

SUPPLEMENTARY INFORMATION

**Controlled Syntheses of Ag Nanoparticles inside MOFs by Using  
Amine-Boranes as Vapour Phase Reductant**

Yohei Takashima,\* Yasushi Sato, Takaaki Tsuruoka and Kensuke Akamatsu\*

*Department of Nanobiochemistry, Frontiers of Innovative Research in Science and  
Technology (FIRST), Konan University,  
7-1-20 Minatojimaminamimachi, Chuo-ku, Kobe 650-0047, Japan*

E-mail: [takashim@konan-u.ac.jp](mailto:takashim@konan-u.ac.jp)

## Experimental

### General methods

All chemicals and solvents used in this research were of reagent grade and used without further purification. X-ray powder diffraction data were collected on a Rigaku RINT-2200 Right System (Ultima IV) diffractometer with  $\text{CuK}\alpha$  radiation. UV-Vis diffused transmission spectra were measured by UV/Vis spectrometer (JASCO V-550) equipped with an integrated sphere ( $\phi 60$  mm, JASCO ISV-469). The TEM observations were performed with a JEOL JEM-1400 transmission electron microscopy (TEM) system operating at 120 kV. ICP analyses were conducted by ICP AES (SPS 7800, Seiko Instruments).

### Synthesis of MIL-101( $\text{SO}_3\text{H}$ )

Monosodium 2-sulfoterephthalic acid (3.35 g, 12.5 mmol),  $\text{CrO}_3$  (1.25 g, 12.5 mmol) and concentrated aqueous hydrochloric acid (0.91 g (12 N), 25 mmol) were dissolved in water (50 ml), then transferred to Teflon-lined stainless steel autoclave. The resulting solution was heated at 453 K for 6 days under hydrothermal conditions. The reaction product was finally obtained after washing three times with DMF under sonication.

### Synthesis of $\text{Ag}^+(\text{x})@\text{MIL-101}(\text{SO}_3^-)$ ( $\text{x} = 20, 200, 2000$ )

To 10 ml of  $\text{x}$  mM  $\text{AgNO}_3$  solution ( $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1/1$ ), added 50 mg of dried MIL-101( $\text{SO}_3\text{H}$ ), and then the resulting suspensions were stirred at r.t. for 12 hrs. After filtration, washing under sonication with 10 ml of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution three times and drying under vacuum,  $\text{Ag}^+(\text{x})@\text{MIL-101}(\text{SO}_3^-)$  were obtained as powder samples.

### Synthesis of $\text{Ag NP}(2000)@\text{MIL-101}(\text{SO}_3\text{H})$ by AB

4 mg of  $\text{Ag}^+(2000)@\text{MIL-101}(\text{SO}_3^-)$  and 4.5 mmol of AB were put into glass tube and then heated at 100 °C for 1.5 hrs under  $\text{N}_2$  flow (20 ml/min). After washing with water,  $\text{Ag NP}(2000)@\text{MIL-101}(\text{SO}_3\text{H})$  was obtained as powder sample.

### Synthesis of $\text{Ag NP}(2000)@\text{MIL-101}(\text{SO}_3\text{H})$ by DMAB

4 mg of  $\text{Ag}^+(2000)@\text{MIL-101}(\text{SO}_3^-)$  and 4.5 mmol of DMAB were put into glass tube and then heated at 70 °C for 1.5 hrs under  $\text{N}_2$  flow (20 ml/min). After washing with water,  $\text{Ag NP}(2000)@\text{MIL-101}(\text{SO}_3\text{H})$  was obtained as powder sample.

### Syntheses of $\text{Ag NP}(\text{x})@\text{MIL-101}(\text{SO}_3\text{H})$ by TMAB

4 mg of  $\text{Ag}^+(\text{x})@\text{MIL-101}(\text{SO}_3^-)$  ( $\text{x} = 20, 200, 2000$ ) and 4.5 mmol of TMAB were put into glass

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tube and then heated at 100, 150, 180 and 200 °C for 30 mins under N<sub>2</sub> flow (20 ml/min). After washing with water, corresponding Ag NP(x)@MIL-101(SO<sub>3</sub>H) were obtained as powder sample.

### **Syntheses of Ag NP(x)@MIL-101(SO<sub>3</sub>H) by TEAB**

4 mg of Ag<sup>+</sup>(x)@MIL-101(SO<sub>3</sub><sup>-</sup>) (x = 20, 200, 2000) and 4.5 mmol of TMAB were put into glass tube and then heated at 100, 150 and 180 °C for 30 mins under N<sub>2</sub> flow (20 ml/min). After washing with water, corresponding Ag NP(x)@MIL-101(SO<sub>3</sub>H) were obtained as powder sample.

