating, the NP decorated PS spheres were slowly cooled to room temperature and isolated via centrifugation. To purify the PS@NPs from any residual suspension of NPs, the isolated pellet was washed twice with water and twice with ethanol. In between each wash step, the decorated spheres were isolated via centrifugation for ~10 min at 10,000 rpm.

Characterization. The purified samples of PS@NPs were analyzed by transmission electron microscopy (TEM) using either a FEI Tecnai G2 field emission or a FEI Osiris X-FEG scanning/TEM operated at an accelerating voltage of 200 keV. Energy dispersive X-ray spectroscopy analysis was performed on the FEI Osiris X-FEG scanning/TEM, which is equipped with a Super-X EDX detection system. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Analytical Axis Ultra DLD spectrometer using a monochromatic aluminum source (Al K α , 1486.6 eV) operating at 150 W (10 mA emission current and 15 kV HT). Fourier transform infrared spectroscopy analysis was performed using a Perkin Elmer Spectrum Two ATR FTIR spectrometer. Sample solutions in ethanol were drop cast onto the single reflection diamond sample window and the ethanol allowed to evaporate prior to obtaining an FTIR spectra.

The catalytic activity of FePt NP decorated PS spheres was evaluated by studying the catalytic degradation of azo dyes in aqueous solution. In a typical experiment, 3 mL of 20 mM of either Bourdeaux Red (Aldrich, dye content ~ 70%) or Methyl Orange (Fisher indicator) azo dye was combined with 20 μ L of freshly prepared 5 mM NaBH₄ and 50 μ L of ~1 wt% aqueous solution of NP decorated PS spheres [25,26]. The catalytic degradation of the azo dye was monitored by UV-Vis spectroscopy with a Varian Cary Win 300 Bio UV-Vis spectrophotometer as a decrease in absorption with time. Reaction rates have not been reported since the time required for degradation depended greatly on how well the NP decorated PS spheres dispersed into the solutions of dye molecules (e.g., agitation of the sample) and the time passed since preparation of the NaBH₄ solution.

3. Results and Discussion

Nanoparticle decorated PS spheres were prepared by a two-step method. Nanoparticles and PS spheres were individually prepared before assembly of the desired PS@NPs. This two-step process enables control over the properties of both the NPs and PS spheres. In contrast to a one-pot method, a two-step process is optimal for tuning the properties, dimensions and shapes of the NPs before assembly onto the PS spheres. In our method, polyvinylpyrrolidone (PVP) stabilized NPs were first synthesized using literature methods [21-24], via routes that could be extended to the preparation of a variety of other metal and metal alloy NPs [27,28], metal oxide NPs [29,30], and semiconducting NPs [31]. These NPs were subsequently added to a suspension of amine functionalized PS spheres under acidic conditions (pH ~3). These conditions produced uniform coatings of evenly dispersed NPs self-assembled onto the surfaces of PS colloids. These coatings are also very stable, with coatings persisting for over 1 year during storage in alcohol or water. Previous work in our group has demonstrated the use of this method to prepare simple coatings of either gold nanorods or lanthanide up-converting NPs on PS spheres (figure S1) [32,33]. The current study demonstrates the general utility of this method by: i) creating PS@NPs from NPs prepared using a diverse range of synthetic routes; ii) preparing multi-component coatings from the simultaneous self-assembly of NPs of different compositions; and iii) controlling the ratio of dissimilar components, as well as the overall loading of NPs in these self-assembled coatings on the PS spheres.

