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To be cited as: *ChemCatChem* 10.1002/cctc.201901710

Link to VoR: http://dx.doi.org/10.1002/cctc.201901710

A Journal of ChemPubSoc Europe

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10.1002/cctc.201901710

Encapsulated gold nanoparticles as a reactive quasi-homogeneous catalyst in base-free aerobic homocoupling reactions

Wongi Jang,[a][b] Hongsik Byun,*[b] and Jun-Hyun Kim*[a]

Abstract: Multiple gold nanoparticles (AuNPs) are physically encapsulated within a poly(N-isopropylacrylamide) particle at room temperature by an *in situ* reduction method using trisodium citrate (Cit) and sodium oxalate (Oxa) to be employed as quasi-homogeneous catalysts for carbon-carbon bond-forming reactions under base-free aerobic conditions. The use of Oxa results in a more rapid formation and higher loading of AuNPs within the polymer particles compared to those prepared with conventional Cit. Upon dispersing both composite particles in EtOH-rich aqueous solvents, the polymer matrices maintain a fully swollen structure while still providing great stability to the AuNPs whose surfaces are analyzed to be nearly free from the reducing/stabilizing agents. As a catalyst in homocoupling reactions, the composite particles prepared with Oxa exhibit higher activity, selectivity, and recyclability with a much lower activation energy than those prepared with Cit. The preparation of the composite particles and their catalytic properties are optimized under environmentally-friendly reaction conditions, and the relationship between structural features and catalytic functions are examined to potentially develop robust, versatile, and green catalytic systems.

The homocoupling of arylboronic acids has been extensively studied because the resulting biaryl products serve as important building blocks to produce specialty chemicals for pharmaceuticals, polymers, agrochemicals, and biomaterials.[1] These carbon-carbon (C-C) bond-forming reactions are typically carried out by homogeneous and heterogeneous reaction systems using transition-metal catalysts under basic conditions. Although palladium has performed as the leading catalyst in the coupling reaction, relatively less toxic gold-based materials have shown the capability to serve as effective catalysts in green solvent environments.[2] As such, the modification of gold–derived catalysts has been widely explored to design homogeneous catalysts with ligands/complexes and heterogeneous catalysts with supported/colloidal nanoparticles, respectively.[1e, 2f, 3] Both of these catalysts have shown some drawbacks associated with their reactivity, selectivity, and recyclability.

Here we prepared a quasi-homogenous catalyst to overcome the limitations for both catalytic systems by integrating gold nanoparticles (AuNPs) into a biocompatible polymer particle. The formation of the composite particles was precisely regulated to maximize the active sites of the physically encapsulated AuNPs, which exhibited an unexpected high catalytic activity in homocoupling reactions.[4] In addition, these composite particles showed an excellent compatibility with various environmentally-friendly solvents (e.g., water and short-chain alcohols) by imparting a long-term stability, enabling their utilization as recyclable catalysts. Although most catalytic homocoupling reactions are generally promoted under basic conditions,[5] controlling the ratio of the water content in alcohol solvents completely eliminates the need for inorganic bases, where the composite particles, acting as a catalyst, only required reactants to form products. Furthermore, these base-free aerobic reaction conditions did not damage the structural features of the composite particles, which allowed for the examination of their recyclability and versatility in the homocoupling of other arylboronic acid derivatives to understand their atypical catalytic performance. Thus, establishing effective modification strategies and reaction conditions to enhance their catalytically active sites, long-term stability, and applicability in green reaction environments is central to the success of AuNP-based catalytic systems.