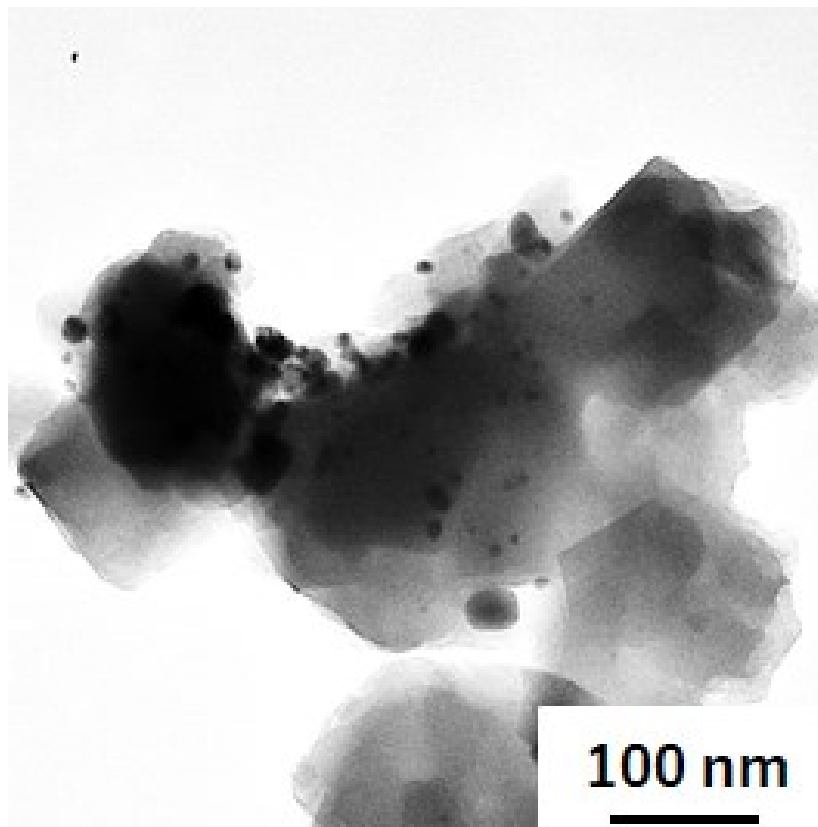
### **Synthesis of Ag NP(2000)@MIL-101(SO<sub>3</sub>H) by H<sub>2</sub> gas**

5 mg of Ag<sup>+</sup>(2000)@MIL-101(SO<sub>3</sub><sup>-</sup>) was put into the hydrothermal bomb and then heated at 200 °C for 2 hrs under 5atm of H<sub>2</sub> gas. After cooling down to r.t., Ag NP(2000)@MIL-101(SO<sub>3</sub>H) was obtained as powder sample.

### **Synthesis of Ag NP(2000)@MIL-101(SO<sub>3</sub>H) by NaBH<sub>4</sub>aq**

60 mM NaBH<sub>4</sub> aq was added to 5 mg of Ag<sup>+</sup>(2000)@MIL-101(SO<sub>3</sub><sup>-</sup>) under vigorous stirring. After 20 mins, the sample was filtered, washed with water and dried in vacuo to obtain Ag NP(2000)@MIL-101(SO<sub>3</sub>H).

