

Supplementary Information (SI) for RSC Applied Interfaces.

Utilizing a Pickering Emulsion for Suzuki-Miyaura Coupling with an Amine-Coordinated Pd Catalyst

Mingshuang Li,^{1,2} Junhao Huang,¹ Xing-Bao Wang,² Yuanyuan Shan,^{1,*}

¹ Institute of New Carbon Materials, College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China

² State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, China

Supporting Information:

Information 1. Preparation of GO.

Information 2. Initial rate kinetics.

Fig. S1 Pd 3d spectra of GO-DAP-PdCl₂.

Fig. S2 Cl 2p spectra of GO-DAP-PdCl₂.

Fig. S3 Water contact angles of GO (a), GO-DAP (b) and GO-DAP-PdCl₂ (c).

Fig. S4 Emulsion effect plots (a–c) and histograms of particle size distribution for base additions of 2, 5 and 10 mmol.

Fig. S5 Emulsion state and droplet size distribution of the Pickering emulsion during the Suzuki-Miyaura coupling reaction (85 °C, 500 rpm) at different time intervals (a–h), with corresponding droplet size distribution histograms (b and i).

Fig. S6 Emulsion states of the conventional surfactant-stabilized emulsion before (a) and after (b) the catalytic reaction.

Fig. S7 TEM images of fresh catalyst (a) and catalyst after cycling 5 and 6 times (b–c).

Fig. S8 Pd 3d Spectra of GO-DAP-PdCl₂ after 6 cycling.

* Corresponding author. Email addresses: shanyuanyuan@tyut.edu.cn (Y.Y. Shan)

Fig. S9 Mechanism Analysis of the Suzuki-Miyaura coupling reaction.

Table S1. Suzuki coupling reaction substrate expansion.

Table S2. Comparison of initial reaction rates (r_0) for Suzuki-Miyaura coupling catalyzed by GO-PdCl₂, homogeneous DAP-PdCl₂, and GO-DAP-PdCl₂ Pickering emulsion under identical conditions.

Table S3. The total interfacial area of the emulsion formed at different oil-water ratios and the corresponding initial reaction rates.

Information 1. Preparation of GO

The specific operation was as follows: firstly, 5 g of graphite and 2.5 g of NaNO₃ were added into 130 mL of concentrated H₂SO₄ and stirred for 2 h in an ice bath. then, 15 g of KMnO₄ powder was added slowly over a period of 3 h at 0–5 °C. The solution was then transferred to a water bath at 35 °C, and 230 mL of deionised water was added slowly with continuous stirring for 1 h. The temperature of the water bath was then adjusted to 98 °C , and the solution was stirred for 30 min. After the heating was turned off, 400 mL of deionised water and 10 mL of H₂O₂ were added to remove the incompletely reacted KMnO₄. Finally, the precipitates were left to settle for a few days, then centrifuged and washed to be neutral, and then finally, the concentration was calibrated and set aside.

Information 2. Initial rate kinetics

Experimental design: Reaction conditions were kept consistent with the main reaction (85 °C, K₂CO₃, identical substrate ratio). Only the reaction conversion within the first 5 min was recorded.

- Calculation formula: $r_0 = \frac{\Delta n_{product}}{\Delta t}$, Here, r_0 represents the initial reaction rate within 5 min (unit: mol/h), $\Delta n_{product}$ represents the amount of product formed within 5 min (calculated based on an initial iodobenzene amount of 1 mmol), and Δt is the reaction time.

Calculation of emulsion interfacial area:

- Calculation formula: $S = \frac{6a \cdot Ve}{D}$, Here, S represents the total interfacial area of the emulsion formed by the emulsifier (unit: m^2), a is the spatial packing efficiency of emulsion droplets (in this case, assuming hexagonal close packing, $a = 74\%$), Ve is the volume of the emulsion formed, and D is the average diameter of the droplets.

