Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Ultrasmall Pd/Au bimetallic nanocrystals embedded in hydrogen-bonding supramolecular structures: facile synthesis and super catalytic activities in the reduction of 4-nitrophenol

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Content list

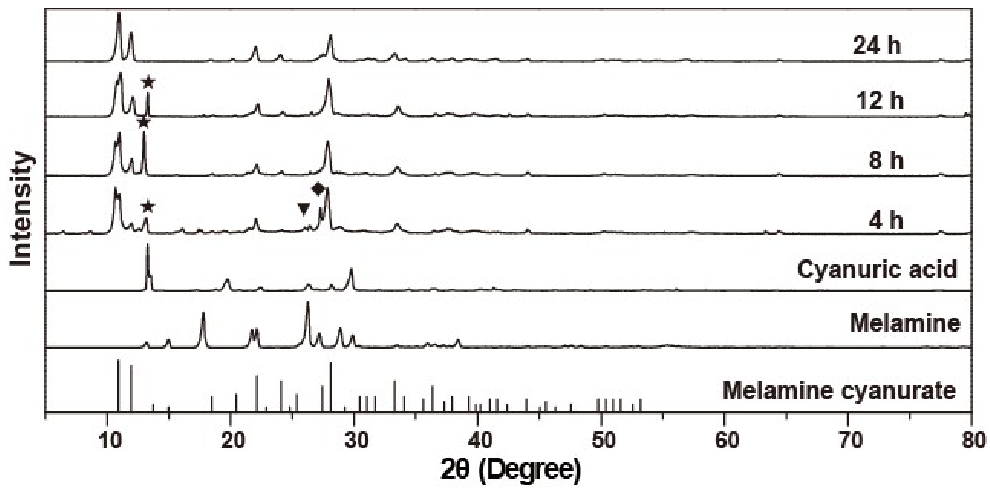

Figure S1 XRD patterns of the hydrothermal products at different time intervals from 4 h to 24 h, cyanuric acid, melamine and melamine cyanurate (JCPDS file No. 00-005-0127).

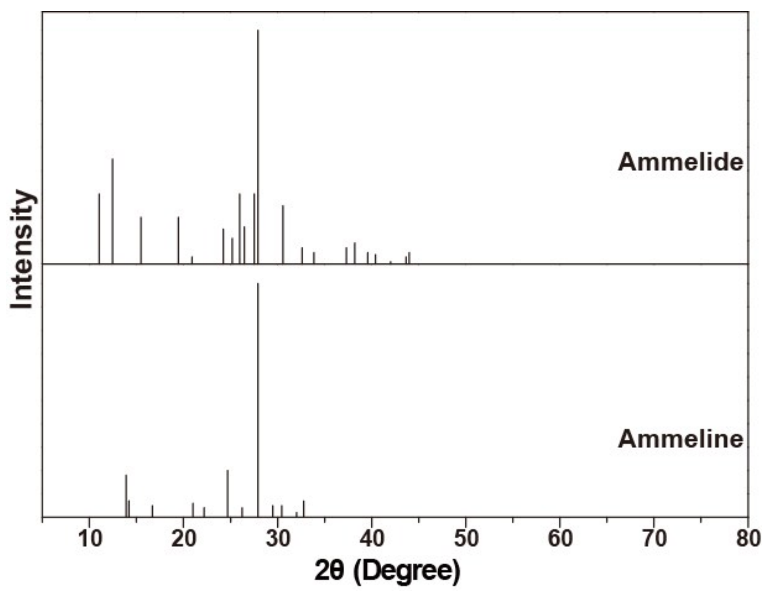

Figure S2 Standard XRD patterns of ammelide (JCPDS file No. 00-031-1527) and ammeline (JCPDS file No. 00-031-1526).

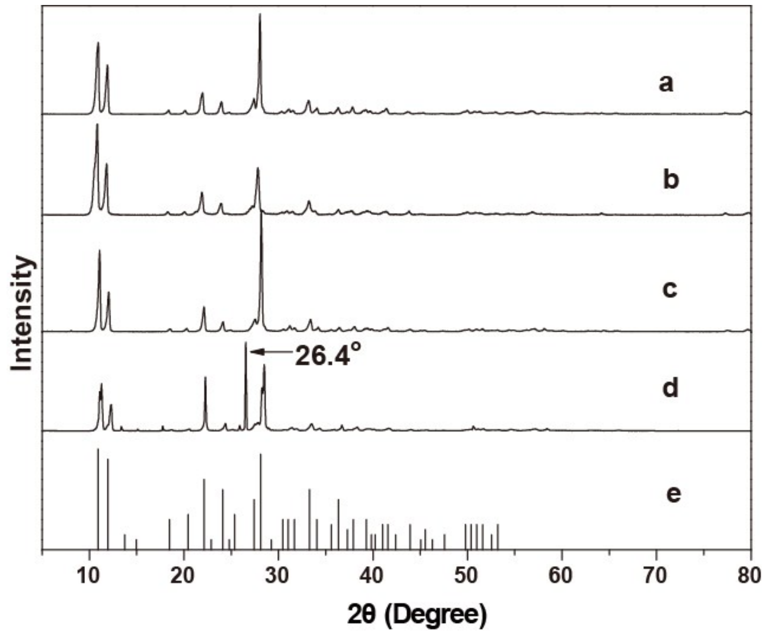

Figure S3 XRD patterns for the hydrothermal products from melamine with oxalic acid (a), acetic acid (b), sulfur acid (c) and from only melamine (d) for 24 h, melamine cyanurate (JCPDS file No. 00-005-0127) (e).

