Supporting Information

New Insights into CdS Quantum Dots in Zeolite Y

Nak Cheon Jeong, Hyun Sung Kim, and Kyung Byung Yoon*

Center for Microcrystal Assembly, Center for Nanoporous Materials, Department of Chemistry, and Program of Integrated Biotechnology, Sogang University, Seoul 121-742, Korea

RECEIVED DATE (**yoonkb@ccs.sogang.ac.kr**)

SI 1. Additional Experimental Details.

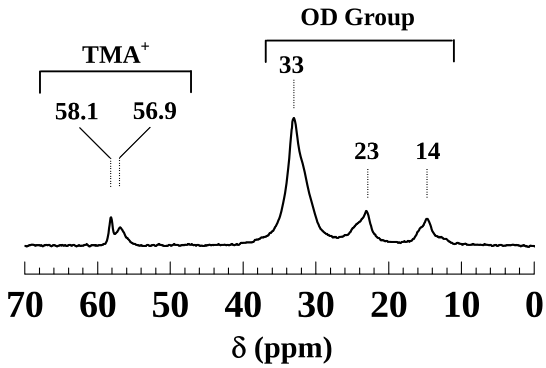
A. Procedure for the synthesis of Na^+-exchanged zeolite-Y having 0.7 TMA^+ ions in each supercage and 1.0 TMA^+ ion in each sodalite cage. We prepared a gel consisting of $Al(iPrO)_3$, TEOS, TMAOH, NaOH, and H_2O, where the mole ratio of the gel in terms of Al_2O_3:SiO_2:TMA:Na_2O:H_2O was 1:3.6:6.2:0.05:250. The procedure for the preparation of the above gel is as follows. TMAOH solution (25%, 112.8 g) was diluted in distilled deionized water (315 g). To this solution, $Al(iPrO)_3$ (20.8 g) was added with stirring, and the mixture was stirred for 1 h to hydrolyze $Al(iPrO)_3$. TEOS (38.3 g) was added to the above mixture, and the solution was stirred for 2 h. A dilute NaOH solution consisting of NaOH (0.2 g) and distilled deionized water (50 g) was added to the above clear solution. The mixture was aged for 12 h at room temperature with continuous stirring. The synthesis gel was then transferred into a polypropylene bottle, and the bottle was placed in an oven heated at 100 °C for 7 d. The produced $[Na(TMA)_{sup}(TMA)_{sod}]$-$Y_{1.8}$ was collected by centrifugation at 9000 rpm, and washed with copious amounts of distilled deionized water.

B. Procedure for the preparation of Cd^{2+}-exchanged $Y_{1.8}$ having 1.0 TMA ion in each sodalite cage {$[Cd_n(TMA)_{sod}]$-$Y_{1.8}$, n = 0.01, 0.1, 1, 6, 12, and 30}. For the preparation of $[Cd_{30}(TMA)_{sod}]$-$Y_{1.8}$, $[Na(TMA)_{sod}]$-$Y_{1.8}$ (0.3 g) was added into a $Cd(NO_3)_2$ solution (400 mM, 50 mL), and the heterogeneous solution was shaken for 24 h at room temperature. Due to a very high preference of $Y_{1.8}$ to Cd^{2+}, the ion exchange of Na^+ with Cd^{2+} was complete even after undergoing the above ion exchange procedure only once. Despite this, we repeated the above ion exchange procedure one more time to ensure a complete ion exchange of Na^+ with Cd^{2+}. For the preparation of $[Cd_n(TMA)_{sod}]$-$Y_{1.8}$ with smaller n (i.e., n = 0.01, 0.1, 1, 6, and 12) five 250-mL flasks and five different aqueous $Cd(NO_3)_2$ solutions with the concentrations of 0.05, 0.46, 2.8, and 5.5 mM, respectively, were prepared. Into each flask, $[Na(TMA)_{sod}]$-$Y_{1.8}$ (0.3 g) and each $Cd(NO_3)_2$ solution (50 mL) of different concentration were introduced, and the flasks were shaken for 24 h at room temperature. The Cd^{2+}-exchanged zeolite-$Y_{1.8}$ crystals were separated from the supernatant solutions by centrifugation at 9000 rpm, and washed with copious amounts of distilled deionized water several times until the supernatant solutions were free from Cd^{2+}. The presence of Cd^{2+} ion in the washes was monitored by dropping a drop of 1 M Na_2S solution into the washes.

