# Heterogeneous Catalysis |Hot Paper|



# Size-Selective Yolk-Shell Nanoreactors with Nanometer-Thin Porous Polymer Shells

Ying Jia,<sup>[a]</sup> Sergey N. Shmakov,<sup>[b]</sup> Paul Register,<sup>[a]</sup> and Eugene Pinkhassik<sup>\*[b]</sup>

**Abstract:** Yolk-shell nanoreactors with metal nanoparticle core and ultrathin porous polymer shells are effective catalysts for heterogeneous reactions. Polymer shells provide size-selectivity and improved reusability of catalyst. Nanocapsules with single-nanometer porous shells are prepared by vesicle-templated directed assembly. Metal nanoparticles are formed either by selective initiation in pre-fabricated nanocapsules or simultaneously with the creation of a crosslinked polymer shell. In this study, we investigated the oxidation of benzyl alcohol and benzaldehyde catalyzed by gold nanoparticles and hydrogenation of cyclohexene catalyzed by platinum nanoparticles. Comparison of newly created nanoreactors with commercially available nanoparticles revealed superior reusability and size selectivity in nanoreactors while showing no negative effect on reaction kinetics.

# Introduction

This work addresses the challenge of creating yolk-shell nanoreactors combining size selectivity and fast reaction rates. These nanoreactors contain gold or platinum nanoparticles entrapped in hollow porous styrene or acrylate polymer nanocapsules with single-nanometer shell thickness that enabled selective permeability and fast mass transfer through the shells.

Hybrid structures composed of nanosized components encapsulated in matrix materials have drawn considerable attention in the past few years. One particularly promising type of these nanostructures known under different names—yolkshell, core@shell, nanorattle, or ship-in-a-bottle nanoreactors (NRs)—consists of metal nanoparticles (NPs) confined within shells or voids of organic or inorganic material.<sup>[1]</sup> Semipermeable walls of NRs act as a physical barrier against large-scale metal NPs aggregation.

The combination of active core and porous shells defines the rapidly developing application of such NRs in heterogeneous catalysis.<sup>[1]</sup> To date, many different reactions were catalyzed by NRs, including reduction,<sup>[2]</sup> oxidation,<sup>[3]</sup> halogenation,<sup>[2a]</sup> and a few others.<sup>[4]</sup>

[a]	Y. Jia, P. Register
	Department of Chemistry
	Saint Louis University
	3501 Laclede Ave, 63103 (USA)
[b]	S. N. Shmakov, E. Pinkhassik
	Department of Chemistry
	University of Connecticut
	55 North Eagleville Road, Storrs, 06269, CT (USA)
	E-mail: eugene.pinkhassik@uconn.edu
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Silica,<sup>[2a-f,n; 3:5a]</sup> carbon,<sup>[2g-i; 5b,c]</sup> TiO<sub>2</sub>,<sup>[2],k]</sup> and CeO<sub>2</sub><sup>[2],m]</sup> have been the most popular materials used to build shells of NRs. Encapsulation of a catalyst often dramatically improves its reusability. Porous structure of the walls of NRs may offer another important advantage over conventional catalysts—the size selectivity. Indeed, several reports showed that careful control of pore sizes and their uniformity makes it possible to discriminate transport of molecules by their size.<sup>[2n;3a,f,g;5a]</sup> However, for the vast majority of reported NRs, the size selectivity remains a challenge and is often achieved at the expense of the diffusion rate or the conversion of substrates due to the thickness of the shells, which are usually much thicker than tens of nanometers. Thicker shells are associated with slower diffusion rates, particularly when well-defined molecular weight cut-off for permeability is required.<sup>[3f; 6]</sup>

Many applications are not compatible with the typical conditions for the synthesis of NRs, harsh reactions conditions, or thick inorganic shells. Although polymer shells may offer substantial advantages in construction and applications of NRs, they are severely underused. Main challenges include difficulties of producing polymer shells allowing selective ultra-fast mass transfer of reactants and products while maintaining structural integrity of NRs.<sup>[7a,b]</sup> In pursuit of new materials for the yolk-shell nanoreactors, it is essential to focus on combining size selectivity with fast mass transfer. Additionally, recyclability is an important consideration for successful practical applications of nanoreactors.