As depicted in Figure S1, the peak located at 13° in XRD patterns of the hydrothermal products from 4 h to 12 h should be attributed to cyanuric acid, an intermediate of melamine and citric acid during the hydrothermal process, the peak at 26.4° should be attributed to the unreacted melamine and the peak at 27.9° should be attributed to incompletely hydrolyzed product, ammelide and ammeline (Figure S2). When other acids such as acetic acid, oxalic acid, or sulfur acid was added instead of citric acid, all of the resulting products were melamine cyanurate (Figure S3). Therefore, citric acid should play a catalytic role in the formation of melamine cyanurate.

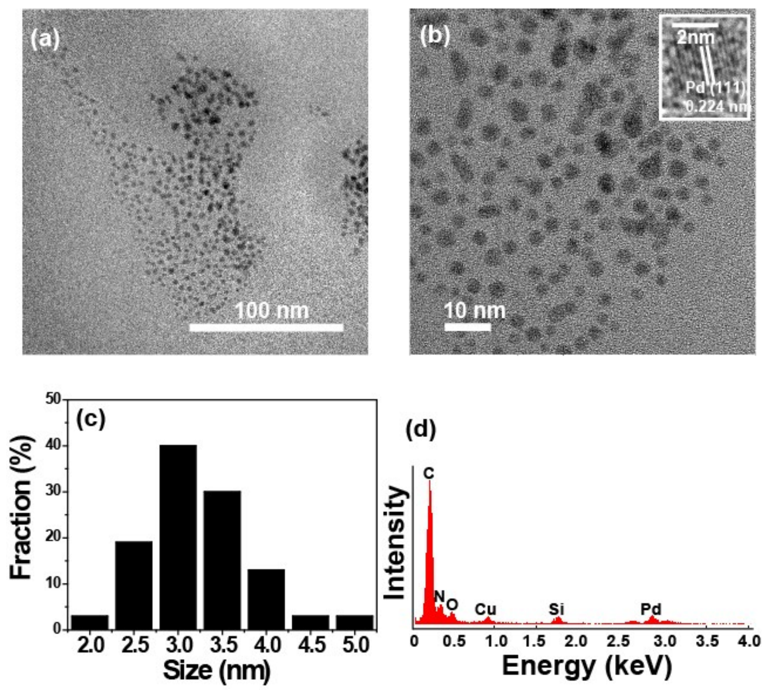

Figure S4 TEM (a), HRTEM images (b), size distribution histogram of Pd NPs embedded in MCA skeleton structure(c) and EDS of MCA-Pd (d). Inset shows one typical Pd NP.

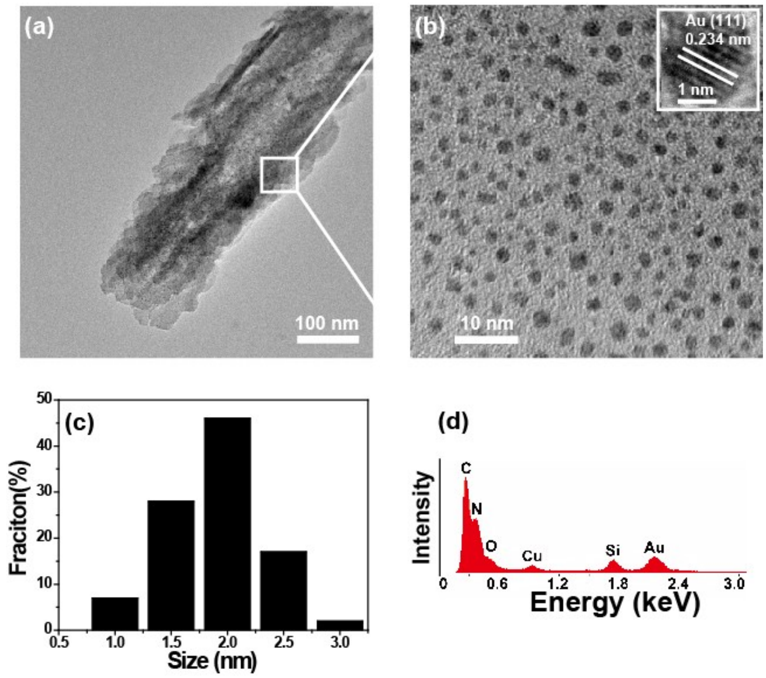

Figure S5 TEM (a), HRTEM images (b), size distribution histogram of Au NPs embedded in MCA skeleton structure (c) and EDS of MCA-Au (d). Inset shows one typical Au NP.