The loading and distribution of NPs self-assembled onto each of the PS spheres has important implications for their utility, such as optimizing these materials for use in a variety of applications [1-20]. The loading of NPs on the PS@NPs is controlled by tuning the relative concentrations of NPs and PS spheres during self-assembly. For example, the average number of NPs assembled onto 200-nm diameter PS spheres can be tuned by nearly one order of magnitude (figure 1). Average distance between the Pt NPs varied in proportion to their surface coverage. Nanoparticles were separated by 10.8 ± 4.3 nm, 9.3 ± 3.6 nm, and 6.2 ± 1.8 nm with corresponding parking areas (average surface area occupied by an individual NP on a PS sphere, figure S2) of $92 \text{ nm}^2 \pm 16\%$, $68 \text{ nm}^2 \pm 15\%$ and $30 \text{ nm}^2 \pm 9\%$ per NP, for PS@NPs with low, medium, and high Pt NP surface coverage, respectively. The NPs were uniformly distributed over the surfaces of the PS spheres as observed by TEM analysis. This uniformity is further supported by the relatively small ($\leq 16\%$) and consistent variation in parking area measured for each sample, even while varying the average loading from ~100 to ~1000 NPs per sphere (the quantification method is described in supporting information; figure S2).

Complex multi-component nanoparticles have been pursued for a range of different applications, with each discrete type of nanoparticle lending unique properties to the final composite [34-36]. In this study, multi-component coatings were prepared through the assembly of a mixture of Pt and Pd NPs onto the surfaces of the PS spheres (figure 2). Three distinct types of multi-component PS@NPs were prepared, each with a different composition (i.e., distinct ratios of Pt to Pd within the coating) as evaluated by XPS (figure S3, table S1). This compositional variation was achieved by tuning the relative concentrations of each component during the self-assembly process. The uniformity of these samples, as measured by the distribution of individual NPs and by overlap between Pt and Pd, was assessed by combining electron microscopy imaging with energy dispersive X-ray spectroscopy to create elemental maps of the PS@NPs (figure 2). Each sample had a distinct composition, and contained a uniform distribution of both Pt and Pd over the surfaces of the PS spheres. These results are the first demonstration of a method to prepare uniform, multi-component PS@NPs with fine control over the concentration of their distinct components. This process also provides a unique ability to further optimize the properties of the assembled colloidal materials for specific applications.

In order to better understand how this method enables the formation of uniform coatings with control over composition and loading of NPs, we took a closer look at the interacting components during the self-assembly process. Many studies have explored the parameters that influence NP self-assembly, such as shape of the particles, surface chemistry, choice of solvent and its ionic strength [37-43]. The processes taking place during the formation of these PS@NPs may be governed by a

number of different mechanisms. It might appear that heterocoagulation plays a significant role in the self-assembly of NPs onto the surfaces of PS spheres. The high ionic strength of our mixture though weakens the polar interactions of PVP with the PS spheres [44]. As well, the addition of increasing amounts of PVP while preparing the NP coatings either improves [32,33] or has no effect (data not shown) on the self-assembly process, which is counter to the effects seen by Li et al. when coating Au NPs onto PS spheres via heterocoagulation [9]. The self-assembly observed in this current study is attributed to the interactions of PVP stabilizing groups with the surfaces of the PS spheres. The dominant interactions are likely hydrogen bonding and electrostatic interactions. This conclusion is based in part on the reported conformation of PVP molecules in solution and the acidic conditions necessary for a successful assembly of the NP coatings [43,44]. Additional observations that support this conclusion include: i) unsuccessful attempts to prepare high-quality NP coatings by the same conditions using different surface chemistries on the NPs (e.g., trisodium citrate) ii) the ability to prepare NP coatings with PS spheres with other functionalities that enable H-bonding (e.g., carboxyl functionalized PS at pH 3, figure S1); iii) uniformity of NP coatings regardless of the type of NP; and iv) homogeneity of the composition over the surfaces of the PS spheres for a multi-component coating. Small amounts of PVP appear to remain associated with the NP decorated PS after purification (figure S4), suggesting that PVP interacts strongly with the PS spheres (enduring the purification process) and may stabilize the NP coatings on the surfaces of the PS spheres. The even distribution of NPs over the surfaces of the PS spheres is most likely due to coulombic repulsion between neighbouring NPs [37]. Altogether, these observations suggest that PVP plays a key role in the self-assembly process, through simultaneous interactions with the surfaces of both the NPs and PS spheres to create stable, tunable and uniform PS@NPs.