We have recently established two methods of synthesis of polymer yolk-shell structures with metal cores. These structures contain single or multiple metal nanoparticles of controlled size ranging from a single nanometer to tens of nanometers entrapped within hollow polymer capsules with typical diameters in the 100–200 nm range. The shells of these nanocapsules have single nanometer thickness and programmed nanopores. One of the synthesis methods uses vesicle-templated simulta-

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neous polymerization of nanocapsules and growth of entrapped NPs.<sup>[8a]</sup> The size of entrapped NPs can be controlled by the concentration of metal ion in the aqueous core of the vesicles and the amount of initiator in the bilayer. In another method, NPs are grown exclusively inside pre-fabricated hollow polymer nanocapsules.<sup>[8b]</sup> In the latter approach, growth of gold NPs is seeded by entrapped sacrificial initiator molecules. The type of initiator, concentration of metal ions, and the length of the synthesis control the size of NPs.<sup>[8b]</sup> Pre-liminary data showed high activity of such yolk-shell Au NRs in catalyzing the reduction of 4-nitrophenol.<sup>[8b]</sup>

Hollow polymer capsules with ultrathin (1-1.5 nm) walls used here for the construction of yolk-shell NRs above are synthesized by using hydrophobic interior of lipid or surfactant bilayers as templating medium.<sup>[9a-d,k]</sup> Hydrophobic monomers are placed into the self-assembled bilayers and then polymerized and crosslinked to create nanocapsule shells. The templating scaffold can be removed and recycled. This directed assembly approach allowed us to create a variety of capsule-based nanodevices.<sup>[9e-h]</sup> The permeability of the polymer nanocapsule shells can be controlled by imprinting uniform molecular size nanopores using different pore-forming templates, as well as by pore functionalization.<sup>[9a,f,i,j]</sup> By controlling the size and chemical environment of nanopores, we were able to achieve size-selective permeability as well as transport regulated by external environment.<sup>[9a,f,i,j]</sup> Bilayer-templated porous polymer walls with single-nanometer thickness enable ultra-fast transport of ions and small molecules while being impermeable to molecules larger than the pore size.<sup>[9b]</sup>

This study describes successful use of hollow polymer nanocapsules in the creation of size-selective and fast-acting nanoreactors. Here we report catalytic performance, recyclability, and size selectivity of NRs with Au and Pt movable cores entrapped in vesicle-templated capsules with porous nanometerthin shells.

### **Results and Discussion**

By varying reaction conditions (concentration, temperature, or time), one can control the size of entrapped NPs. In this work, we used polyether dendrimer DE-(OH)<sub>12</sub> as a sacrificial molecule to initiate and grow gold NPs exclusively inside nanocapsules (Figure 1 A,B; Figures S1 and S2, Supporting Information). This approach produced NPs with the average size of 5.4 nm, as determined from TEM data.<sup>[8b]</sup> Atomic absorption experiments showed 0.4–0.6 wt.% of gold loading in NRs. The total surface area of gold NPs was calculated from the average size of NPs to be approximately 56 m<sup>2</sup>g<sup>-1</sup>.

Commercially available Au NPs supported on TiO<sub>2</sub> were used as a reference. They have been extensively studied in alcohol oxidation and esterification reactions.<sup>[10]</sup> The total accessible area of TiO<sub>2</sub>-supported NPs was calculated according to published procedures<sup>[11]</sup> to be approximately 112 m<sup>2</sup>g<sup>-1</sup>. Benzyl alcohol esterification is a one-pot cascade reaction in which Au NPs catalyze both steps (formation of benzaldehyde intermediate and its conversion to an ester). Studying the behavior of Au NRs in this process should provide an important insight

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**Figure 1.** TEM (A) and SEM (B) micrographs of a typical polymer NC containing entrapped Au NP early stage kinetics of methyl benzoate formation. Au-Cat = reference Au@TiO<sub>2</sub> (circles, -----) and Au NRs ( $\Box$ , -----); MeONa, 30 °C, O<sub>2</sub> 3 atm.

into catalytic performance of polymer nanoreactors under oxidative conditions.

To compare activities of Au NRs and reference catalyst, we studied the early stage kinetics of benzyl alcohol esterification (Figure 1C; Figures S3 and S4, Supporting Information). At conversion rates below 10%, the reaction kinetics can be adequately approximated with a linear fit. When two catalysts were used in amounts corresponding to the same total surface area of Au NPs, we observed the same reaction rates for Au NRs and the reference catalyst. This observation suggests that shells do not slow down the diffusion of reactants and the products in and out of nanocapsules. The rate-limiting step in the overall process is the catalytic reaction rather than the mass-transfer though the shells.