Supporting data

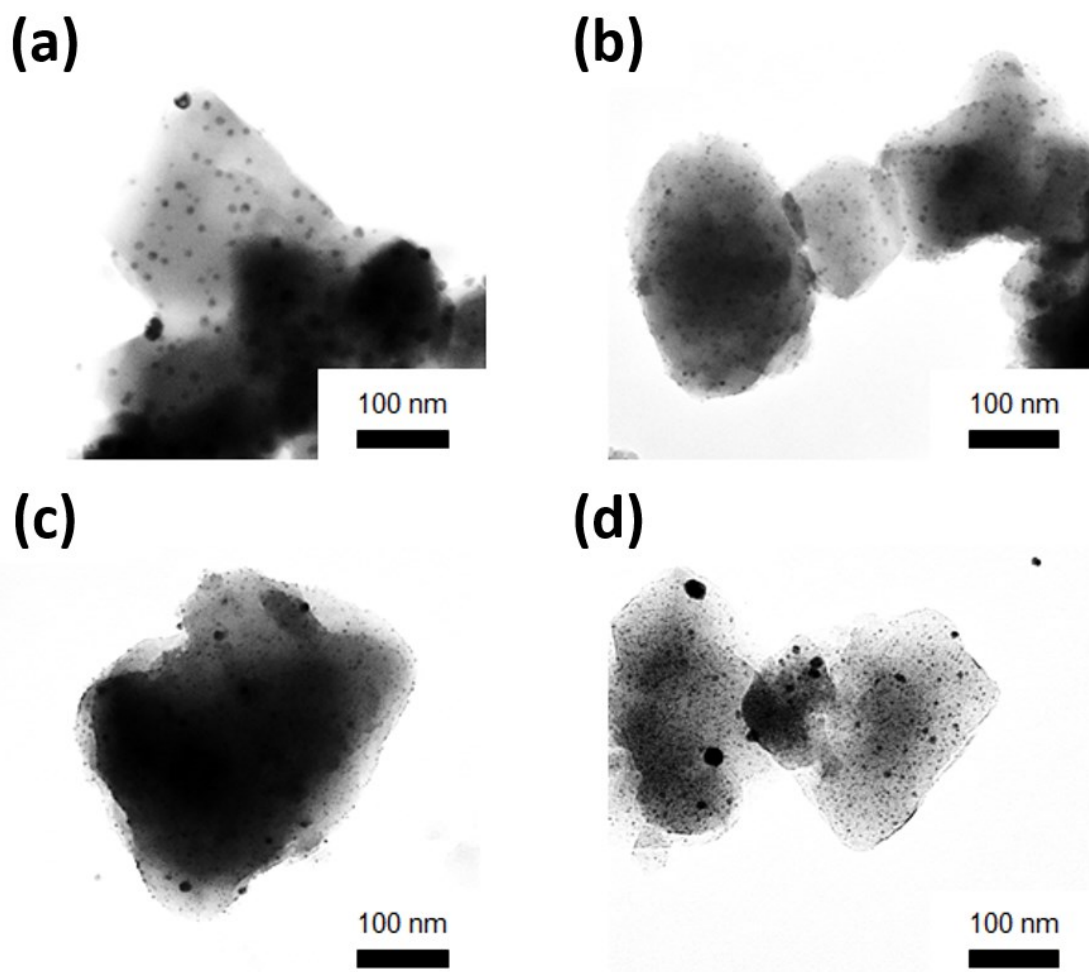


**Fig. S1.** TEM picture of Ag NP(2000)@MIL-101(SO<sub>3</sub>H)

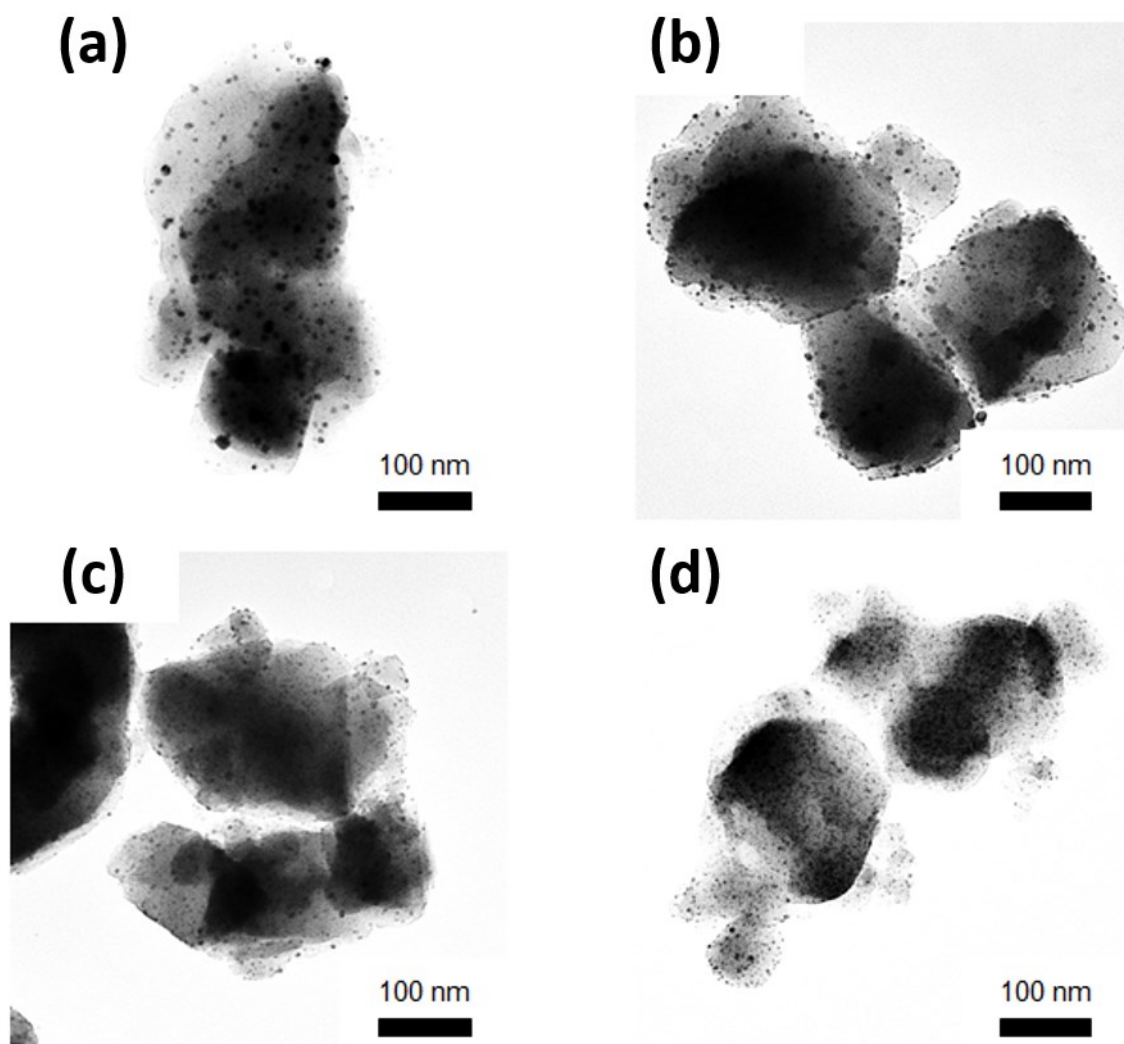
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amine-boranes	reaction temp./ °C	reaction time/ hr	Vaporization amount/ $\mu\text{mol}$
AB	100	1.5	70
DMAB	70	1.5	280
TMAB	100	0.5	2357
	150	0.5	4500
	180	0.5	4500
	200	0.5	4500
TEAB	100	1.0	808
	150	1.0	4500
	180	1.0	4500