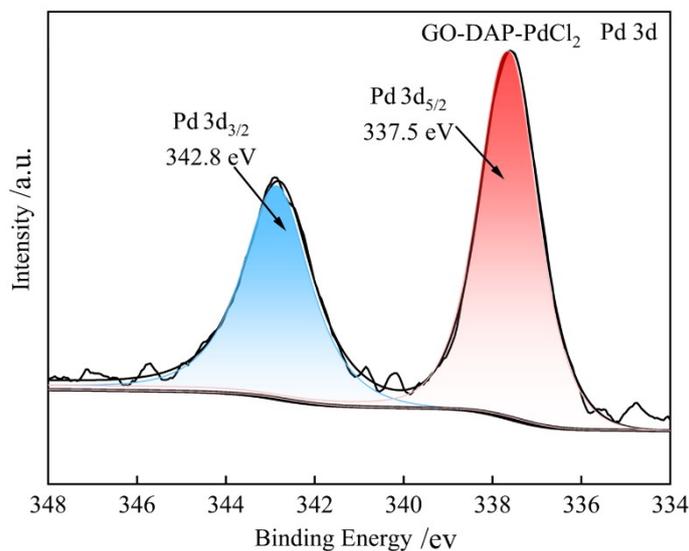


Fig. S1 Pd 3d spectra of GO-DAP-PdCl₂.

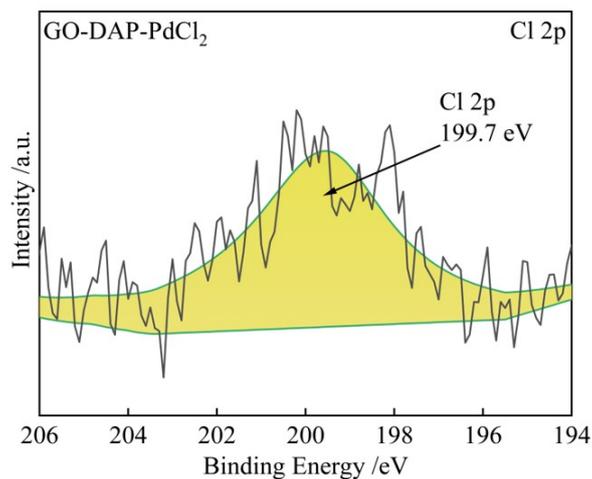


Fig. S2 Cl 2p spectra of GO-DAP-PdCl₂.

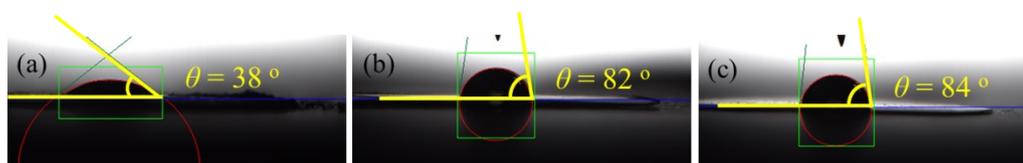


Fig. S3 Water contact angles of GO (a), GO-DAP (b) and GO-DAP-PdCl₂ (c).

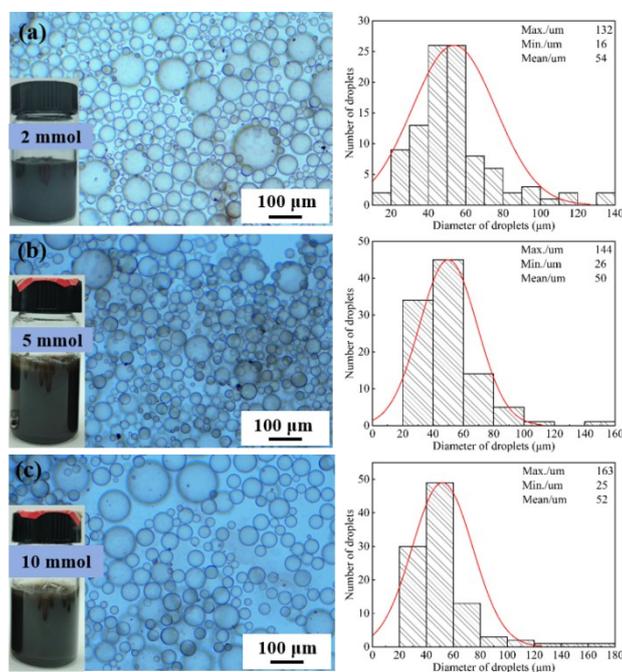


Fig. S4 Emulsion effect plots (a–c) and histograms of particle size distribution for base additions of 2, 5 and 10 mmol.

