Experimental

Materials synthesis: For the synthesis of Bis-urea, 3-(isocyanatopropyl)triethoxysilane (20 mmol, 5 mL) was added dropwise to 3-aminopropyltriethoxysilane (20 mmol, 4.5 mL) for 5 minutes at room temperature and stirred vigorously under solvent-free conditions until a white solid was obtained. Then the reaction temperature was raised to 60 °C to melt the white solid and held for 15 min. After cooling the reaction down to room temperature, the solid product was recovered and washed with petroleum ether and then dried under vacuum. $C_{16}TMA^+$-oct (300 mg), was prepared according to the previously reported method,[1] and then dispersed in a solution of toluene (20 mL) containing Bis-urea (20 mmol). This mixture was refluxed at 120 °C for 48 h. The solid product was separated by centrifugation, washed with ethanol, and dried at 60 °C, to obtain Urea-oct. Urea-oct (200 mg) was dispersed in an ethanolic solution of $AgNO_3$ (0.01 M, 20 mL). The mixture was stirred in dark at room temperature for the defined reaction time. The products were separated by centrifugation, washed with ethanol, and dried at 60 °C in vacuum to obtain Ag/Urea-oct(X) (X = reaction time). Ag@$C_{16}TMA^+$-oct was prepared by a similar procedure as the synthesis of Ag/Urea-oct(20), except that the dried product was further dispersed in aqueous solution (5 mL) containing $NaBH_4$ (0.01 M) reducing agent and NH_3 (1 M). The dispersion was stirred at room temperature for 25 min. Pt@TiO_2 was prepared by using P25 TiO_2 according to the literature.[2] The Pt content was adjusted to 0.2 wt%.

Catalytic activity test: The samples (20 mg) were mixed in an aqueous solution (5 mL) containing NH_3BH_3 (20 μmol) in Pyrex glass tube (34 mL), ultrasonicated, and deaerated by Ar bubbling. The glass tube was sealed with a rubber septum. The dispersion was stirred during the reaction. The gas in the glass tube was withdraw from the headspace with a gas-tight syringe and analyzed with a Shimadzu GC-8A gas chromatograph equipped with a SHINCARBON-ST 50-80 column. For the investigation of light irradiation effects, the glass tube was irradiated with a solar simulator (San-Ei Electric, λ > 300 nm, 1 SUN) with or without a longpass filter (λ > 420 nm) and then measured with a gas chromatograph.

References

1. M. Ogawa and D. Iwata, *Cryst. Growth Des.,* 2010, **10**, 2068
2. F. Amano, O.-O. Prieto-Mahaney, Y. Terada, T. Yasumoto, T. Shibayama and B. Ohtani, *Chem. Mater.,* 2009, **21**, 2601.

Tables and Figures

	C (wt%)[a]	N (wt%)[a]	Si (wt%)[b]	Ag	N/Si_8O_{17}

Table S1. Composition of Urea-oct and Ag/Urea-oct(12).

				(wt%)[b]	(mol)
Urea-oct	17.5	3.8	30.2	-	2.3
Ag/Urea-oct(12)	13.4	3.6	30.4	4.9	2.3

[a] Determined by CHN elemental analysis. [b] Determined by ICP of the dissolved samples.

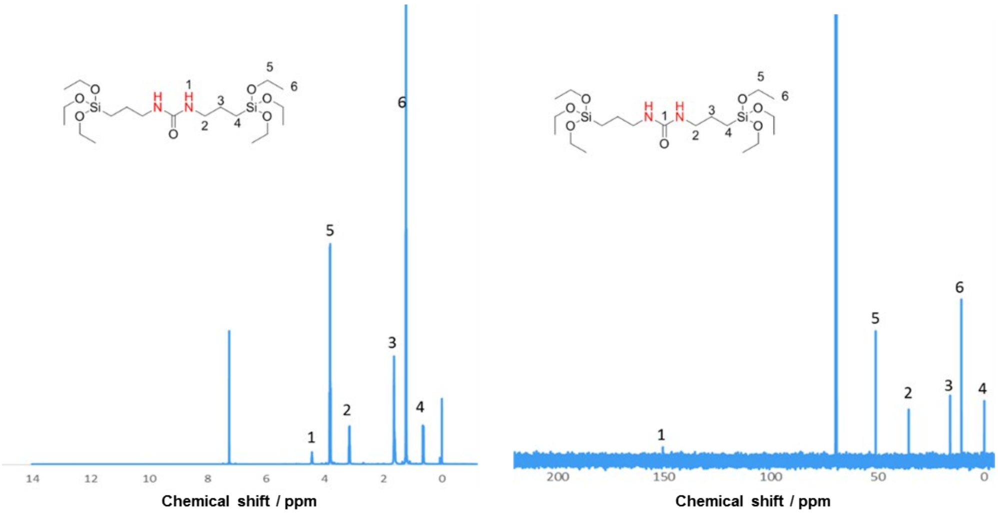

Fig. S1. ^{1}H NMR (left) and ^{13}C NMR (right) spectra of Bis-urea.