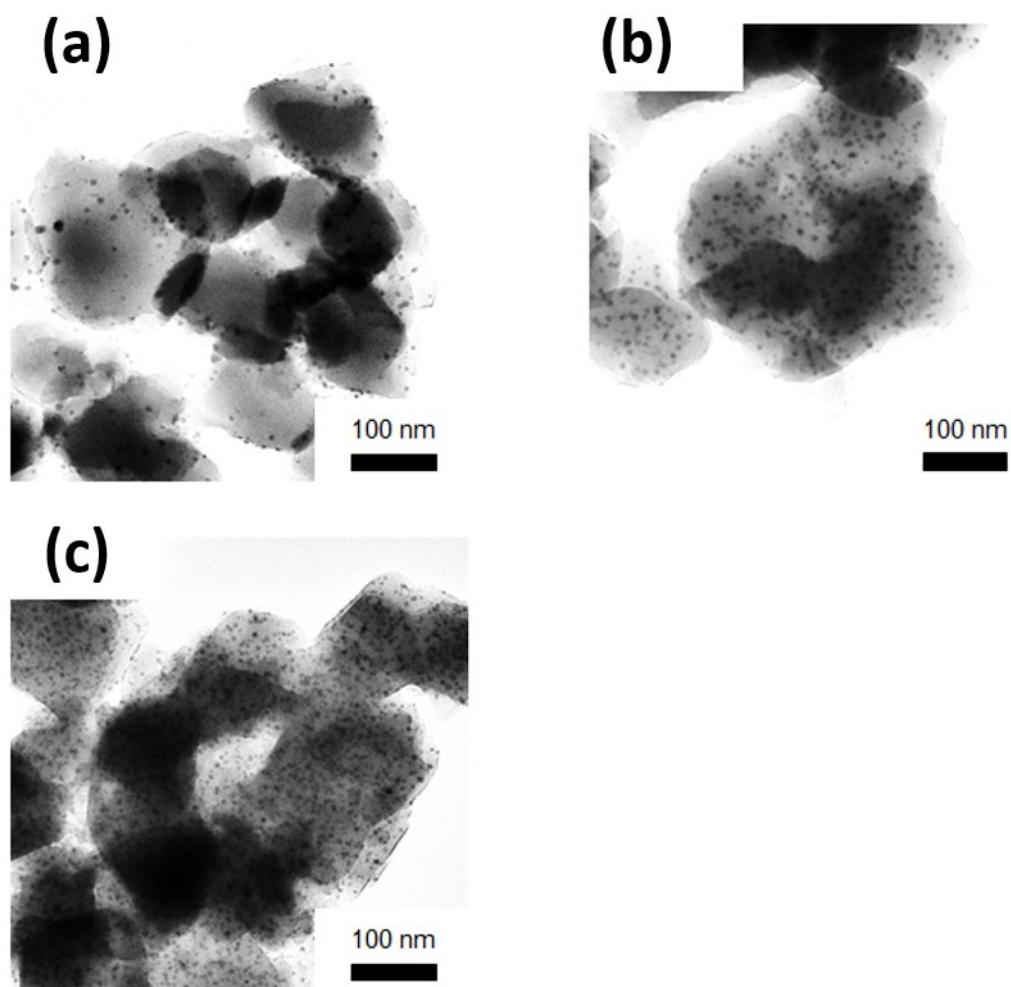
**Table S1.** Amount of amine-boranes consumed during the reactions.



**Fig. S2.** TEM pictures of Ag NP(20)@MIL-101(SO<sub>3</sub>H) by TMAB reduction at (a) 100 °C, (b) 150 °C, (c) 180 °C and (d) 200 °C. Size of Ag NPs: (a)  $11.2 \pm 1.7$  nm; (b)  $5.9 \pm 0.9$  nm; (c)  $4.7 \pm 0.6$  nm; (d)  $3.2 \pm 0.6$  nm.

