

An Ideal Catalyst Carrier: Patchy Nanoparticles with Dual Functional Domains of Substrates Enrichment and Catalysis

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Experimental Section

Materials.

Methyl methacrylate (MMA) was purchased from Damao Chemical Reagent and further purified by distillation. 2,2'-azobis(isobutyronitrile) (AIBN) was purchased from Adamas-beta. Poly(vinylpyrrolidone) (PVP) was purchased from Alfa Aesar. 3-(2-Benzothiazolyl)-N,N-diethylumbelliferylamine Coumarin 6, Potassium persulfate (KPS), were purchased from J&K. Polyoxy ethylene nonyl phenyl ether (NP-40), 2-(methacryloyloxy) ethyl trimethylammonium chloride ([MTMA]-Cl) lithium bis(trifluoromethanesulfonyl)amide (Li-[TFSA]) were purchased from Aladdin. phosphotungstic acid was purchased from Meryer. Benzaldehyde was purchased from TCI. Ethylene glycol was purchased from General-Reagent. N-hexane, menthol were purchased from Beijing Chemical Works.

Synthesis of [MTMA][TFSA] monomer

The ionic liquid monomer was synthesized by just mixing the aqueous solutions of 2.0 g [MTMA]-Cl and 2.3 g Li-[TFSA]. After mixing at room temperature for 12 h, phase separation occurred, and the lower oil phase (ionic liquid monomer, [MTMA][TFSA]) was washed with water.

Preparation of PMMA Seed Particles

3.0 g of MMA, 0.30 g of PVP, and 0.030 g of AIBN were dissolved in a methanol/water medium (1/1 v/v, 60 mL). The homogeneous solution was degassed by several vacuum/N₂ gas exchanges in a round-bottomed flask. After ultrasonic dispersing, the polymerization was carried out at 70 °C for 11 h with stirring by a magnetic stirrer. After reaction, the PMMA seeds were obtained by centrifugation (5000 rpm) and washing with 20 mL of deionized water for 5 times.

Preparation of PMMA@PIL-TFSA Patchy NPs and PMMA@PIL-TFSA Core-shell NPs

PMMA@PIL-TFSA Patchy NPs was prepared by mixing the 0.20 g of PMMA Seed Particles and 1.0 g of NP-40 in 10.0 mL deionized water ($\mu = 1.0/10$ NP-40/ deionized water). For getting well PMMA seeds dispersion, the mixture was ultrasonic dispersed for 10 min and stirring vigorously for 2 h. After adding 0.20 g of [MTMA][TFSA] monomer (ILs) and stirring for 11 h to fully swell the ILs into the PMMA seeds, 1.0 g of KPS aqueous solution (1 wt %) was added and the polymerization was carried out at 70 °C for 24 h with stirring by a magnetic stirrer. After reaction, the PMMA@PIL-TFSA Patchy NPs was obtained by centrifugation (5000 rpm) and washing with 20 mL of deionized water for 5 times. PMMA@PIL-TFSA Core-shell NPs was prepared by changing $\mu = 1.0/10$ to $1.5/10$.

Preparation of PMMA@PIL-PA Patchy NPs and PMMA@PIL-PA Core-Shell NPs

0.020 g of PMMA@PIL-TFSA Patchy NPs or PMMA@PIL-TFSA Core-shell NPs was dispersed in 20 mL of deionized water and ultrasonic for 20 min. To the dispersion liquid, 60 mg of H₃PW₁₂O₄₀ was add. The mixture was allowed to stir at room temperature for 3 h. After anion exchange, PMMA@PIL-PA Patchy NPs or PMMA@PIL-PA Core-Shell NPs was obtained by centrifugation (5000 rpm) and washing with 20 mL of deionized water for 5 times.

Adsorption performances of PIL-Covered PMMA@PIL-TFSA Patchy NPs, PMMA@PIL-PA Patchy NPs and PMMA@PIL-PA Core-Shell NPs for

coumarin 6.