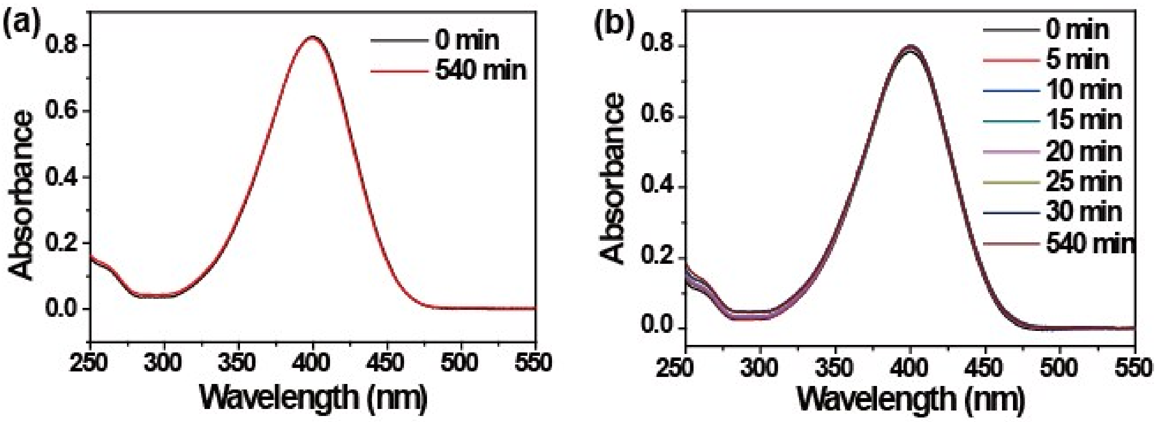

Figure S6 Typical time-dependent evolutions of UV/Vis spectra of the reduction of 4NP with $NaBH_4$ at room temperature in absence of any catalyst (a) and in the presence of MCA (b), showing the reduction reaction doesn't occur without the help of catalyst and MCA alone doesn't have any catalytic activity to reduce 4-NP even in the presence of $NaBH_4$.

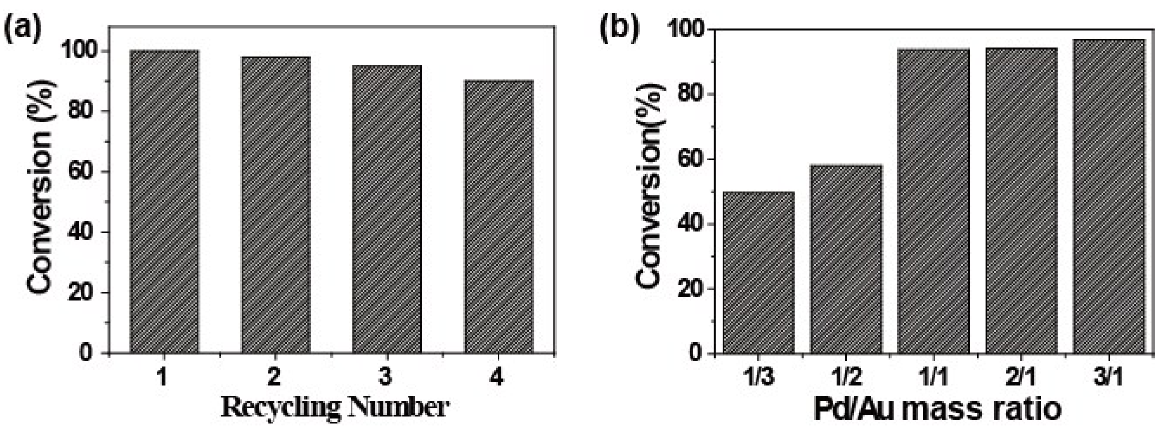

Figure S7 Four-run durability test of the MCA-Pd/Au (1/1) catalyst (a), and the conversion of 4-NP when catalysed by MCA-Pd/Au catalysts with different Pd/Au mass ratios at 6 min (b).

Table S1 Binding energies for N 1s, Pd 3d and Au 4f in MCA and MCA loaded with Au, Pd and Pd/Au bimetallic NPs.

	N 1s (eV)			Pd 3d (eV)		Au 4f (eV)			
	NH_2 group	C=N group	NH group	$3d_{5/2}$	$3d_{3/2}$	$4f_{7/2}(0)$	$4f_{5/2}(0)$	$4f_{7/2}(III)$	$4f_{5/2}(III)$
MCA	398.77	399.28	400.40						
MCA-Au	398.67	399.54	400.60			85.05	88.70	87.37	91.02
MCA-Pd	399.07	399.67	400.53	338.50	343.75				
MCA-Pd/Au	398.82	399.60	400.46	338.30	343.55	85.30	88.95	87.62	91.27