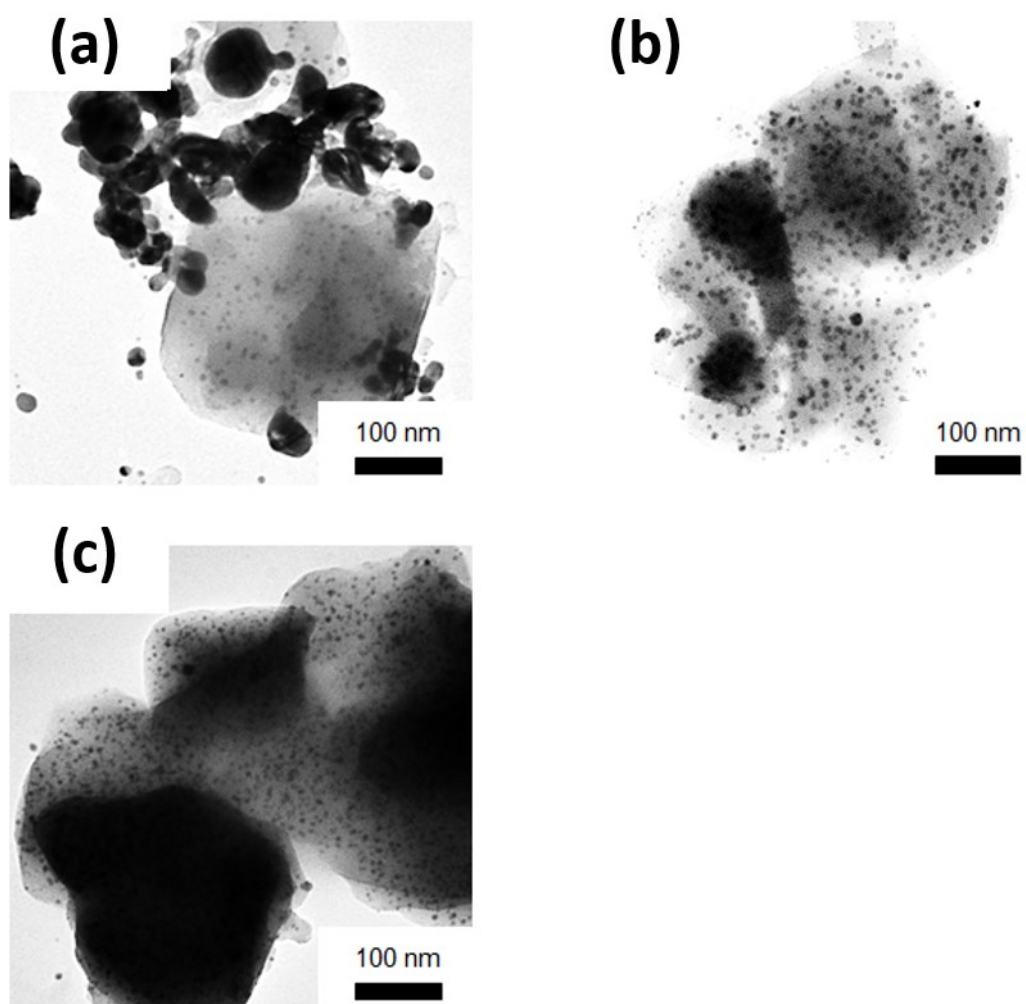


**Fig. S3.** TEM pictures of Ag NP(200)@MIL-101(SO<sub>3</sub>H) by TMAB reduction at (a) 100 °C, (b) 150 °C, (c) 180 °C and (d) 200 °C. Size of Ag NPs: (a)  $8.1 \pm 1.6$  nm; (b)  $6.5 \pm 1.4$  nm; (c)  $4.9 \pm 0.8$  nm; (d)  $3.3 \pm 0.3$  nm.