20 μ L n-hexane solution (50 mg/L) of coumarin 6 was add to 5 mL deionized water dispersion of PMMA@PIL-TFSA Core-Shell NPs, PMMA@PIL-PA Patchy NPs and PMMA@PIL-PA Core-Shell NPs (2.0 mg) respectively. After stirring vigorously, the particles were centrifugated (5000 rpm) and washed with 3 mL of deionized water for 3 times, and their adsorption for coumarin 6 was observed by a confocal laser-scanning microscope (CLSM, Nikon, Ti2)

Adsorption performances of PIL-Covered PMMA@PIL-TFSA Patchy NPs, PMMA@PIL-PA Patchy NPs and PMMA@PIL-PA Core-Shell NPs for benzaldehyde

100 μ L n-hexane solution of benzaldehyde (1.0 mg/L) was add to 5 mL 2.0mg of deionized water dispersion of PIL-Covered PMMA@PIL-TFSA Patchy NPs or PMMA@PIL-PA Patchy NPs or PMMA@PIL-PA Core-Shell NPs. After stirring vigorously, the particles were centrifugated (5000 rpm) and benzaldehyde in supernatant was detected by a UV spectrophotometer (TU1901).

Catalytic performances of PMMA@PIL-PA Patchy NPs and PMMA@PIL-PA Core-Shell NPs for the acetal reaction of benzaldehyde and ethylene glycol

To the solution of benzaldehyde (2.0g) in ethylene glycol (2.0 g), 0.060 g (1.5 %, wt%) of PMMA@PIL-PA Patchy NPs or PMMA@PIL-PA Core-Shell NPs was added. The mixture was heated to reflux and allowed to stir at 90°C for 0.5 h, 1 h, 2 h, 3 h and 4 h. After reaction, the patchy particles were removed by centrifugation (5000 rpm) and the lower oil phase were detected by ^1H NMR.

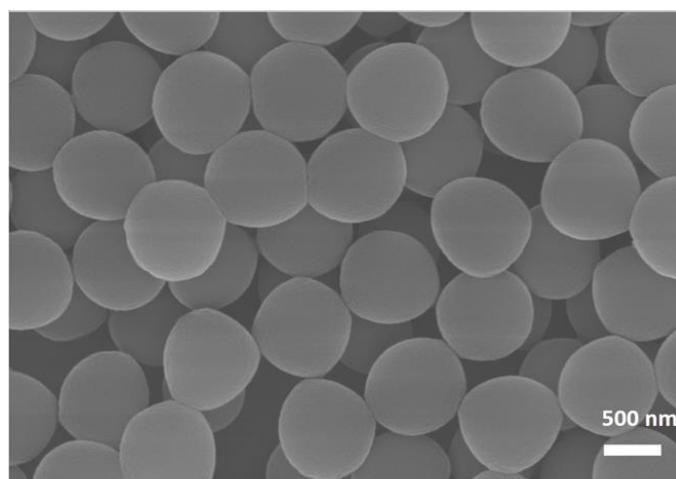
Recycling of catalyst

PMMA@PIL-PA Patchy NPs were separated from the reaction system by centrifugation (5000 rpm). The patchy particles were obtained after washing three times with water, and repeated the catalytic performances for multiple times.

Characterization

The morphology of the sample was observed by scanning electron microscopy (SEM) at 15 KV (JEOL JSM-7900F and Hitachi SU-8010) and transmission electron microscopy (TEM) at 200 KV (JEOL JEM-2100Plus). The sample was prepared via Pt sputtering in vacuum for SEM observation and dropping suspension on a copper grid for TEM observation. After the sample was mixed with KBr, Fourier transform infrared spectroscopy (FT-IR) was used to analyze the characteristic peaks of the sample by the FT-IR spectrometer (Bruker EQUINOX 55).

(a)



(b)

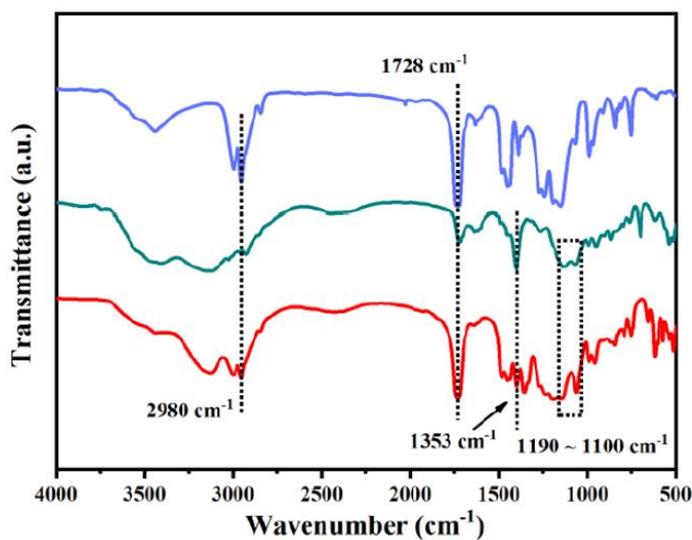


Fig.S1 (a) SEM of PMMA microspheres. Scale bar: 500 nm; (b) FT-IR spectra of PMMA microspheres (blue curve), IL monomer (green curve) and PMMA@PIL-TFSA Patchy NPs (red curve)