Coating NPs onto the surfaces of PS spheres prior to use in a catalytic reaction imparts several advantages. These advantages include, but are not limited to, stabilization of the NPs during the catalytic reaction and simplification of the process required to isolate these particles from solution following the reaction. For example, the PVP stabilized Pt NPs could not be readily isolated from the solution by centrifugation (at force < 3000xg) or filtration following their initial synthesis. Upon coating onto the PS spheres, these NPs were quickly separated from solution via centrifugation at a relatively low force (e.g., 3 min at 1000xg for Pt NP decorated 200-nm diameter PS spheres) or filtration. The catalytic degradation of azo dyes, a potentially harmful environmental contaminant, using FePt NP decorated PS spheres demonstrates the utility of these materials in catalytic reactions. These studies also provided further insight into the colloidal stability of the decorated PS spheres. The FePt NPs were chosen for this study due to their monodisperse size and shape, which was necessary in order to appropriately assess changes in the loading and distribution of NPs within the coatings. In contrast to our demonstration of multi-component Pt/Pd NP decorated PS spheres, the FePt NPs were not prepared from two different types of particles, but rather one particle that is composed of a FePt alloy (figure S5). Suspensions of the FePt NP decorated PS spheres (figure 3) were combined with either methyl orange (MO) or Bordeaux red (BR) azo dyes along with a dilute solution of NaBH₄ (as a co-catalyst) [25,26]. Degradation of the dyes was monitored by UV-Vis spectroscopy through a decrease in absorption by the dyes (figure 3). A complete loss of the dye's absorption peak was typically observed after about 10 minutes. The addition of only the NP decorated spheres or the dilute NaBH₄ solution had no measurable impact on the absorption of the dye in solution. These results indicate that the assembled coatings of NPs were catalytically active; the observed decrease in UV-Vis absorption did not result from a reaction with NaBH₄ alone or from adsorption of dye molecules onto the NP decorated PS spheres. The PS@NPs were isolated from solution by centrifugation and re-used in five separate catalytic reactions. The FePt NPs remained adhered to the surfaces of the PS spheres after the five catalytic cycles. Approximately one third of the NPs appear to be lost from the coatings by the end of the fifth catalytic reaction (without accounting for aggregation or agglomeration of the FePt NPs remaining adhered to the surfaces of the PS spheres). Further analysis of the TEM images (figure S6) suggests that agglomeration of NPs on the surfaces of the PS spheres could be a predominant route for the observed NP "loss". This observation indicates that the PVP continues to

interact with the surfaces of the PS spheres (and adhere the NPs to those surfaces), but a disruption of the coulombic repulsion between the NPs results in a change in NP distribution. Overall, the PS@NPs exhibit desirable properties for potential use in aqueous and alcohol based catalytic reactions, such as tunability of the NP coatings, ease in separating the PS@NPs from reactant solution and their stability over multiple catalytic cycles in the degradation of azo dyes.

4. Conclusions

A tunable method has been demonstrated for the preparation of uniform NP decorated PS spheres by self-assembly of NPs onto the surfaces of PS spheres. Uniformity of these coatings, regardless of the composition of the NP, is attributed to interactions between the PVP stabilizing groups on the NPs and the functionalized surfaces of the PS spheres, as well as from coulombic repulsion between the NPs. The NP surface coverage was tuned from 1.1×10^4 to 3.3×10^4 Pt NPs per μm^2 of PS surface area, providing the ability to optimize NP density as necessary for future applications. Multi-component coatings of NPs were prepared by the co-assembly of Pt and Pd NPs. The relative ratio of each component could be readily tuned during the self-assembly process. The distribution of NPs over the surfaces of the PS spheres appeared uniform by electron microscopy analysis and energy dispersive X-ray spectroscopy elemental mapping (in the case of multi-component NP coatings). This uniformity was statistically confirmed for Pt NP decorated PS spheres of varying NP loading by analysis of the average particle spacing. Polystyrene spheres decorated with FePt NPs were also prepared and shown to be active in the catalytic degradation of azo dyes, a toxic environmental contaminant. These NP coatings were generally stable following several subsequent catalytic reactions. A change in NP distribution was observed (e.g., aggregation of the NPs on the surfaces of the PS spheres), but the NPs appeared to remain adhered to the PS spheres surfaces as a result of persistent PVP interactions. The two-step method described here for creating NP decorated PS spheres has been demonstrated to be highly versatile for the preparation of PS@NPs that retain their colloidal stability, exhibit uniform composition over the PS sphere surfaces, and have a tunable loading of NPs. The adaptability of this method enables its use in preparing designer PS@NPs that exhibit properties suitable for a diverse range of potential applications.