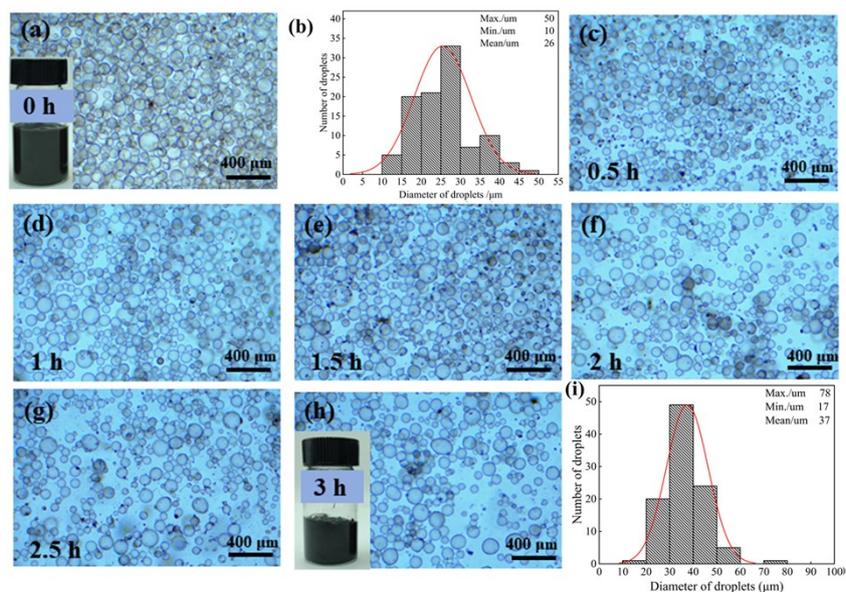


Fig. S5 Emulsion state and droplet size distribution of the Pickering emulsion during the Suzuki-Miyaura coupling reaction (85 °C, 500 rpm) at different time intervals (a–h), with corresponding droplet size distribution histograms (b and i).

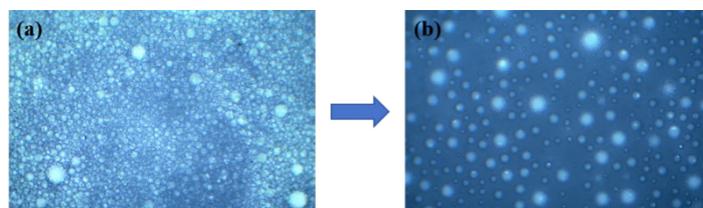


Fig. S6 Emulsion states of the conventional surfactant-stabilized emulsion before (a) and after (b) the catalytic reaction.

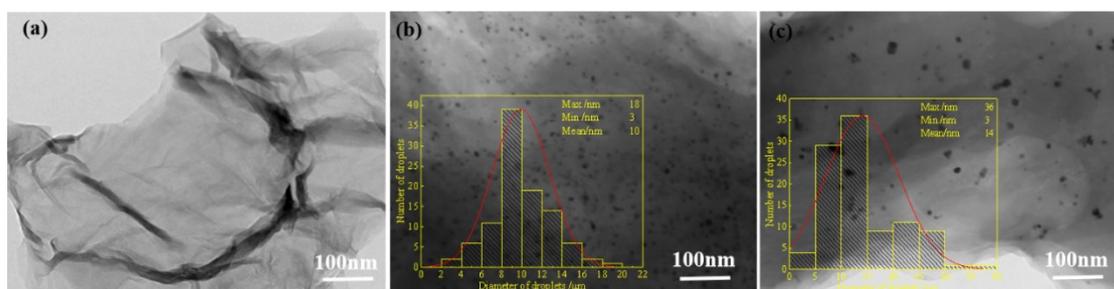


Fig. S7 TEM images of fresh catalyst (a) and catalyst after cycling 5 and 6 times (b–c).