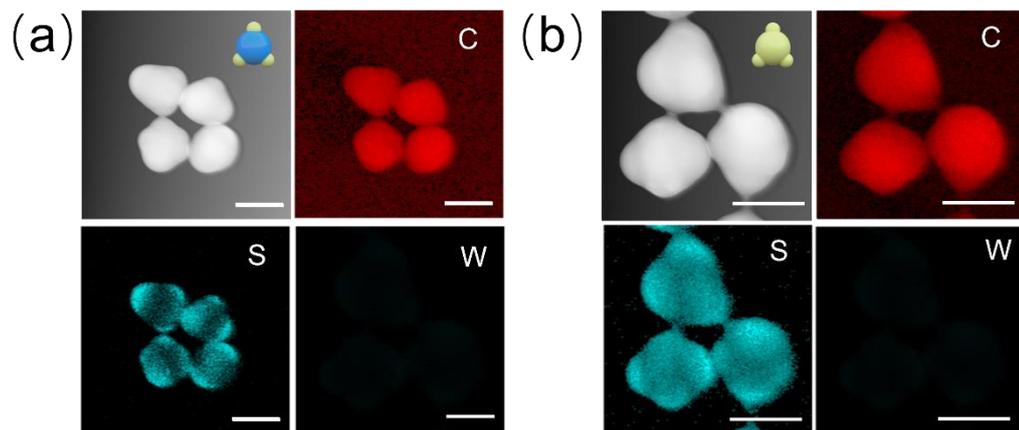
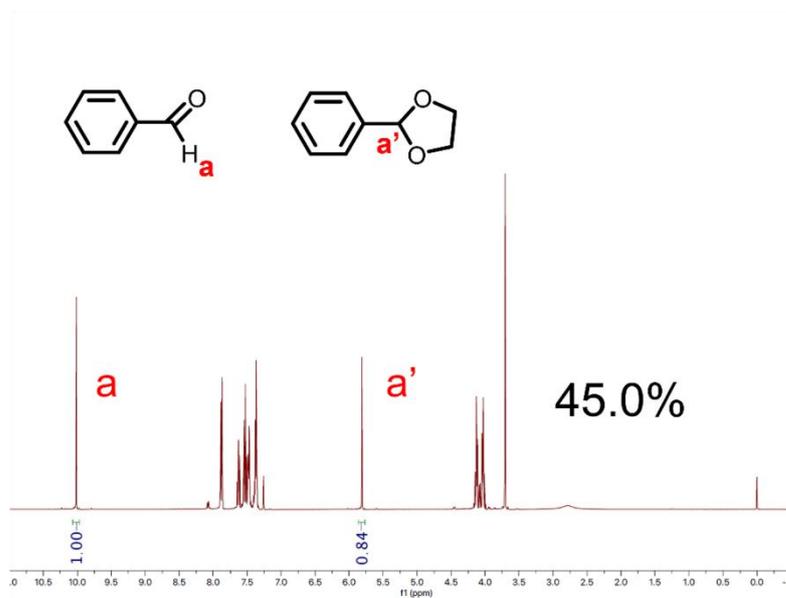


Fig.S2 TEM-EDS mapping images of PMMA@PIL-TFSA Patchy NPs (a) and PMMA@PIL-TFSA Core-shell NPs (b). Scale bar: 1 μ m.