To expand the range of catalytic applications, we prepared Pt NRs by vesicle templated synthesis using acrylate monomers (Figure 2A,B; Figure S5, Supporting Information). The growth of Pt NPs was initiated simultaneously with the formation of the polymer shell of the nanocapsules, similarly to our previous report on the creation of silver nanorattles.<sup>[8a]</sup> Dynamic light scattering data showed no effect of Pt ions on the formation of polymer shells (Figure S6, Supporting Information). Reaction conditions were selected to create Pt NPs with the sizes close to commercially available Pt NPs supported on activated carbon (Figure S7 and S8, Supporting Information).

Hydrogenation of alkenes by supported Pt or Pd nanoparticles has been widely used as a popular benchmark of catalyst efficiency due to its simplicity and substantial industrial relevance.<sup>[2g,n; 7d]</sup>

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**Figure 2.** TEM micrographs of Pt NRs (A) and expanded view of Pt NPs entrapped within nanocapsules (B). Early stage kinetics of cyclohexene hydrogenation (C). PtCat = reference Pt/C ( $_{\circ}$ , -----) and Pt NRs ( $_{\Box}$ , -----); 40 °C; H<sub>2</sub> 1 atm.

We used catalytic hydrogenation of alkenes to evaluate the performance of Pt NRs and to compare it with commercially available Pt NPs supported on activated carbon (Pt/C; Figure 2C; Figures S9 and S10, Supporting Information). Similarly to the experiments above, kinetic studies were done using samples containing the same amount of Pt NPs. Atomic absorption experiments showed approximately 4.6 wt.% of platinum loading in NRs.

Again, shells of Pt NRs did not show any negative effect on the reaction rates, which suggests rapid diffusion of reactants and the products. No side product formation was detected.

To study reusability of catalysts, we investigated the formation of methyl benzoate described above. Esterification of benzyl alcohol proceeds through the formation of benzaldehyde as an intermediate in the rate-limiting step (Figures S3 and S4, Supporting Information). To simplify the experiments, we used benzaldehyde as a substrate for the study of reusability of catalysts.

In four sets of experiments, Au NRs showed no loss of activity (Figure 3; Figure S11, Supporting Information). In contrast, the activity of catalyst supported on TiO<sub>2</sub> decreased dramatically (Figure 3; Figure S12, Supporting Information). Calculated turnover number, TON, for Au NRs was approximately 2200 for the four reactions. Under identical conditions, the yield in the reaction catalyzed by Au@TiO<sub>2</sub> dropped by the fourth run from ~71 to ~25%. Calculated TON for four runs was approximately 1600. Apparent reasons for the activity loss could be the Ostwald ripening process and leaching of gold ions during the washing step. TEM images indicate growth of TiO<sub>2</sub> supported



Figure 3. Performance of Au NP catalysts in multiple subsequent reactions measured by the yield of the ester for Au NRs (striped bars) and  $Au@TiO_2$  (solid bars).



**Figure 4.** Size distribution of Au NPs in Au@TiO<sub>2</sub> and Au NRs. Sizes of Au NPs were measured from TEM micrographs. Samples A and C show Au NPs in Au@TiO<sub>2</sub> before the reaction (A) and after 4th run of esterification reaction (C). Samples B and D show Au NPs in Au NRs before the reaction (B) and after 4th run of esterification reaction (D).

Au NPs from 2.8 nm in starting material to 3.8 nm on average after the fourth run (Figure 4A,B; Figure S13, Supporting Information). This growth alone would result in the decrease of the total surface area of Au NPs by approximately 27%. In addition, atomic absorption measurements showed overall Au loss of  $9 \pm 1.3$ % after the fourth run.

Combined Ostwald ripening and leaching of gold ions accounts for only a fraction of the activity loss, which strongly suggests that the surface of Au NPs was partially fouled during these repeated reactions. In contrast, encapsulated Au NPs neither changed in size nor leached out of nanocapsules upon repeated experiments (Figure 4C,D). Polymer shells likely protected Au NPs from surface fouling.

Pt NRs showed similar repeatable performance. In six subsequent experiments, we found no evidence of the loss of activity (Figures S14 and S15, Supporting Information).