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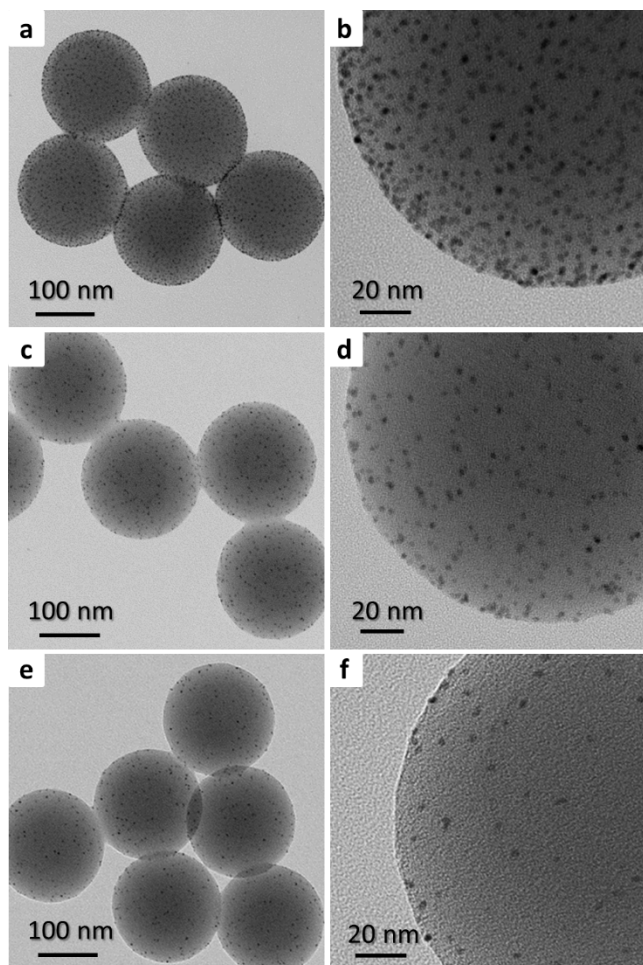


Figure 1. Low (left column) and high (right column) magnification transmission electron microscopy (TEM) images of Pt nanoparticle (NP) decorated 200-nm diameter polystyrene (PS) spheres with a high (a,b), medium (c,d) and low (e,f) NP surface coverage. The average number of NPs per PS spheres is 1026 ± 29 NPs for the sample with a high surface coverage, 362 ± 5 at a medium surface coverage and 116 ± 7 NPs for the sample with lowest surface coverage.