(a)



(b)

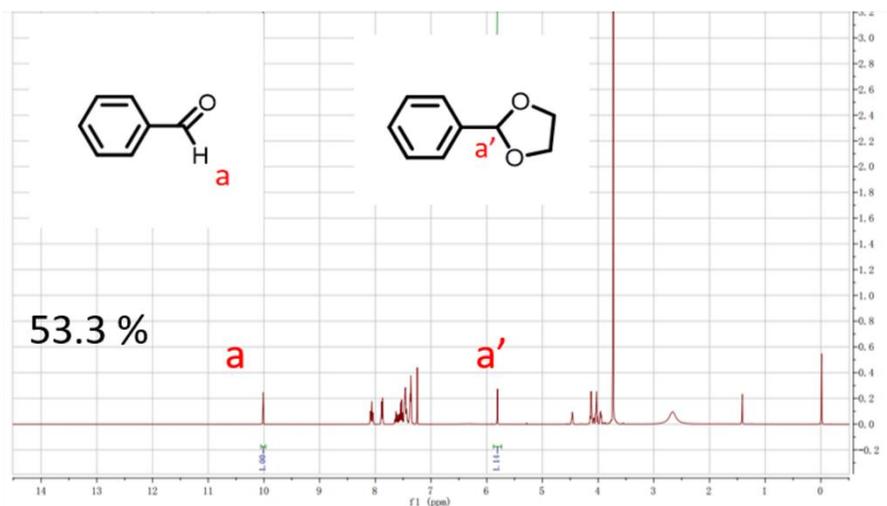


Fig.S3 ^{1}H NMR spectra (400 MHz, CDCl_3) of the products of acetal reaction for 4 h at 90°C without any particles (a) and with PMMA@PIL-TFSA Patchy NPs (b).