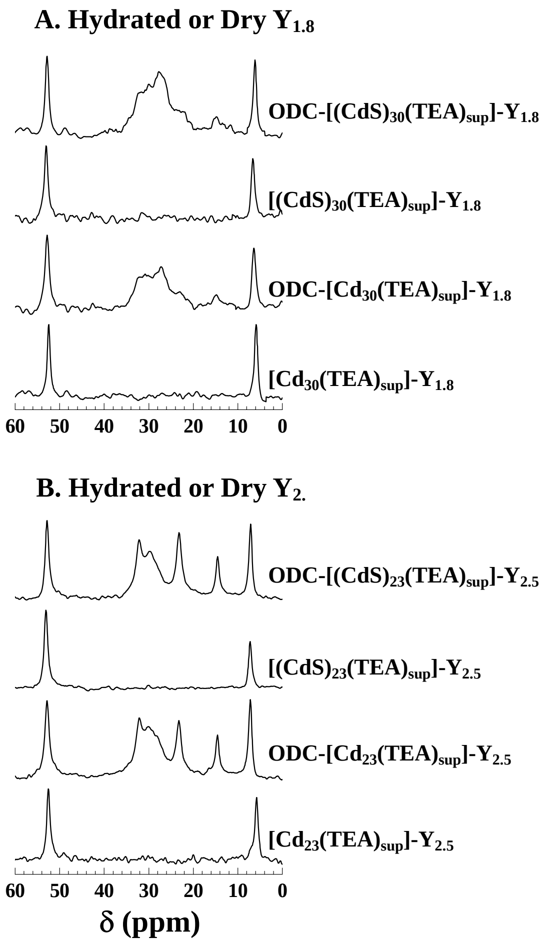
C. Additional instrumentation. The scanning electron microscope (SEM) images of zeolites were obtained from a FE-SEM (Hitachi S-4300) operated at an acceleration voltage of 20 kV. On top of the samples platinum/palladium alloy (in the ratio of 8 to 2) was deposited with a thickness of about 10 nm. The elemental analyses of the zeolite samples were carried out by both the energy dispersive X-ray spectroscopy (EDX) analyses and chemical analyses. The EDX spectra were obtained from a Horiba EX-400 EDX analyzer attached to our FE-SEM. The chemical analyses of Cd and S were carried out by ICP-AES (Shimadzu ICPS-1000IV) and those of Si and Al were carried out by XRF (Shimadzu XRF-1700). The chemical analyses were done by the National Center for Inter-University Facilities located in Seoul National University. X-ray powder diffraction patterns of the samples were obtained from from a Rigaku diffractometer (D/MAX-1C) with the monochromatic beam of Cu Kα. The thermogravimetric analyses (TGA) of the zeolite Y samples were performed on a TA instrument (TGA 2050). The rate of temperature increase was 10 °C min^{-1}, using air as the eluting gas. The flow rates to the balance and furnace were 10 and 90 mL min^{-1}, respectively. The transmission electron microscope (TEM) images of zeolite were obtained from a FE-TEM (JEOL JEM-2100F) at an acceleration voltage of 200 kV.

SI 2. **Table**. Denotations and Compositions of Various Zeolites Used in This Study.

