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COMMUNICATION

Preparation and catalytic evaluation of ruthenium–nickel dendrimer encapsulated nanoparticles *via* intradendrimer redox displacement of nickel nanoparticles†Katherine A. Marvin,^a Nicole N. Thadani,^b Corinne A. Atkinson,^c Emily L. Keller^c and Keith J. Stevenson^{*c}

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Ru and Ru_xNi₃₀ dendrimer encapsulated nanoparticles (DENS) were synthesized using a redox-displacement method. DEN catalytic activity for the reduction of *p*-nitrophenol was evaluated and found to be dependent on the ratio of metals present.

Dendrimer-templated nanoparticle synthesis is an efficient method for preparing a variety of mono- and bimetallic nanomaterials, whose sizes are constrained by the loading capacity of the dendrimer template.^{1,2} A common commercially available dendrimer is composed of repeating amino-amide units (polyamidoamine, PAMAM), whose internal amines coordinate with free metal ions in solution.³ The metal ion affinity for these amine groups strongly influences their partitioning into the dendrimer interior; metal ions such as Cu²⁺ and Pd²⁺ will readily complex within dendrimers under the appropriate conditions and may be directly reduced to metal nanoparticles.^{4,5} However, weakly coordinating metal ions require either a dendrimer template with more appropriate interior groups for coordinating metal cations, which may not be readily available, or an indirect synthetic route. Intradendrimer redox displacement, which involves the formation of dendrimer encapsulated nanoparticles (DENS) of one metal followed by exchange for a second, more noble metal, has been previously reported.⁶ Zhao *et al.*⁶ synthesized Cu₅₅ DENS using generation 6, hydroxyl-terminated (G6-OH) PAMAM dendrimers. Galvanic displacement of Cu⁰ ($E_{\text{ox}} = -0.342$ V) with Ag⁺ to form Ag⁰ ($E_{\text{red}} = 0.777$ V) was then performed. Subsequent displacement of Ag⁰ with Pd²⁺, Pt²⁺ and Au³⁺ to form the corresponding DENS can also be accomplished.

Here, we describe the preparation of ruthenium–nickel dendrimer encapsulated nanoparticles (RuNi DENS) in generation 4 hydroxyl-terminated (G4-OH) PAMAM dendrimers. Previously reported syntheses of Ru DENS used sodium borohydride (NaBH₄)⁷ as well as H_{2(g)}⁸ as reductants, following complexation of the Ru³⁺ for 2–3 days. In this report, we investigated Ni as a potential partner in a displacement scheme to form Ru and RuNi DENS; the displacement was evaluated for 5–20 molar excess (ME) of Ru³⁺ and Ni²⁺, and the resulting effects on the DEN catalytic efficiency for a model reduction reaction were evaluated. This method of preparation eliminates significant metal ion complexation time and results in RuNi DENS that are stable for at least a week under an inert atmosphere.

The galvanic displacement of Ni⁰ with Ru⁰ is based on the following set of half-reactions:⁹

During synthesis, 30 ME of Ni(NO₃)₂ was added to a 10 μM aqueous solution of G4-OH PAMAM dendrimer at pH ~5 and placed on a VWR nutating mixer. After 60–90 min, the UV-Visible absorption spectrum showed a very weak band at 272 nm and no bands associated with Ni²⁺ in solution, indicating that (Ni²⁺)₃₀ was complexed within the dendrimer interior (Fig. 1A). After purging with Ar_(g) for 20 min, the solution was reduced with 5 ME of NaBH₄; the colorless solution turned translucent brown, the spectrum shifted upward, and the distinctive peak at 272 nm flattened. The solution pH was adjusted to ≤ 8 using ~0.010 mL (per mL of solution) of 0.10 M HCl *via* a gas-tight syringe; the approximate solution pH was checked using pHydration paper. The solution was gently purged a second time to remove all residual reductant, and the desired ME of Ar-purged RuCl₃ solution was added drop-wise to the solution with mixing. Over a period of several minutes, the absorbance at wavelengths below 500 nm increase in intensity slightly, and a peak at ~279 nm with a broad shoulder at ~318 nm is observed. These spectral features are consistent

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Fig. 1 UV-Visible absorption spectra of the uncomplexed and complexed Ni²⁺ and Ru³⁺ in the G4-OH dendrimer template (A), and comparison of the formation of G4-OH Ru₂₀(Ni²⁺)₃₀ DENs via direct reduction and Ni⁰ displacement (B).

with those we observed when an anaerobic solution of G4-OH (Ru²⁺)₃₀ was reduced with 20 ME of NaBH₄ (Fig. 1B). Transmission electron microscopy (TEM) images and energy dispersive X-ray spectroscopy data (EDS) of the G4-OH Ru₂₀(Ni²⁺)₃₀ DENs were collected. Analysis of TEM images showed an average particle size of 1.0 ± 0.1 nm with an estimated 1:1 Ru:Ni metal ratio, though the extent of clustering made particles difficult to isolate for single particle EDS analysis (Supplementary Information Fig. S1 and S2†).