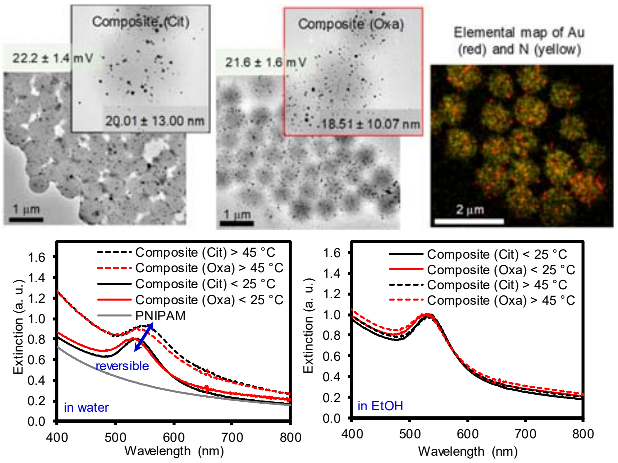

Figure 1. Encapsulated AuNPs with PNIPAM particles prepared with Cit and Oxa under fluorescent light irradiation as well as their corresponding absorption patterns in water and EtOH upon heating and cooling.

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In this work, gold ions were effectively reduced by trisodium citrate (Cit) and sodium oxalate (Oxa) under a fluorescent light source in the presence of functional-group-free poly(N-isopropylacrylamide), PNIPAM, particles (Figure 1 and S1). This *in situ* process reliably resulted in the encapsulation of multiple gold nanoparticles (AuNPs) within the biocompatible polymer networks to form composite particles where the host polymer particles encapsulated the guest AuNPs without any strong electrostatic and/or covalent interactions.[4a, 6] Unlike the formation of bare AuNPs with different sizes in the absence of the PNIPAM particles, the ability to control the size and shape of the encapsulated AuNPs is somewhat limited (~20 nm in diameter) in the presence of the PNIPAM particles using these reducing agents (Figure 2S). The formation processes of these AuNPs under various reaction conditions were thoroughly examined by the distinctive peak position and width of the surface plasmon resonance (SPR).[7] Under the optimized reaction conditions, the use of Oxa as the reducing agent resulted in the more rapid and controlled formation of AuNPs (e.g., narrower size distribution and better loading efficiency) within the polymer particles compared to those prepared with conventional Cit, as supported by the TEM images (Figure 1 and Figure S3).

Subsequent purification and redispersion of the composite particles in EtOH effectively removed the unreacted species and reduced the amount of stabilizing agents from the surface of the loaded AuNPs,[4d, 8] which was verified by the significant decrease in the zeta potential (from -45 mV to -22 mV) regardless of the reducing agents. Minimizing the role of the surface stabilizing agents around the AuNPs could be advantageous for their use as a catalyst because these stabilizers often serve as a physical barrier to decrease the reactivity.[4b-d] In addition, the use of pure EtOH and EtOH-rich aqueous solvents readily eliminated the cononsolvency and thermosensitivity of the composite particles to maintain the fully swollen structures, which was confirmed by the negligible changes of the SPR bands in the temperature range from 20 °C to 65 °C. However, the composite particles in water promptly underwent temperature-induced swelling and deswelling structural changes at the lower critical solution temperature (LCST),[6, 9] which were characterized by reversible SPR bands. The detectable redshift of the SPR bands above the LCST was presumably induced by the interparticle coupling of the encapsulated AuNPs. The subsequent blueshift of the SPR bands upon cooling below the LCST implied that the composite particles returned to their swollen structure in water. The overall SPR bands and their reversibility patterns also indicated the successful formation of the comparable composite particles using the two different reducing agents with the light-induced synthetic method. To quantify the amount of the encapsulated AuNPs within the polymer particles, thermogravimetric analysis (TGA) and atomic absorption (AA) measurements were performed (Figure 2 and Figure S4). The weight loss for the composite particles prepared using Oxa was slightly less (~2 wt%) than those with Cit whereas the bare PNIPAM particles exhibited a notably greater weight loss (5-7 wt%). Similarly, the AA spectroscopy also confirmed that the composite particles prepared with Oxa embraced a slightly more amount of AuNPs within the polymer particles (0.81 mg/mL) than those with Cit (0.77 mg/mL).