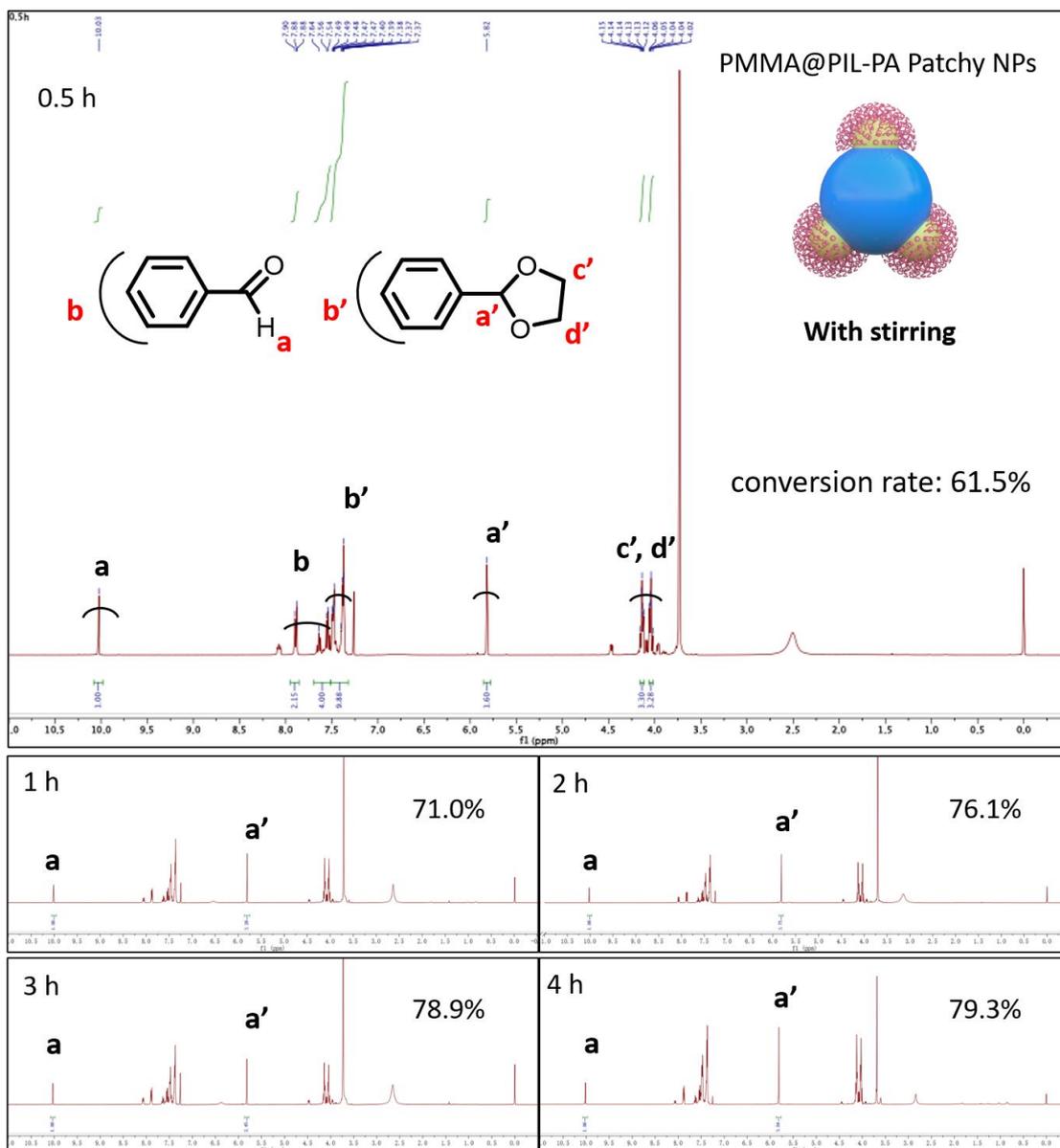


Fig.S4 ¹H NMR spectra (400 MHz, CDCl₃) of the products of acetal reaction catalyzed by PMMA@PIL-PA Patchy NPs for different hours at 90 °C with stirring.