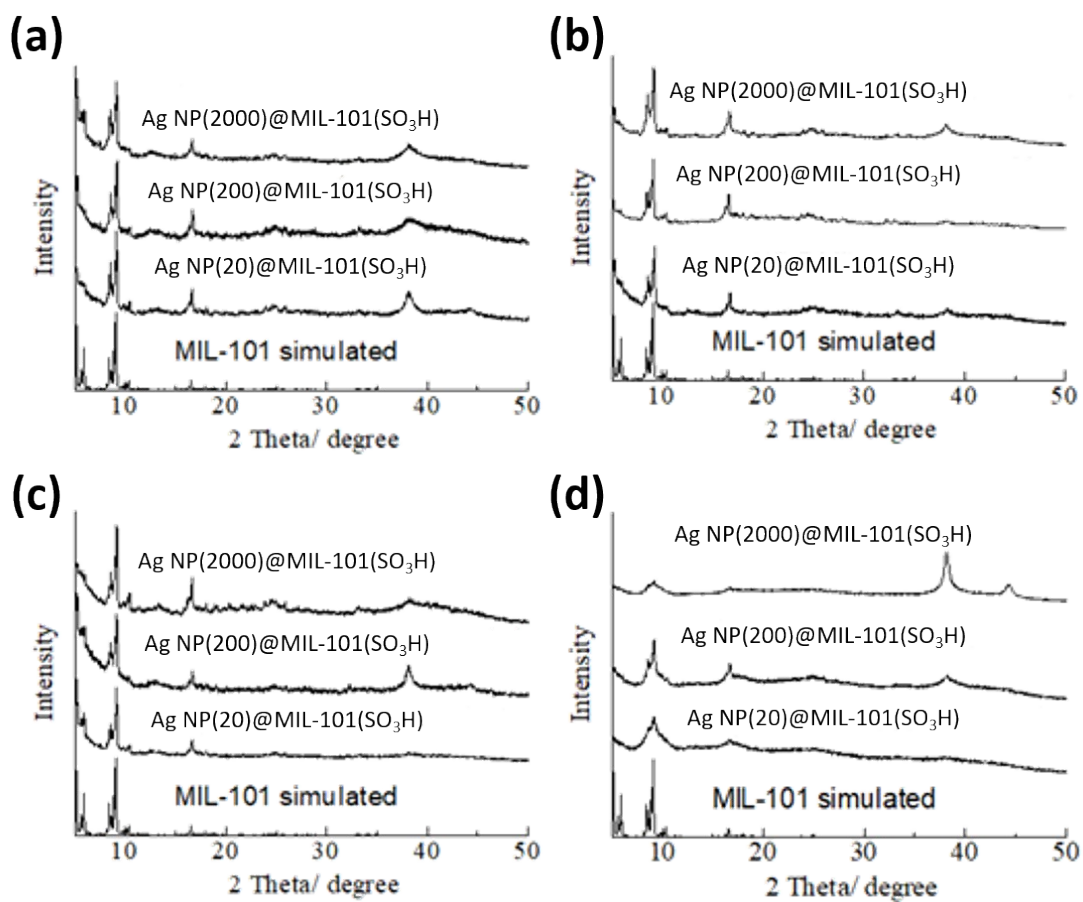


**Fig. S4.** TEM pictures of Ag NP(20)@MIL-101(SO<sub>3</sub>H) by TEAB reduction at (a) 100 °C, (b) 150 °C and (c) 180 °C. Size of Ag NPs: (b)  $8.9 \pm 0.8$  nm; (c)  $6.4 \pm 0.8$  nm.