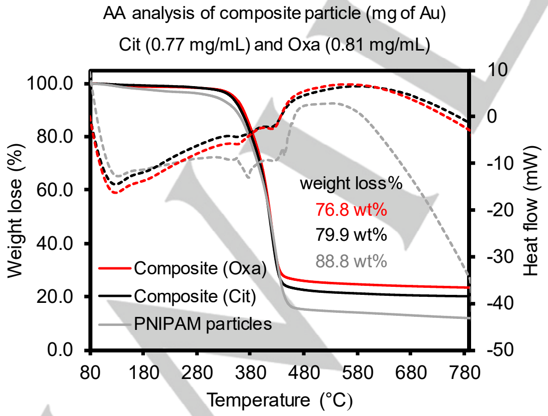


Figure 2. Thermogravimetric and differential scanning calorimetric analysis (TGA/DSC) of bare PNIPAM and composite particles prepared with Cit and Oxa, as well as the amount of loaded gold content examined by atomic absorption spectrometer.

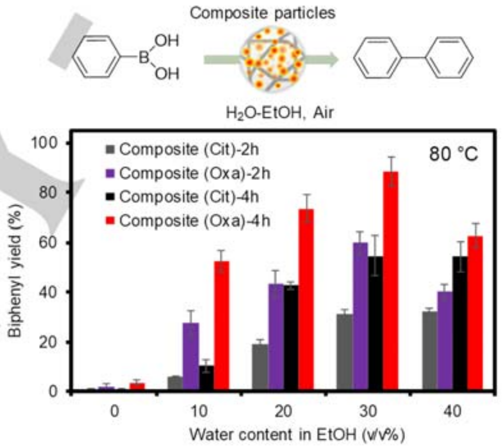


Figure 3. Base-free homocoupling of phenylboronic acid using the composite particles in various EtOH-rich aqueous solvents at 80 °C (all reaction produced less than 3% of phenol byproduct).

Our previous work demonstrated the capability of improving the aerobic homocoupling of arylboronic acid derivatives in alcohol-rich aqueous solvents using inorganic bases and encapsulated AuNPs within PNIPAM particles under ambient conditions.[4a] As the use of Oxa allowed for the rapid preparation of the composite particles with an improved loading efficiency and greater uniformity of AuNPs, both the composite particles (~2.3 mol% of the Au atoms based on the total amount of AuNPs) and ~0.13 mol% of the Au atoms based on the outer surface of the AuNPs were employed in the homocoupling of phenylboronic acid to compare their catalytic properties at 22 °C and 50 °C as a function of time (Figure S5; calculations shown in the supporting information section). In contrast to the bare AuNPs prepared with Cit and Oxa, which exhibited poor catalytic activities due to their instability (the digital photos in Figure S5a), both composite particles in pure EtOH easily yielded over 90% regardless of the reaction temperature. Interestingly, the formation of the biphenyl product was notably faster with the composite particles prepared

10.1002/cctc.201901710

with Oxa than those prepared with Cit (Figure S5b and S5c). This fast conversion rate led us to revisit the homocoupling reactions in the absence of K_2CO_3 base because of the limited solubility of the inorganic base in pure EtOH. The initial base-free homocoupling of phenylboronic acid using both types of composite particles in EtOH only showed a trace level of biphenyl formation, implying the important role of the base in the reaction. As the alcohol-rich aqueous solvents readily eliminated the cononsolvency and temperature-responsiveness of PNIPAM-based particles,[10] introducing a small quantity of water into EtOH only disturbed the pH of the solvent (i.e., possibly creating a slightly basic environment) where the composite particles exhibited atypical catalytic activity in the homocoupling reaction. Figure 3 shows the unexpectedly high catalytic property of both composite particles upon the addition of varying amounts of water at 80 °C. The use of 20-30 vol% water greatly improved the yields of biphenyl, particularly with the composite particles formed with Oxa (presumably due to the slightly greater amount of loaded AuNPs and their uniform size distribution). The presence of a small amount of water evidently played an important role in increasing the catalytic function of the composite particles. It is worth mentioning that the desired biphenyl product has a good solubility in the EtOH-rich solvents and so can avoid an additional extraction step, which enables the composite particles to serve as a quasi-homogeneous catalyst after a brief recovery step by centrifugation.