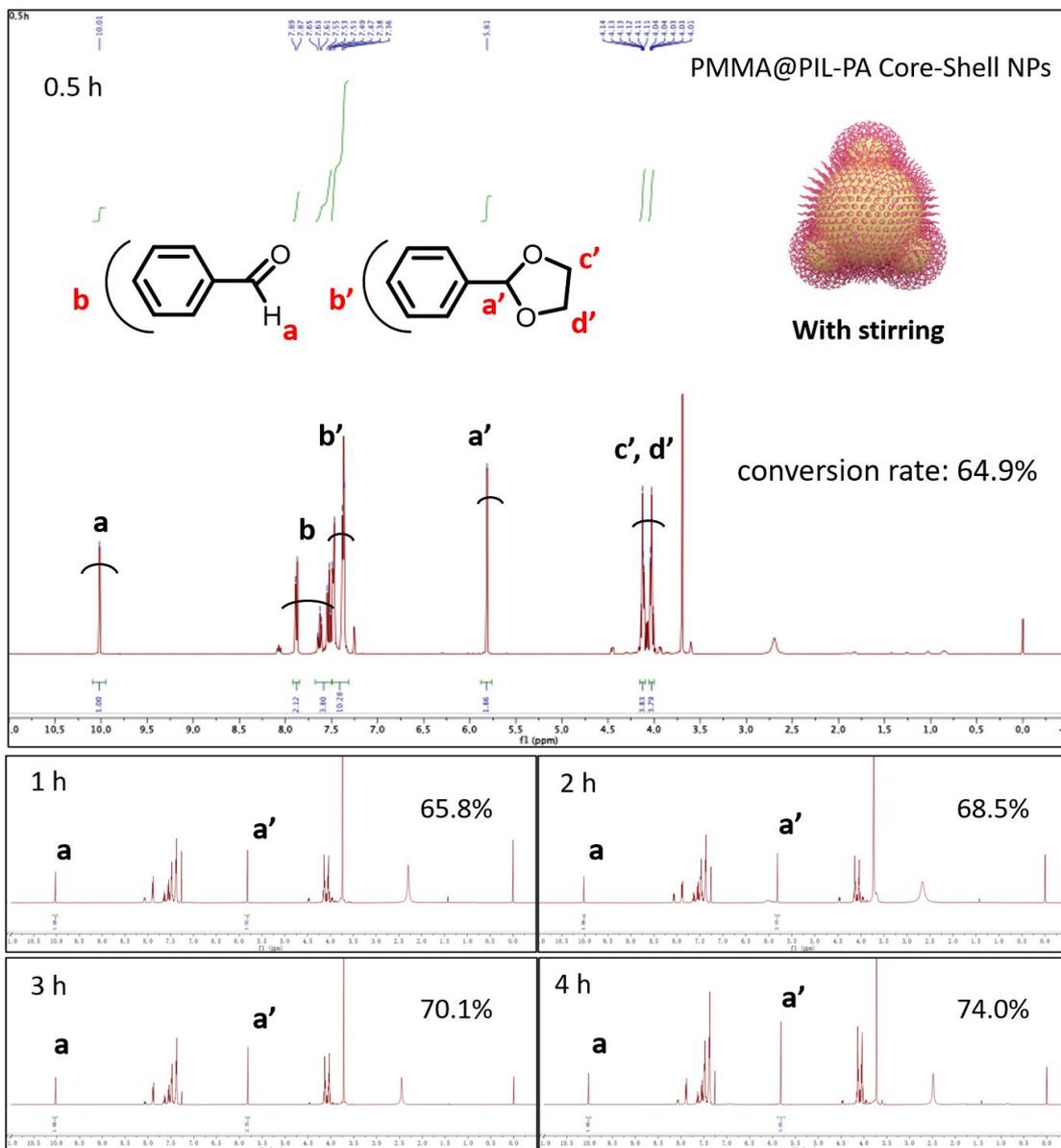


Fig.S5 ^1H NMR spectra (400 MHz, CDCl_3) of the products of acetal reaction catalyzed by PMMA@PIL-PA Core-Shell NPs for different hours at 90 $^\circ\text{C}$ with stirring.

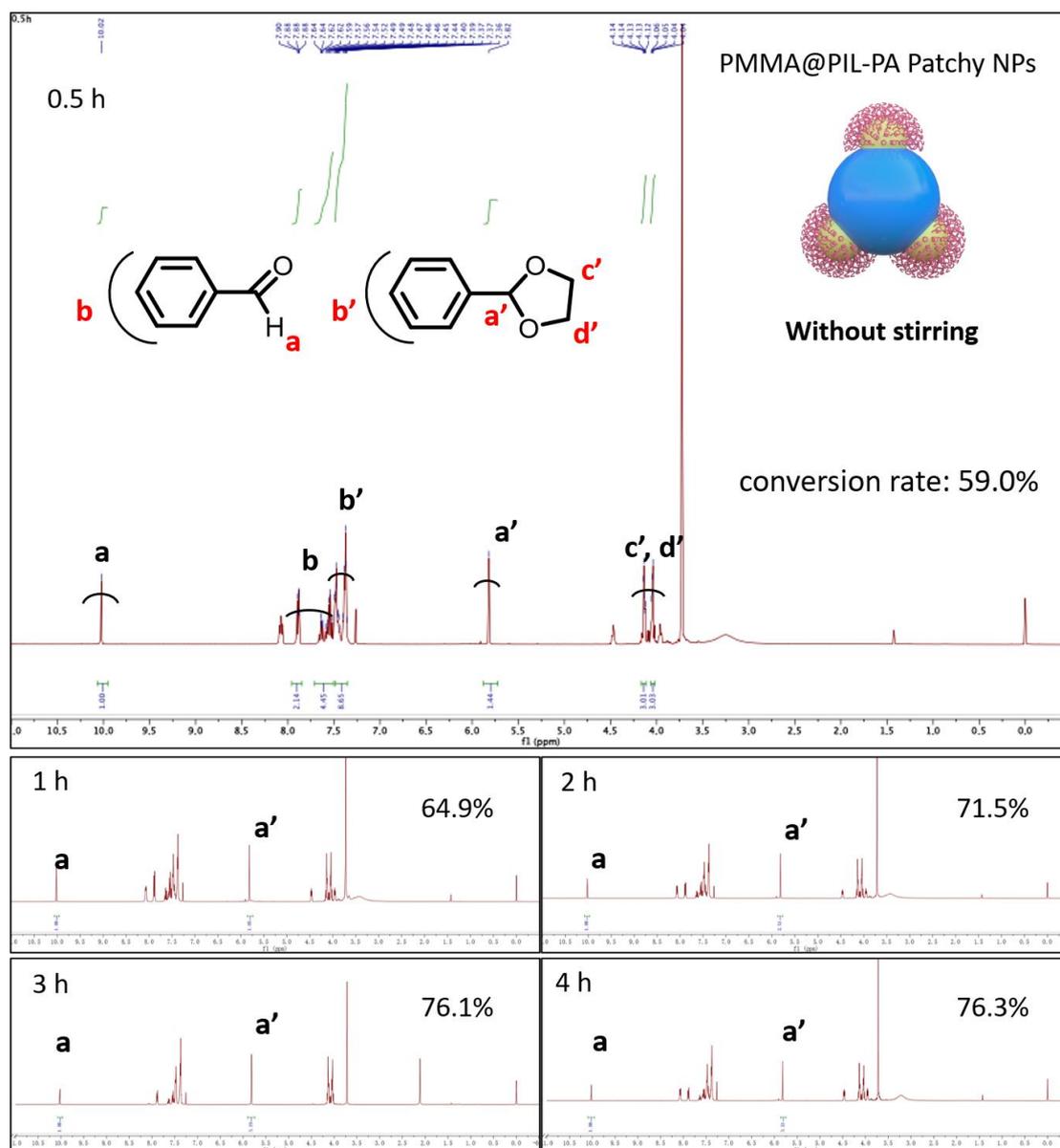


Fig.S6 ¹H NMR spectra (400 MHz, CDCl₃) of the products of acetal reaction catalyzed by PMMA@PIL-PA Patchy NPs for different hours at 90 °C without stirring.