Each of the prepared DENs was then evaluated as a catalyst for the reduction of *p*-nitrophenol (*p*-NP). At alkaline pH, *p*-NP is highly colored, and reduction to the colorless *p*-aminophenol occurs very slowly in the presence of excess NaBH₄ but may be increased several orders of magnitude using a catalyst.^{10,11} This reaction may be followed as the intensity at 400 nm (*p*-NP) decreases (Supplementary Information Fig. S3†). The rate of reduction has been observed to be pseudo-first order in the presence of a large ME of NaBH₄:

$$\text{Rate} = k [\text{p-NP}] \quad (1)$$

where the concentration of *p*-NP is directly related to the absorbance at 400 nm via Beer's Law:

$$A = \epsilon l C \quad (2)$$

The rate constant, k (s⁻¹), of the reaction is determined by plotting the corrected natural log of the Absorbance₄₀₀ vs. time (s) via the first order integrated rate law:

$$\ln[\text{Abs}_{400}] = -kt + \ln[\text{Abs}_{400}]_{t=0} \quad (3)$$

Abs₄₀₀ values used to determine rate constants were baseline corrected; the baseline absorbance at 600 nm was subtracted

from the raw Abs₄₀₀ value, giving Abs₍₄₀₀₋₆₀₀₎. The minimum value of Abs₍₄₀₀₋₆₀₀₎ was then subtracted from each Abs₍₄₀₀₋₆₀₀₎ to give the final, baseline corrected Abs₄₀₀ value. Kinetic experiments were performed using Ar-purged solutions and septa-sealed polystyrene cuvettes to maintain anaerobic conditions for the air-sensitive Ru–Ni DENs.

When the reduction of *p*-NP is catalyzed by the individual monometallic G4-OH Ru₃₀ or Ni₃₀ DENs, a significant difference in catalytic activity is noted (Table 1). G4-OH Ru₃₀ DENs exhibited very low to negligible catalytic activity under these reaction conditions (<0.003 s⁻¹); in contrast, G4-OH Ni₃₀ DENs exhibited a high relative efficiency, but were found to demonstrate zero-order behavior for the *p*-NP reaction, with an observed average rate constant of ~ 0.22 s⁻¹ derived from the linear correlation of the final, corrected Abs₄₀₀ vs. time (s).

Following redox displacement of Ni to form bimetallic Ru_xNi₃₀ DENs, it is expected that the displaced, oxidized Ni²⁺ metal ions will remain complexed within the dendrimer as long as the pH is high enough to prevent H⁺ competition for interior amine sites. In addition, the terminal –OH groups are not expected to complex with Ni²⁺, making the formation of intra-dendrimer particles unlikely. The absorption features of Ru⁰ within the dendrimer obscure spectral features that would indicate the presence of Ni²⁺ ions in solution; however, when the reduction of *p*-NP was initiated with an excess of NaBH₄, precipitation was not observed, which is consistent with the formation of fully reduced bimetallic particles, e.g., Ru₅Ni₃₀, present as the catalyst. However, the formation of nickel oxides cannot be ruled out.

The collected kinetic data for the selected combinations of Ru_xNi₃₀ indicate that the ME of Ru present in the DEN may be correlated to the magnitude of the observed rate constant, k (s⁻¹) (Table 1). Ru_xNi₃₀ DENs exhibit first-order behavior as well as variable, and significant, increases in the rate constant as compared to either of the monometallic Ru or Ni DENs. A maximum average rate is observed for G4-OH Ru₁₀Ni₃₀ DENs at 2.21 s⁻¹, and each of the other DEN combinations of Ru and Ni exhibit altered catalytic activity, with the smallest rate observed for nickel-enriched Ru₅Ni₃₀ DENs at 0.96 s⁻¹. It is worth noting that the optimal catalyst, Ru₁₀Ni₃₀, outperformed the best monometallic catalyst (Pd₃₀) we have tested in this size regime (Table S1†).

In conclusion, a redox-displacement method was employed to prepare Ru and Ru_xNi₃₀ dendrimer-encapsulated nanoparticles (DENs). The catalytic activities of alloys containing variable

Table 1 Comparison of the observed kinetic rate constants (k , s⁻¹) using Ru, Ni and RuNi DENs. All solutions were Ar(g)-purged, and each kinetic trial was prepared by adding 1.75 mL of nanopure water and 0.2 mL of 600 μM *p*-NP (pH ~ 12) to the septum-sealed polystyrene cuvette via gas-tight syringe; 0.6 mL of 0.2 M NaBH₄ was then added to the cuvette, and the reaction was initiated by injecting 0.4 mL of 10 μM DEN solution into the stirred solution. Kinetics were monitored using UV-vis spectrophotometry (Ocean Optics USB4000, LoggerPro 3.8)

DEN	Rate constant, k_{avg} , s ⁻¹
Ru ₃₀	<0.003
Ni ₃₀	0.22 ± 0.05
Ru ₅ Ni ₃₀	0.95 ± 0.03
Ru ₁₀ Ni ₃₀	2.21 ± 0.11
Ru ₁₅ Ni ₃₀	1.84 ± 0.02
Ru ₂₀ Ni ₃₀	1.45 ± 0.03

Ru:Ni ratios were evaluated and found to reach a maximum at an intermediate molar ratio of Ru:Ni metals.

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