An additional interesting finding was the trace amount of phenol formation in the base-free reaction conditions. To examine this atypical catalytic selectivity, the same reaction was performed with and without the K_2CO_3 base at 50 °C and 80 °C. The use of the base greatly accelerated the coupling reaction to yield 75% of biphenyl in 1 h, but rapidly formed the phenol by-product up to 25% as well, obviously limiting the selectivity (Figure S6). Both composite particles in the base-free reaction conditions resulted in the modest yields of biphenyl with the undetectable formation of phenol at 50 °C in 8 h. Raising the reaction temperature to 80 °C promptly resulted in a biphenyl yield of over 80% with the negligible formation of phenol (≤ 3%) in 4 h, evidently suggesting a high selectivity in the absence of a base. As the temperature-dependent reactivity is often explained by the collision theory, the activation energies of the reaction were calculated from the Arrhenius plot (Figure S7). Apparently, the base-free homocoupling reaction with the composite (Oxa) (~31.8 kJ/mol) is easier than that with the composite (Cit) (~41.4 kJ/mol), which were within the range of reported values.[2c, 5b, 11]

The recyclability of both composite particles was then tested under the base-free aerobic homocoupling reactions (Figure 4). The catalytic activity of the composite particles gradually diminished from third batch, possibly due to the loss of catalytic activity and/or amount of the composite particles. The latter speculation was withdrawn by our extensive washing of the composite particles (e.g., minimum of three times for precipitation and resuspension) in this recycling test in order to completely remove remaining reactants and products although the recovery of the particles was simply achieved by centrifugation. The detectable reduction of SPR band intensities without changing their shapes after being recycled six times evidently indicated the loss of the composite particles. In addition, a detectable leaching of the encapsulated AuNPs (1.67 ± 0.11 ppm for composite by Cit and 3.39 ± 0.11 ppm for composite by Oxa in each cycle) was also observed by atomic emission analysis (Figure S8). By simply extending the reaction time, recycling the decreased amount of the composite particles (i.e., the amount recovered after the 6th cycle) significantly improved the conversion yield of biphenyl, particularly for the composite particles prepared with Oxa, strongly supporting the idea that the reduced catalytic activity was somewhat caused by the loss of the composite particles rather than their complete deactivation. As such, the greatly improved stability and easily accessible surfaces of the encapsulated AuNPs synergistically influenced the overall catalytic performance of the composite particles.

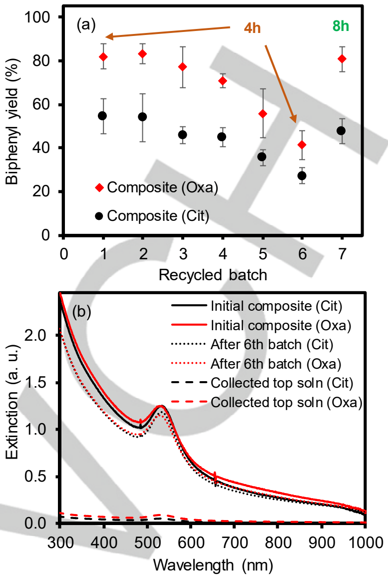
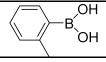
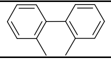
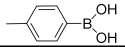
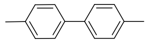
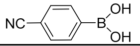
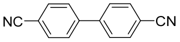
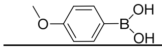
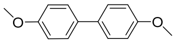
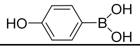
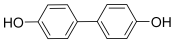


Figure 4. Recyclability of the composite particles under base-free aerobic homocoupling of phenylboronic acid at 80 °C for 4 h (a) and their representative absorption patterns before and after the 6th batch (b).