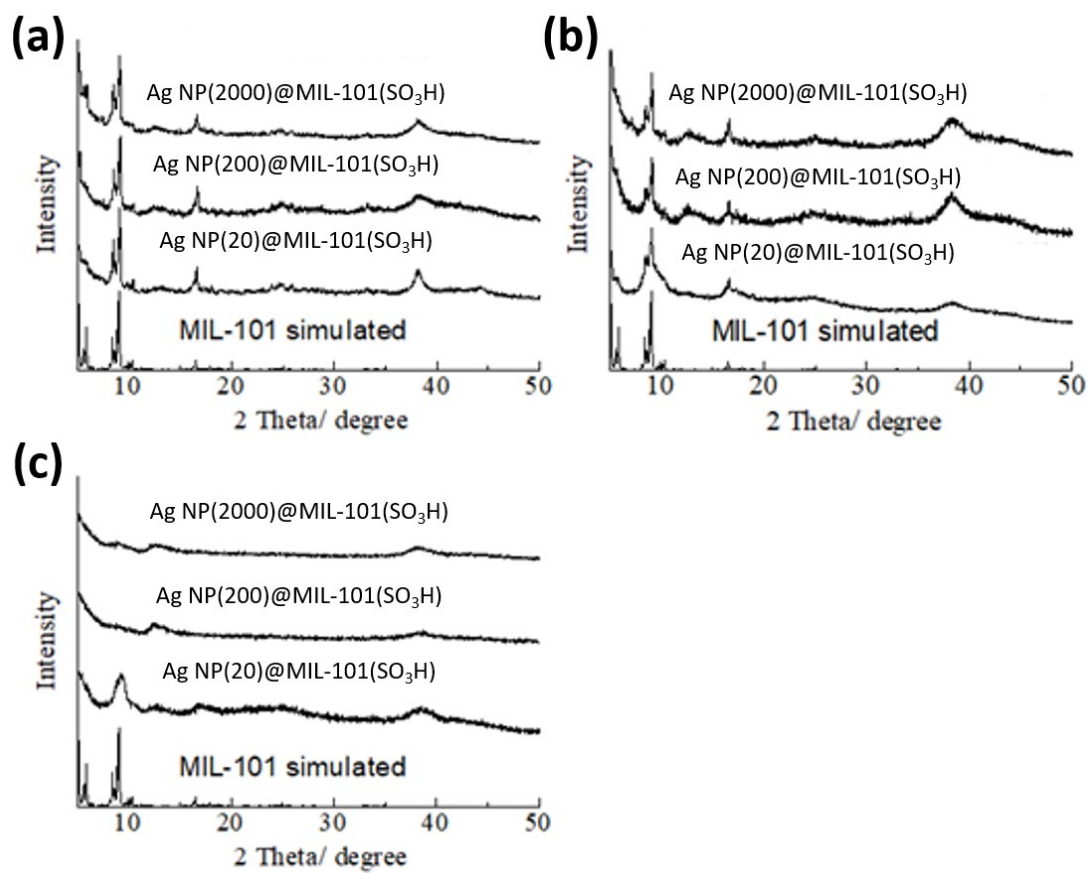




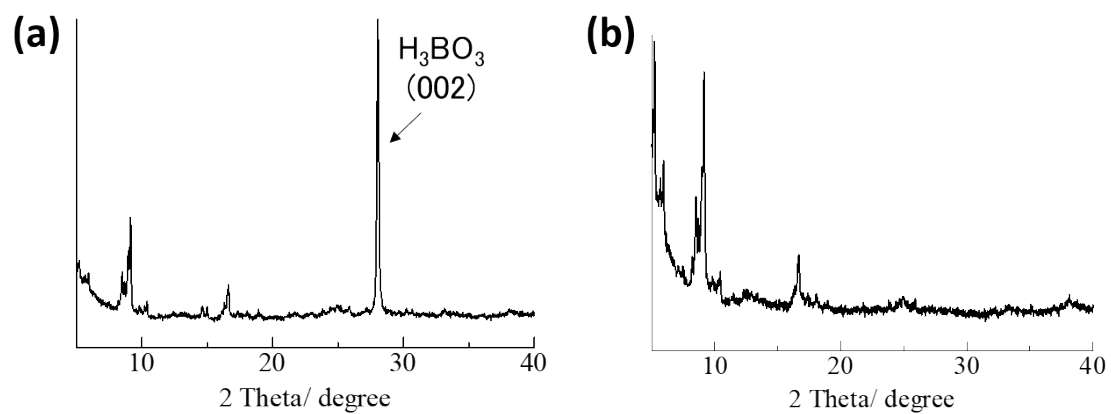
**Fig. S5.** TEM pictures of Ag NP(200)@MIL-101(SO<sub>3</sub>H) by TEAB reduction at (a) 100 °C, (b) 150 °C and (c) 180 °C. Size of Ag NPs: (b)  $9.5 \pm 1.2$  nm; (c)  $7.0 \pm 0.8$  nm.



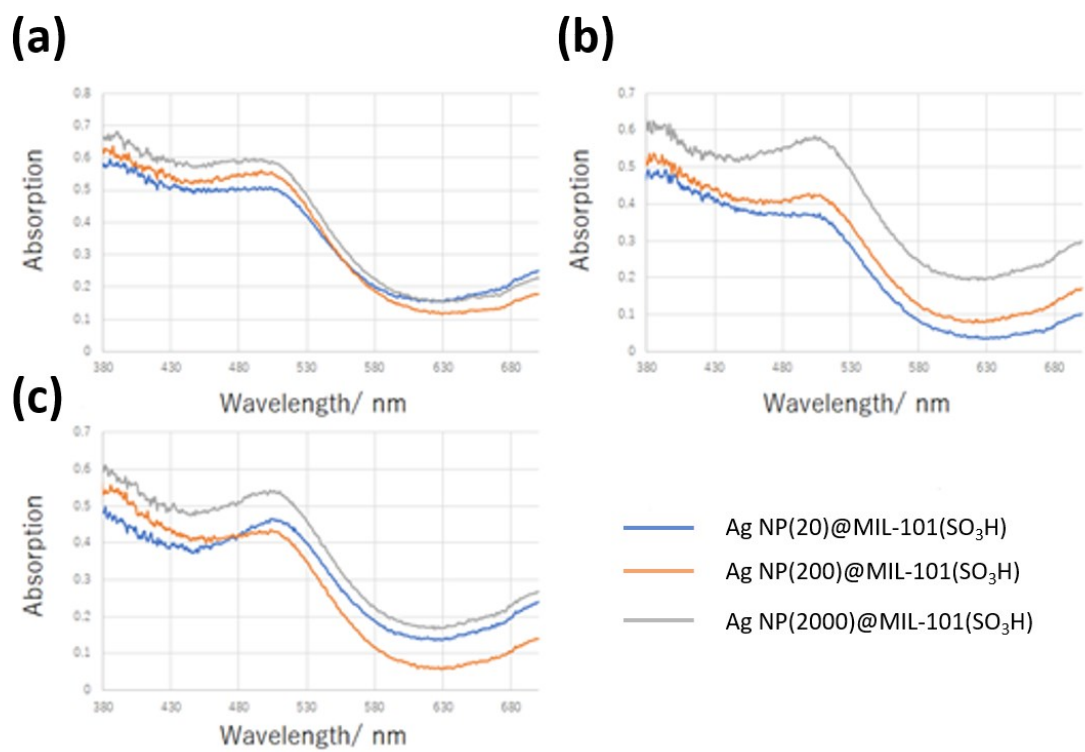
**Fig. S6.** XRD patterns of Ag NP@MIL-101(SO<sub>3</sub>H) generated by TMAB reduction at (a) 100 °C, (b) 150 °C, (c) 180 °C and (d) 200 °C.



**Fig. S7.** XRD patterns of Ag NP@MIL-101(SO<sub>3</sub>H) generated by TEAB reduction at (a) 100 °C, (b) 150 °C and (c) 180 °C.

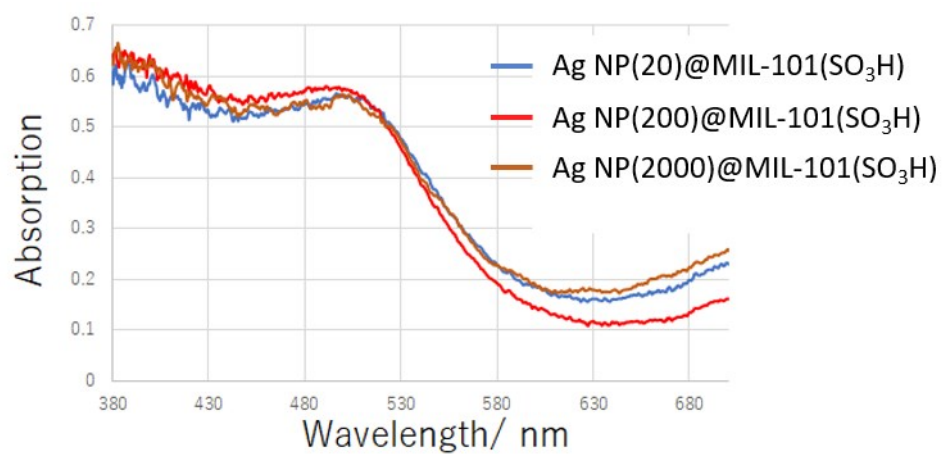


**Fig. S8.** XRD patterns of Ag NP@MIL-101(SO<sub>3</sub>H) generated by TMAB reduction (a) before and (b) after water washing.