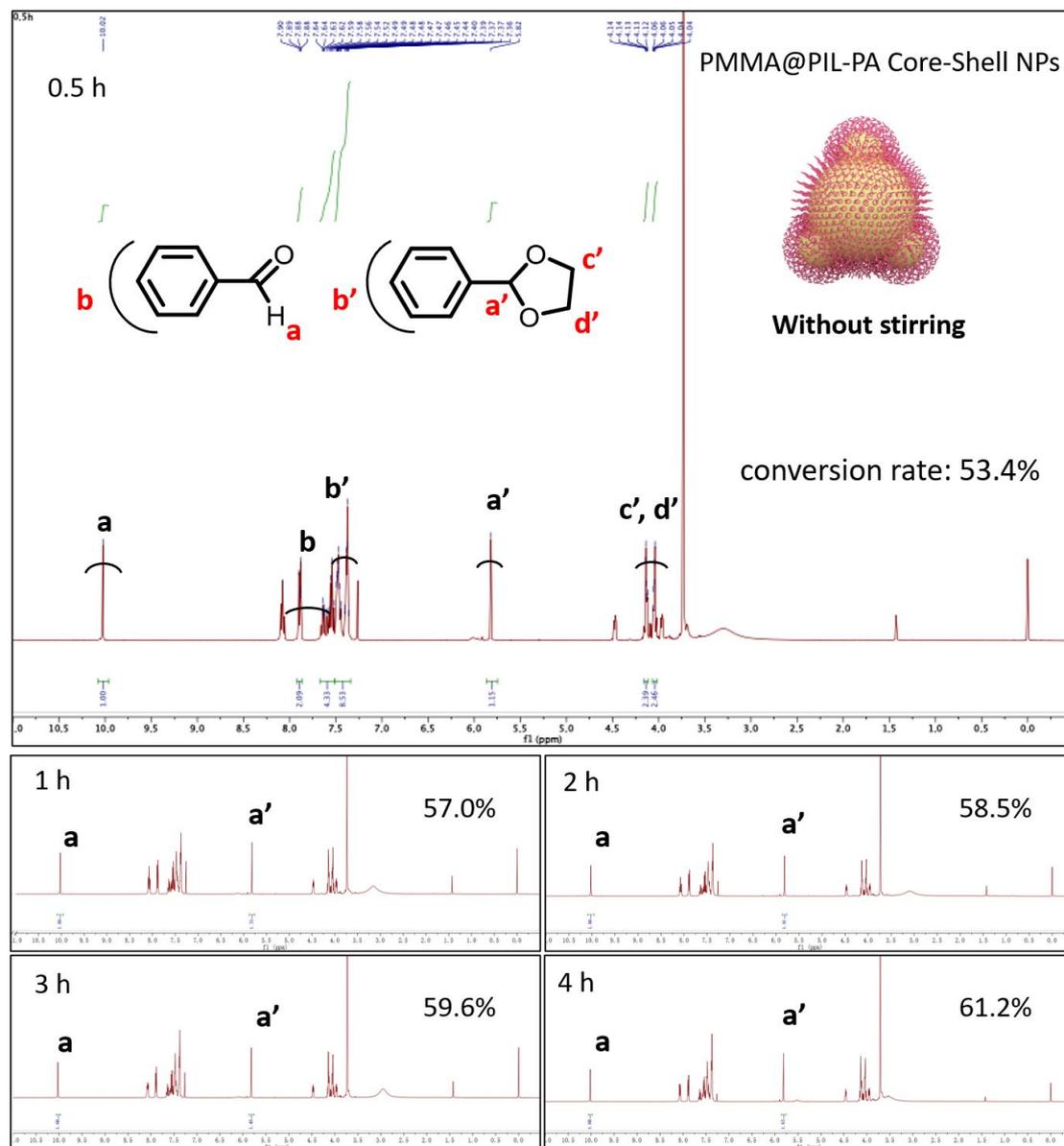


Fig.S7 ¹H NMR spectra (400 MHz, CDCl₃) of the products of acetal reaction catalyzed by PMMA@PIL-PA Core-Shell NPs for different hours at 90 °C without stirring.