Given their atypical catalytic activity, selectivity, and recyclability in the base-free reaction conditions, we took one further step to screen the homocoupling reactions of the arylboronic acid derivatives (Table 1). The coupling of 4-methylphenylboronic acid easily reached the over 90% yield in 4 h, whereas 2-methylphenylboronic acid generally exhibited a low yield, presumably due to the steric hindrance. Slightly hydrophilic 4-cyano and 4-methoxyphenylboronic acids resulted in moderate yields, possibly due to the dissimilar solubility in the EtOH-rich aqueous solvent conditions. The coupling of hydrophilic 4-hydroxyphenylboronic acid led to a relatively low yield, which was possibly caused by the deprotonation of the slightly acidic alcohol in the phenol group. This process might compete against the formation of 4-hydroxyphenyl-$B(OH)_3^-$ species in the base-free coupling reactions.[3d, 11] Extending the reaction time (e.g., 8 h) appreciably increased the yields of all products to moderately overcome the steric and miscibility barriers under the same reaction conditions.

Table 1. Base-free homocoupling of phenylboronic acid derivatives in a mixed solvent of water and EtOH (30:70 v/v%) at 80 °C for 4 h using the composite particles prepared with Oxa.

Reactant	Product	Yield (%)

		30[a)] (38)
		≥ 90[a]
		65[b] (75)
		50[c] (57)
		30[d] (56)

[a] GC; [b] GC extraction with acetonitrile; [c] GC extraction with toluene; [d] HPLC, all parentheses indicate the yields of the same reactions for 8 h
*Trace level of byproduct formation (≤ 3%)

In summary, the light-induced synthetic method allowed for the rapid and controlled formation of AuNPs within the PNIPAM particles. Simply controlling the solvent conditions not only decreased the role of the stabilizing agents around the encapsulated AuNPs, but also eliminated the cononsolvency effect and thermo-responsiveness of the composite particles to render a greater stability. Given these features, the resulting composite particles exhibited atypical catalytic reactivity, selectivity, versatility, and recyclability in the base-free aerobic homocoupling reactions in green solvent environments, which can support the development of industrially practical quasi-homogeneous catalysts.

Experimental Section

Encapsulation of multiple gold nanoparticles within a polymer particle

Cross-linked poly(N-isopropylacrylamide), PNIPAM, particles were synthesized via the radical polymerization of NIPAM (1.00 g) and BIS (0.10 g) using the APS initiator (0.12 g) in a 500 mL round bottom flask containing 200 mL water. The solution was purged with argon gas for 1 h and then heated to 70 °C in an oil bath for 4 h. The resulting milky white polymer solution was cooled to room temperature and filtered through a filter paper (Whatman #40) prior to use. An aliquot of the PNIPAM particle solution (10 mL) was then mixed with 1.0 ml of the $HAuCl_4.3H_2O$ solution (1.0 wt% in water) for at least 45 min. Varying amounts of trisodium citrate solution (Cit, 1.0 wt% in water) and sodium oxalate solution (Oxa, 1.0 wt% in water) were then added into the mixture, which was placed in a water-jacketed beaker and exposed to a fluorescent light (~80 mW/cm^2) equipped with a UV filter. The light intensity was estimated by a handheld optical power meter (1916-C Power Meter, Newport Inc.) in the range of 520 to 550 nm. This *in situ* reduction method allowed for the formation of multiple gold nanoparticles (AuNPs) within the polymer particle template under light irradiation while keeping the temperature of the reaction vial below 25 ºC. The formation of AuNPs was easily confirmed by the solution color change from yellow to red in 1 h with Cit and 30 min with Oxa. The composite particles prepared with Cit were additionally stirred overnight after 3 h of light irradiation, while the composite particles prepared with Oxa were stirred for 2 h after 2 h of light irradiation. The controlled formation of the composite particles with their kinetics was monitored by the absorption measurements to optimize the reaction conditions (Figure S1 and S2). The final solution was centrifuged at 5000 rpm for 25 min twice (Sorvall Legend X1 Centrifuge Series, Thermo Scientific) in EtOH to remove any free AuNPs and reducing agents. The purified composite particles were then resuspended in various volume ratios of water and EtOH (0 - 40 v/v% in ethanol) prior to use in the catalytic reactions. The bare AuNPs were also prepared under the same process in the absence of PNIPAM particles. After purification, the bare AuNPs were resuspended in water for the UV-vis measurements and in EtOH for the homocoupling reactions (Figure S3).