As shown previously, the size of intrinsic pores in the wall of vesicle-templated nanocapsules is less than 0.8 nm.<sup>[9a-c]</sup> To probe the size-selective permeation through the walls of nano-capsule, we compared the conversion of benzaldehyde and its sterically crowded analogue, 3,5-di-*tert*-butyl benzaldehyde

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**Figure 5.** Size-selective oxidation of benzaldehyde and DTBBA by  $Au@TiO_2$  (solid bars) and Au NRs (striped bars). Conversion of DTBBA required a longer reaction time than benzaldehyde. For each substrate, the reaction was carried out by using the amount of catalyst corresponding to the same total surface area of gold.

(DTBBA), on Au NRs and on Au@TiO<sub>2</sub>. Smallest cross-sections of benzaldehyde and DTBBA are 0.6 and 0.9 nm, respectively (Figure 5). Conversion of DTBBA required a longer reaction time. Figure 5 clearly shows size selectivity of Au NRs, as compared with no selectivity by TiO<sub>2</sub>-supported catalyst (Figure S16, Supporting Information). This remarkable size selectivity is achieved without compromising the mass-transfer rate through the shell.

To test the durability of ultrathin polymer shells we designed control experiments simulating reaction conditions. SEM analysis and permeability studies with nanocapsules containing entrapped dyes confirmed that the structural integrity of NRs remained intact under both oxidative and reductive reaction conditions (Figure 6). In these experiments, tetrasodium-*meso*tetra(4-sulfonatophenyl) porphine (TSPPNa) was entrapped in polymer nanocapsules. Samples were repeatedly subjected to



**Figure 6.** A) SEM micrograph of Au NRs after 4th run in benzyl alcohol esterification confirming preservation of spherical shape of nanocapsules; B) Retention of fluorescent molecules supporting lack of degradation of capsule shells: aqueous dispersions of nanocapsules with entrapped water-soluble fluorescent tetrasodium-*meso*-tetra(4-sulfonatophenyl) porphine (TSPPNa) molecules (smallest cross-section 1.5 nm): control sample (1), nanocapsules containing Au NPs and TSPPNa after 4th run in benzyl alcohol esterification (2), nanocapsules containing Pt NPs and TSPPNa after 4th run in 1-hexene reduction (3). Lack of release of TSPPNa from samples 2 and 3 supports structural integrity of nanocapsule shells under the reaction conditions.

the same reaction conditions as described above. After each reaction step, nanocapsules were redispersed in water. During these steps, any released TSPPNa molecules would be separated from the nanocapsules. The smallest cross-section of TSPPNa is approximately 1.5 nm. No escape of fluorescent TSPPNa molecules was observed under reaction conditions used here. Retention of the originally encapsulated TSPPNa (Figure 6) suggests that the capsules did not break or develop pinhole defects.

# Conclusion

In summary, encapsulation of metal NPs in hollow nanocontainers with porous polymer walls with single-nanometer thickness offers size selectivity and improved catalyst recycling without compromising reaction kinetics. Au NRs maintain the same level of catalytic activity and withstand relatively harsh reaction conditions (high concentration of a base, oxidizing agent, high pressure, etc.) in repeated catalytic reactions, while the activity of reference catalyst degrades significantly. Nanoreactors based on encapsulated metal NPs proved to be efficient catalysts for different types of reactions. As shown previously, the permeability of the polymer nanocapsule shell can be controlled by imprinting uniform molecular size nanopores using different pore-forming templates, as well as by pore functionalization.<sup>[9f,i,j]</sup> Considering straightforward control of size and chemical environment of nanopores,<sup>[9a,f,i,j]</sup> we anticipate that ultrathin polymer-based NRs will be easily expanded to different types of catalysts and catalytic processes.

## **Experimental Section**

#### General

Chemicals were purchased from Sigma–Aldrich unless noted otherwise. 1,2-Dimyristoyl-sn-glycero-3-phosphocholine (DMPC) was purchased from Avanti Polar Lipids, Inc. as a dry powder. Gold 1% on TiO<sub>2</sub> (Au@TiO<sub>2</sub>) was purchased from STREM Chemicals. 3,5-Di-*tert*butylbenzaldehyde (DTBBA) was purchased from Frontier Scientific. All chemicals were used as received, unless noted otherwise. Butyl methacrylate (BMA), *tert*-butyl methacrylate (tBMA), *tert*-butylstyrene (*t*BuSt), ethylene glycol dimethacrylate (EGDMA), and *p*-divinylbenzene (DVB), were passed through an alumina column to remove the inhibitor shortly before the polymerization. Solvents (Fisher Scientific) were HPLC-grade and used as received. All glassware was washed with aqua regia prior to synthesis of gold nanoparticles. Polyether dendrimer DE-(OH)<sub>12</sub> was prepared as described previously (Figure S2, Supporting Information).<sup>[8b]</sup>