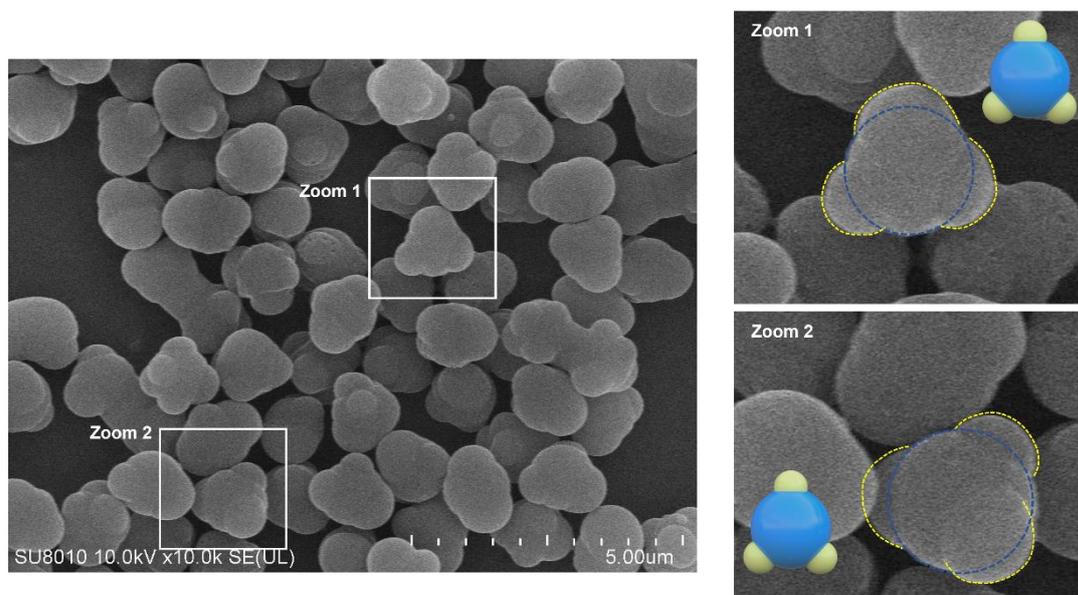


Fig.S8 Magnified SEM images of PMMA@PIL-TFSA Patchy NPs.

Table S1. Summary of conversion rates with different nanoparticles

Nanoparticles	Conversion Rates (90 °C, 4 h)
None	45.0%
PMMA@PIL-TFSA Patchy NPs	53.3%
PMMA@PIL-PA Core-Shell NPs	74.0%
PMMA@PIL-PA Patchy NPs	79.3%

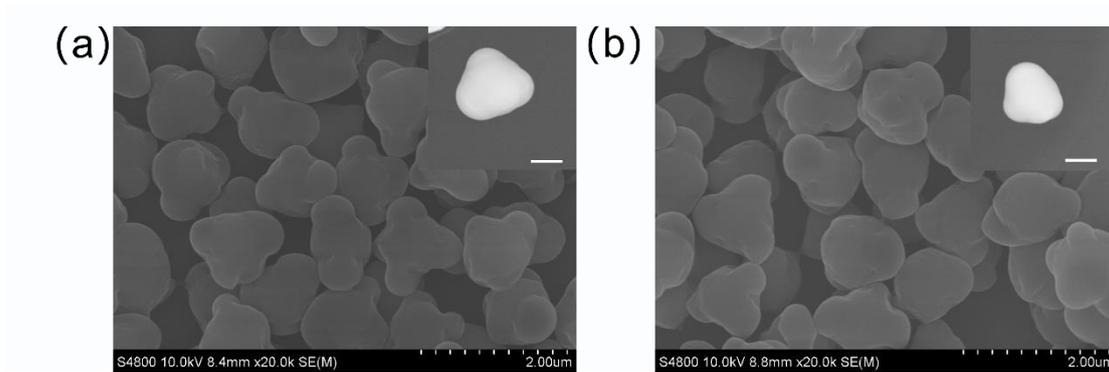


Fig. S9 SEM and TEM (inset) images of PMMA@PIL-PA Patchy NPs before (a) and after five cycles (b).
Scale bar: 500 nm for TEM (inset).