Homocoupling of arylboronic acid derivatives

The homocoupling of phenylboronic acid was carried out with the composite particles and bare AuNPs in pure EtOH and a mixture of water-EtOH solvents (Figure S5a). For example, an aliquot (2.0 mL) of the composite particles in EtOH was mixed with phenylboronic acid (21 mg, 0.17 mmol) and K_2CO_3 (67.0 mg, 0.48 mmol) in a capped glass vial. After stirring at ambient conditions for 24 h, the resulting solutions were centrifuged at 10,000 rpm for 5 min (Sorvall Legend Micro17 centrifuge, Thermo Scientific) to separate the composite particles, and the top liquid layer (1.0 mL) was directly subjected to GC analysis. Similarly, the homocoupling reaction was performed under various conditions, including the temperature, solvents, and time, in the presence and absence of the K_2CO_3 base. For the recyclability tests, the composite particles were suspended in a pre-prepared EtOH-rich aqueous solvent (30 v/v% of water and EtOH) solution for the homocoupling reaction at 80 °C for 4 h. After the reaction, the composite particles were quantitatively transferred to an Eppendorf tube and purified three times by repeating the centrifugation (10,000 rpm for 30 min) and redispersion of the composite particles in the solvent to completely remove the organic reactants and products. The recovered composite particles were then redispersed in 2 mL of the solvent prior to the next cycle. The base-free homocoupling of the arylboronic acid derivatives containing the methyl, cyano, methoxy, and hydroxyl groups was performed under the same reaction conditions. In the case of the products exhibiting a poor solubility in the mother liquor, the reaction mixture was completely dried by a rotary evaporator and redispersed in the proper solvent (e.g., 4,4'-dicyanobiphenyl in acetonitrile and 4,4'-dimethoxybiphenyl in toluene). After a brief sonication, the mixture was centrifuged to collect the top solution for the GC and HPLC analyses.

Acknowledgements

This work is supported by the National Research Foundation of Korea Grant funded by the Korean Government (NRF-2018R1A2B6008854). This work is also supported by Illinois State University's Department of Chemistry.

Conflict of interest

The authors declare no conflict of interest.

Keywords: poly(N-isopropylacrylamide) • encapsulated gold nanoparticles • base-free homocoupling • sodium citrate • sodium oxalate

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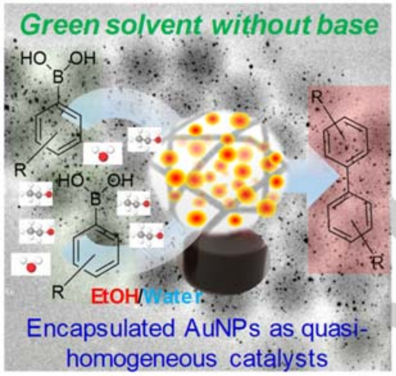
Entry for the Table of Contents

Layout 1:

COMMUNICATION

Encapsulated gold nanoparticles within a polymer particle exhibit a high reactivity, selectivity, and recyclability in base-free aerobic homocoupling reactions to serve as a green catalyst.



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Encapsulated gold nanoparticles as a reactive quasi-homogeneous catalyst in base-free aerobic homocoupling reactions