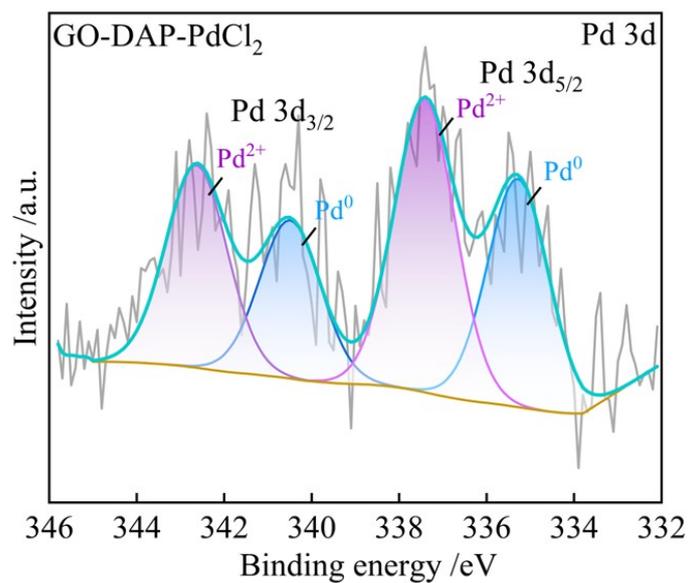


Fig. S8 Pd 3d Spectra of GO-DAP-PdCl₂ after 6 cycling.

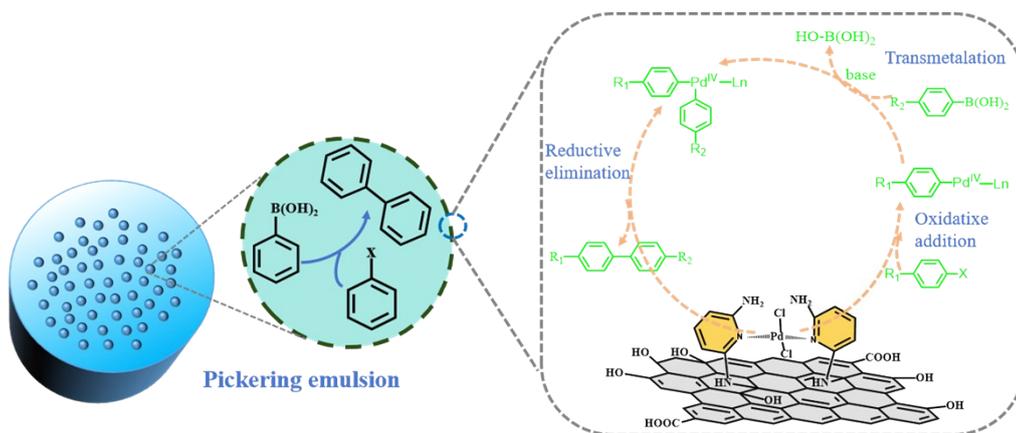
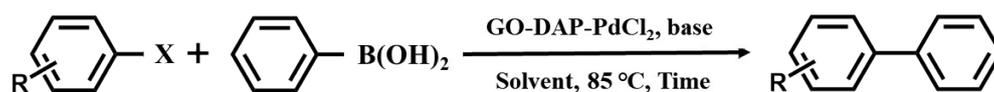


Fig. S9 Mechanism Analysis of the Suzuki-Miyaura coupling reaction.

Table S1. Suzuki coupling reaction substrate expansion.

Entry	R	X	Conversion (%)
1	H	I	95
2	2-MeO	I	91
3	3-MeO	I	93
4	4-MeO	I	83
5	4-Me	I	84
6	4-NO ₂	I	90
7	H	Br	58
8	H	Cl	2

Reaction conditions: 1 mmol iodobenzene, 2 mmol phenylboric acid, 2 mmol K₂CO₃, 6 mg GO-DAP-PdCl₂, 8 mL H₂O, 85 °C

Table S2. Comparison of initial reaction rates (r_0) for Suzuki-Miyaura coupling catalyzed by GO-PdCl₂, homogeneous DAP-PdCl₂, and GO-DAP-PdCl₂ Pickering emulsion under identical conditions.

Catalytic system	Conversion rate within 5min	r_0 (mol/h)
GO-DAP-PdCl ₂	8%	9.6×10^{-4}
DAP-PdCl ₂ (Homogeneous)	22%	2.64×10^{-3}
GO-DAP-PdCl ₂	78%	9.36×10^{-3}

Table S3. The total interfacial area of the emulsion formed at different oil-water ratios and the corresponding initial reaction rates.

oil-water ratios	$S (m^2)$	r_0 (mol/h)
1: 7	45.54	7.44×10^{-3}
1: 10	52.24	7.92×10^{-3}
1: 14	57.29	8.16×10^{-3}
1: 23	71.04	8.76×10^{-3}
1: 70	84.57	9.36×10^{-3}