#### Methods

Shimadzu GC 2010-Plus equipped with FID and Shimadzu GCMS 2010 were used to monitor reaction kinetics. Hydrodynamic diameter measurements were performed on a Malvern Nano-ZS Zetasizer (Malvern Instruments Ltd., Worcestershire, U.K.). SEM and Scanning Transmission Electron Microscopy (STEM) images were acquired on FEI Inspect F50 microscope. TEM was carried out on FEI Tecnai Spirit and JEOL JEM-2010 FasTEM microscopes. Atomic absorption experiments were carried out on GBC 908AA instrument equipped with a graphite furnace.

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#### Synthesis of styrene nanocapsules

Nanocapsules were prepared using a previously described procedure.<sup>[9c]</sup> Two monomers solutions containing (S1) Cetyltrimethylammonium tosylate (CTAT) and (S2) sodium dodecylbenzenesulfonate (SDBS) were prepared. Solution S1: tBuSt (105 µL, 0.57 mmol), DVB (81 µL, 0.57 mmol), 2,2-dimethoxy-2-phenyl-acetophenone, DMPA, (3 mg, 0.01 mmol), and CTAT (200 mg, 0.438 mmol) were added to a test tube, followed by addition of 2.5 mm DE-OH<sub>12</sub> aqueous solution (20 mL). Solution S2: tBuSt (105 µL, 0.57 mmol), DVB (81 µL, 0.57 mmol), DMPA, (3 mg, 0.01 mmol), and SDBS (200 mg, 0.57 mmol) were added to a test tube, followed by addition of 2.5 mm DE-OH<sub>12</sub> aqueous solution (20 mL). Solutions were kept at 35-40 °C for 15 min, then shaken or briefly sonicated to give homogeneous dispersion. Then solutions were quickly mixed up in the desired proportion. In a typical experiment, solutions were mixed in the ratio S1/S2=2:8 (i.e., 2 mL of S1 and 8 mL of S2), shaken several times and then bathed undisturbed for 30 min at 35 °C. The resulting suspension containing vesicles of different sizes was extruded 4-5 times at 35 °C through a track-etched polyester membrane with 200 nm pore size. Oxygen was removed by passing argon through the solution. The sample was irradiated  $(\lambda = 254 \text{ nm})$  in a photochemical reactor equipped with a stirrer (10 lamps of 32 W each; 10 cm distance between the lamps and the sample) for 60 min. Methanol (10 mL) was added, and the precipitate was washed 3-5 times with methanol and then 3 times with acetonitrile over a period of 24 h.

#### Au-loaded polymer nanoreactors (Au NRs)

A slurry of precipitated nanocapsules (ca. 5 mg of dry material) was transferred to a screw-capped test tube equipped with a stir bar and dispersed in 2 mL of acetonitrile. The test tube was placed in water bath and stirred at 60 °C. Then 100 mM HAuCl<sub>4</sub> aqueous solution (10  $\mu$ L) was added to nanocapsules dispersion and the mixture was agitated for 5 min at 60 °C. Then 1 M NaOH (10  $\mu$ L) was added. After 15 min, the mixture was removed from the bath and ice-cold water (8 mL) was added. The resulting colored precipitate was washed with water and methanol.

#### Pt-loaded polymer nanoreactors (Pt NRs)

Pt NRs were prepared by a method similar to the liposome-templated method described earlier for silver loaded nanocapsules.<sup>[8a]</sup> In a typical experiment, tBMA (43 µL, 0.193 mmol), BMA (42 µL, 0.199 mmol), EGDMA (32  $\mu$ L, 0.17 mmol), and DMPA, (1 mg, 3.9 $\times$  $10^{-6}$  mol) were added to a solution of DMPC (0.4 mL, 160 mg, 0.236 mmol) in CHCl<sub>3</sub>. The CHCl<sub>3</sub> was evaporated using a stream of argon to form a lipid/monomer mixture on the wall of a test tube. The film was further dried under vacuum for 5 min to remove traces of CHCl<sub>3</sub>. The dried film was hydrated with 10 mm aqueous solution of neutralized H<sub>2</sub>PtCl<sub>6</sub> (8 mL) to give a dispersion of multilamellar vesicles. During the hydration of the lipid/monomer mixture, the test tube was briefly agitated on a Vortexer every 5 min. The suspension was extruded 16 times at 35 °C through a tracketched polyester Nucleopore membrane (Sterlytech) with 0.2 µm pore size using a Lipex stainless steel extruder (Northern Lipids). Prior to polymerization, unloaded platinum ions were removed from the mixture by size-exclusion chromatography on Sephadex G-50 column. Oxygen was removed by passing argon through the solution. Polymerization was carried out as described above. Methanol (10 mL) was added, and the precipitate was washed 3-5 times with methanol and then 3 times with ethanol.