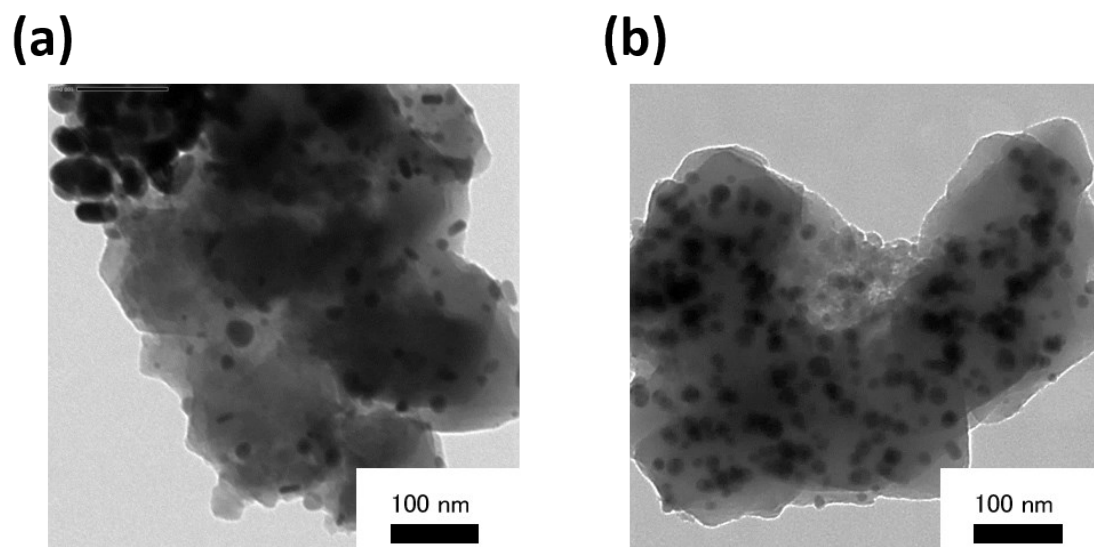


**Fig. S9.** Difference spectra obtained by the absorption spectra of Ag NP@MIL-10(SO<sub>3</sub>H) by TMAB reduction and MIL-101(SO<sub>3</sub>H). Reaction temperatures: (a) 100 °C; (b) 150 °C; (c) 180 °C.

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**Fig. S10.** Difference spectra obtained by the absorption spectra of Ag NP@MIL-10(SO<sub>3</sub>H) by TEAB reduction at 150 °C and MIL-101(SO<sub>3</sub>H).



**Fig. S11.** TEM pictures of Ag NP@MIL-10(SO<sub>3</sub>H) generated by the reduction with (a) NaBH<sub>4</sub> aq. and (b) H<sub>2</sub> gas.

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Sample	Ag content (weight%)	Amine-boranes	Reaction temp./ °C	Average Size of Ag NPs/ nm
Ag NP(2000)@MIL-101(SO <sub>3</sub> H)	21	AB	100	Aggregated
Ag NP(2000)@MIL-101(SO <sub>3</sub> H)	21	DMAB	50	5.4
			60	5.4
			70	5.2

**Table S2.** Summary of AgNP generations with AB or DMAB as reductant.

sample	Ag content (weight%)	Amine-boranes	Reaction temp./ °C	Average Size of Ag NPs/ nm
Ag NP(20)@MIL-101(SO <sub>3</sub> H)	7.4	TMAB	100	11.2
			150	5.9
			180	4.7
			200	3.2
Ag NP(200)@MIL-101(SO <sub>3</sub> H)	11	TMAB	100	8.1
			150	6.5
			180	4.9
			200	3.3
Ag NP(2000)@MIL-101(SO <sub>3</sub> H)	21	TMAB	100	9.4
			150	6.8
			180	5.4
			200	4.8

**Table S3.** Summary of AgNP generations with TMAB as reductant.



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sample	Ag content (weight%)	Amine-boranes	Reaction temp./ °C	Average Size of Ag NPs/ nm
Ag NP(20)@MIL-101(SO <sub>3</sub> H)	7.4	TEAB	100	Aggregated
			150	8.9
			180	6.4
Ag NP(200)@MIL-101(SO <sub>3</sub> H)	11	TEAB	100	Aggregated
			150	9.5
			180	7.0
Ag NP(2000)@MIL-101(SO <sub>3</sub> H)	21	TEAB	100	Aggregated
			150	8.8
			180	6.8

**Table S4.** Summary of AgNP generations with TEAB as reductant.