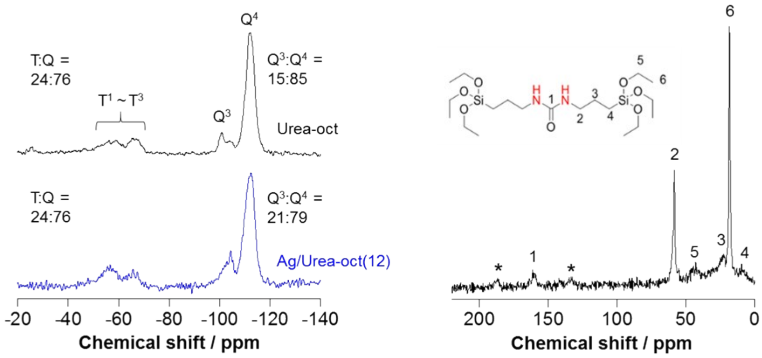

Fig. S2. ^{29}Si MAS NMR (left) and ^{13}C CP/MAS NMR (right) spectra of Urea-oct.

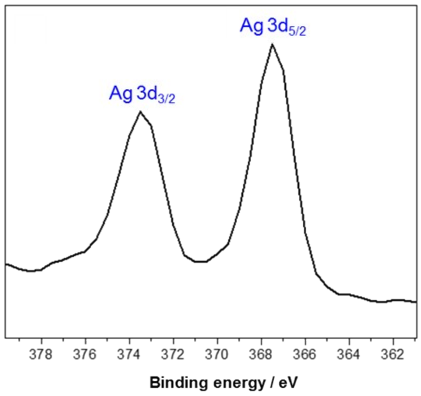

Fig. S3. XPS spectrum of Ag/Urea-oct(12).

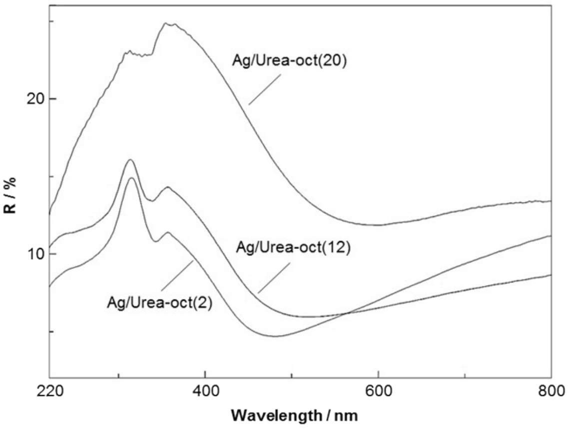

Fig. S4. UV-vis spectra of Ag/Urea-oct(2), Ag/Urea-oct(12) and Ag/Urea-oct(20).

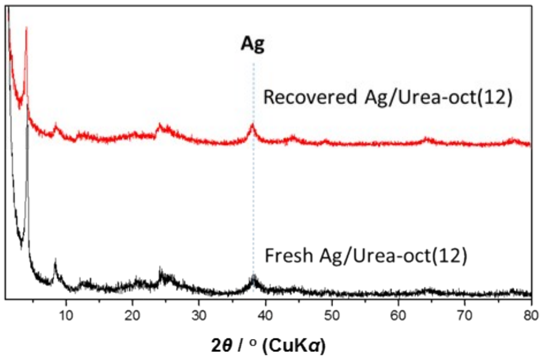

Fig. S5. XRD patterns of Ag/Urea-oct(12) before and after performing catalytic hydrolysis of NH_3BH_3 in water.

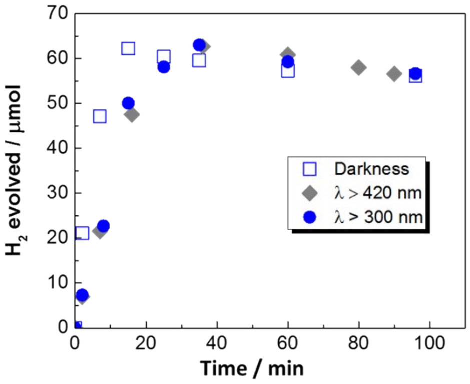

Fig. S6. Time-dependent H_2 evolution for Ag/Urea-oct(12) with HN_3BH_3 in water. The reaction was conducted both in dark and under irradiated of a solar simulator (λ > 300 nm, 1 SUN) with or without a longpass filter (λ > 420 nm)