#### Size of Au and Pt nanoparticles

The size of Au and Pt nanoparticles was determined from TEM micrographs. Size distributions were calculated by measuring more than 300 nanoparticles from a collection of several micrographs. In these measurements, several micrographs were taken from random areas of the sample. Each nanoparticle within each of these micrographs was measured and the results were plotted on a histogram.

#### Dye loading and retention experiments

Dye loading and retention experiments were performed according to a previously described procedure.<sup>[8b]</sup> Polymer nanocapsules with entrapped tetrasodium-*meso*-tetra(4-sulfonatophenyl) porphine (TSPPNa) were prepared by following the same procedures described above for synthesis of liposome-templated nanocapsules except for the hydration step, in which 2.5 mM aqueous solution of TSPPNa was used instead of solution of DE-(OH)<sub>12</sub>. After dye encapsulation, nanocapsules were thoroughly washed with methanol and finally with water until complete disappearance of the Soret band at 416 nm in the UV/Vis spectra of the supernatant was observed. Nanocapsules were subjected to the same reaction conditions followed by addition of water, precipitation, and recording of the UV spectrum of the supernatant.

#### Catalysis

All experiments were carried out in a heavy-walled glass reactor equipped with magnetic stir bar. For kinetic studies, the corresponding reaction was stopped and an aliquot was tested by GC analysis.

#### Esterification of benzyl alcohol

Benzyl alcohol (10.4 uL) was added to a reactor containing 25 wt.% sodium methoxide solution (2.7 g) in methanol, methanol (7.5 mL), powdered Au@TiO<sub>2</sub> (2.6 mg, ~0.13 mol%). *tert*-Butylbenzene or mesitylene were used as an internal standard. The reaction was carried out under 3 atm. of oxygen at 30 °C.

#### Esterification of benzaldehyde and DTBBA

Benzaldehyde (10.1 uL, 0.1 mmol) or 3,5-ditertbutylbenzaldehyde (21.8 mg, 0.1 mmol) was added to a reactor containing 25 wt.% sodium methoxide solution (2.7 g) in methanol, methanol (7.5 mL), powdered Au@TiO<sub>2</sub> (2.6 mg, ~0.13 mol%). *tert*-Butylbenzene or mesitylene were used as an internal standard. The reaction was carried out at 30 °C under 3 atm. of oxygen.

#### Catalytic reactions with Au NRs

Catalytic reactions with Au NRs were carried out in the same way as described above, but instead of  $Au@TiO_{2^r}$  the precipitate of Au NRs was used. Calculated total accessible surface area of Au nanoparticles and  $Au@TiO_2$  were equivalent.

#### Hydrogenation of cyclohexene with Pt/C

Cyclohexene (100 uL) was added to a reactor containing Pt/C (0.25 mg, 0.013 mol% of 10 wt.% Pt/C) in ethanol (4.4 mL) at 40  $^\circ$ C under 1 atm. of hydrogen.

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#### Hydrogenation of cyclohexene with Pt NRs

Cyclohexene (100 uL) was added to a reactor containing a suspension of Pt NRs (0.5 mL) in ethanol (4.5 mL) at 40  $^\circ\text{C}$  under 1 atm. of hydrogen. Total amount of Pt in NRs and in reference Pt/C was equivalent.

In recycling experiments, cyclohexene (507 uL) was used in a mixture of Pt NRs (ca. 4 mg of dry basis) in ethanol (4.4 mL) at 75  $^\circ\text{C}$  under 1 atm. of hydrogen.

#### Calculation of surface area of encapsulated nanoparticles

Surface area of Au nanoparticles in Au@TiO2 was estimated according to calculations used earlier by Bi et al. for supported nanoparticles.<sup>[11]</sup> The calculation of particle surface area was based on a quasi-hemispherical model of gold particles (Supporting Information).

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