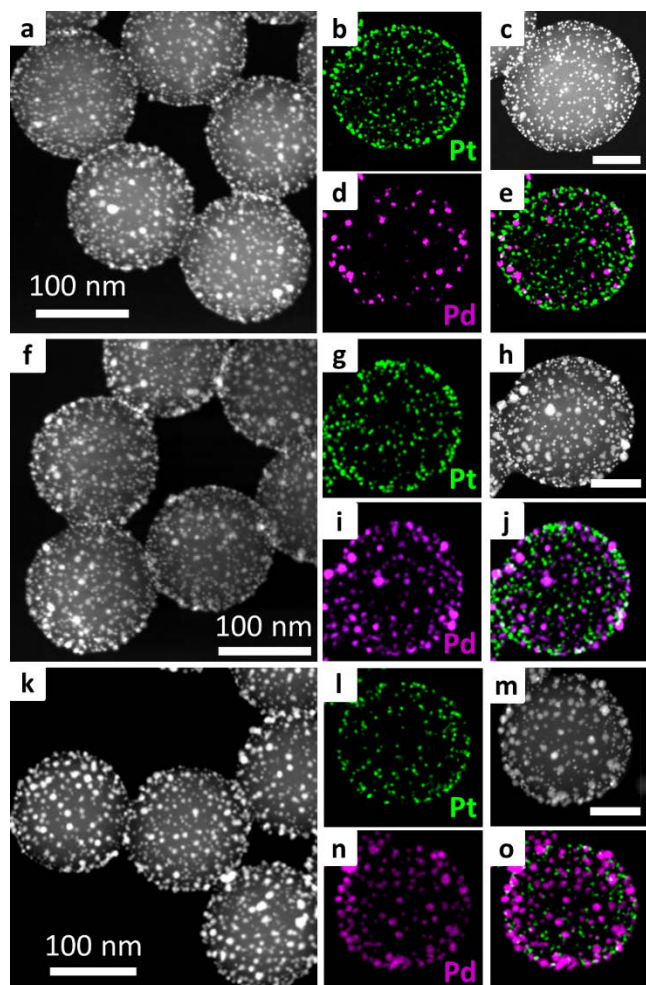


Figure 2. (a,f,k) Low and (c,h,m) high magnification (50 nm scale bars) scanning TEM (STEM) images and elemental mapping by energy dispersive X-ray spectroscopy (EDS) (b,d,e,g,i,j,l,n,o) of multi-component NP decorated 180-nm diameter PS spheres with a tuned ratio of Pt to Pd. Analysis by X-ray photoelectron spectroscopy determined the relative atomic concentrations for the ratio of Pt:Pd to be approximately 44:56, 22:78 and 12:88 for samples 1 (a-e), 2 (f-j) and 3 (k-o), respectively.

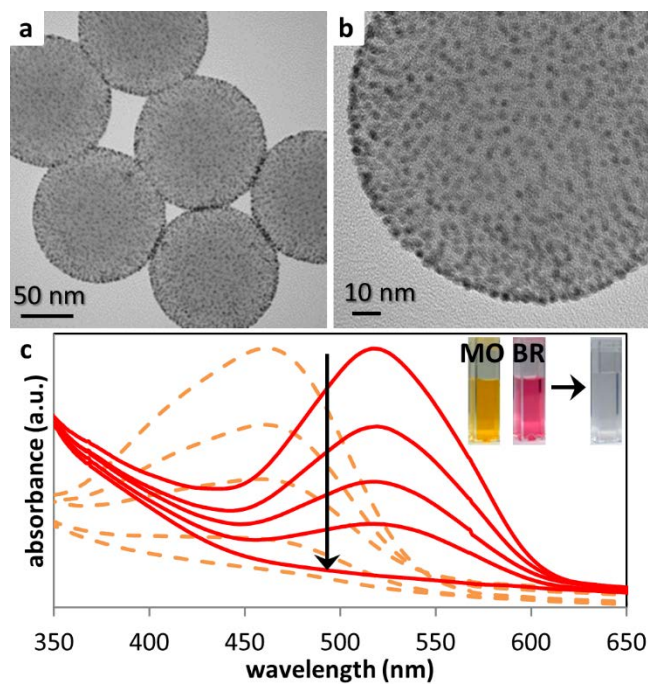


Figure 3. (a) Low and (b) high magnification TEM images of FePt NP decorated PS spheres. (c) UV-Vis absorbance spectrum of methyl orange (MO, orange dashed traces) and Bourdeaux red (BR, solid red traces) dyes recorded during a catalytic degradation facilitated by FePt NP decorated PS spheres. The first spectrum was recorded shortly after addition of these PS@NPs to each solution of dye. The remaining spectra were obtained at approximately equal intervals of time between the first and last spectra (approximately 10 min overall). Inset optical images show solutions of MO and BR dyes before (left) and after (right) catalytic degradation.