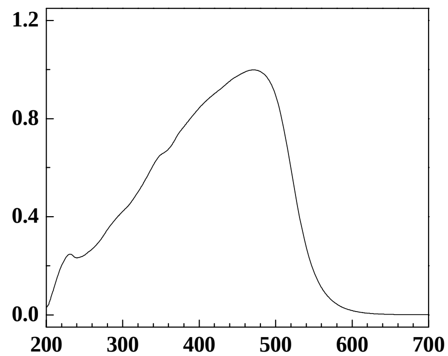
Type of Zeolite	Composition	CdS contents (wt%)
$[Na(TMA)_{sup}(TMA)_{sod}]$-$Y_{1.8}$	$Na_{53.3}[TMA_{5.8}]_{\alpha}[TMA_{7.9}]_{\beta}Al_{67}Si_{125}O_{384}$	
$[Na(TMA)_{sod}]$-$Y_{1.8}$	$Na_{59.1}TMA_{7.9}Al_{67}Si_{125}O_{384}$	
$[Na_{53}H_{14}]$-$Y_{1.8}$	$Na_{53.3}H_{13.7}Al_{67}Si_{125}O_{384}$	
$[Na]$-$Y_{1.8}$	$Na_{67.0}Al_{67}Si_{125}O_{384}$	
$[Na]$-$Y_{2.5}$	$Na_{54.0}Al_{54}Si_{138}O_{384}$	
$[H]$-$Y_{1.8}$	$H_{67.0}Al_{67}Si_{125}O_{384}$	
$[H]$-$Y_{2.5}$	$H_{54.0}Al_{54}Si_{138}O_{384}$	
$[Cd_{0.01}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{0.01}Na_{59.08}TMA_{7.9}Al_{67}Si_{125}O_{384}$	
$[Cd_{0.1}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{0.1}Na_{58.9}TMA_{7.9}Al_{67}Si_{125}O_{384}$	
$[Cd_{1}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{1.1}Na_{56.9}TMA_{7.9}Al_{67}Si_{125}O_{384}$	
$[Cd_{6}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{6.2}Na_{46.7}TMA_{7.9}Al_{67}Si_{125}O_{384}$	
$[Cd_{12}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{11.8}Na_{35.5}TMA_{7.9}Al_{67}Si_{125}O_{384}$	
$[Cd_{30}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{29.5}Na_{0.1}TMA_{7.9}Al_{67}Si_{125}O_{384}$	
$[Cd_{0.01}]$-$Y_{1.8}$	$Cd_{0.01}Na_{66.98}Al_{67}Si_{125}O_{384}$	
$[Cd_{0.1}]$-$Y_{1.8}$	$Cd_{0.1}Na_{66.8}Al_{67}Si_{125}O_{384}$	
$[Cd_{1}]$-$Y_{1.8}$	$Cd_{1.2}Na_{64.6}Al_{67}Si_{125}O_{384}$	
$[Cd_{6}]$-$Y_{1.8}$	$Cd_{5.8}Na_{55.4}Al_{67}Si_{125}O_{384}$	
$[Cd_{12}]$-$Y_{1.8}$	$Cd_{11.6}Na_{43.8}Al_{67}Si_{125}O_{384}$	
$[Cd_{34}]$-$Y_{1.8}$	$Cd_{33.5}Na_{0.0}Al_{67}Si_{125}O_{384}$	
$[Cd_{0.01}]$-$Y_{2.5}$	$Cd_{0.01}Na_{53.98}Al_{54}Si_{138}O_{384}$	
$[Cd_{0.1}]$-$Y_{2.5}$	$Cd_{0.1}Na_{53.8}Al_{54}Si_{138}O_{384}$	
$[Cd_{1}]$-$Y_{2.5}$	$Cd_{1.3}Na_{51.4}Al_{54}Si_{138}O_{384}$	
$[Cd_{6}]$-$Y_{2.5}$	$Cd_{6.1}Na_{41.8}Al_{54}Si_{138}O_{384}$	
$[Cd_{12}]$-$Y_{2.5}$	$Cd_{12.4}Na_{29.2}Al_{54}Si_{138}O_{384}$	
$[Cd_{30}]$-$Y_{2.5}$	$Cd_{27.0}Na_{0.0}Al_{54}Si_{138}O_{384}$	
$[Cd_{0.01}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{0.01}Na_{59.78}TEA_{7.2}Al_{67}Si_{125}O_{384}$	
$[Cd_{0.1}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{0.1}Na_{59.6}TEA_{7.2}Al_{67}Si_{125}O_{384}$	
$[Cd_{1}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{1.2}Na_{57.4}TEA_{7.2}Al_{67}Si_{125}O_{384}$	
$[Cd_{6}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{6.3}Na_{47.2}TeA_{7.2}Al_{67}Si_{125}O_{384}$	
$[Cd_{12}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{12.1}Na_{35.6}TEA_{7.2}Al_{67}Si_{125}O_{384}$	
$[Cd_{30}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{29.4}Na_{1.0}TEA_{7.2}Al_{67}Si_{125}O_{384}$	
$[Cd_{0.01}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{0.01}Na_{47.08}TEA_{6.9}Al_{54}Si_{138}O_{384}$	
$[Cd_{0.1}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{0.1}Na_{46.9}TEA_{6.9}Al_{54}Si_{138}O_{384}$	
$[Cd_{1}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{1.1}Na_{44.9}TEA_{6.9}Al_{54}Si_{138}O_{384}$	
$[Cd_{6}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{6.0}Na_{35.1}TEA_{6.9}Al_{54}Si_{138}O_{384}$	
$[Cd_{12}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{11.7}Na_{23.7}TEA_{6.9}Al_{54}Si_{138}O_{384}$	
$[Cd_{30}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{22.5}Na_{2.1}TEA_{6.9}Al_{54}Si_{138}O_{384}$	
$[(CdS)_{0.01}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{0.01}S_{0.01}H_{0.02}Na_{59.08}TMA_{7.9}Al_{67}Si_{125}O_{384}$	0.01
$[(CdS)_{0.1}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{0.1}S_{0.1}H_{0.2}Na_{58.9}TMA_{7.9}Al_{67}Si_{125}O_{384}$	0.11
$[(CdS)_{1}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{1.1}S_{1.0}H_{2.0}Na_{56.9}TMA_{7.9}Al_{67}Si_{125}O_{384}$	1.2
$[(CdS)_{6}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{6.2}S_{6.0}H_{12.0}Na_{46.7}TMA_{7.9}Al_{67}Si_{125}O_{384}$	6.3
$[(CdS)_{12}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{11.8}S_{11.2}H_{22.4}Na_{35.5}TMA_{7.9}Al_{67}Si_{125}O_{384}$	11.6
$[(CdS)_{30}(TMA)_{sod}]$-$Y_{1.8}$	$Cd_{29.5}S_{29.2}H_{58.4}Na_{0.1}TMA_{7.9}Al_{67}Si_{125}O_{384}$	26.0
$[(CdS)_{0.01}]$-$Y_{1.8}$	$Cd_{0.01}S_{0.01}H_{0.02}Na_{66.98}Al_{67}Si_{125}O_{384}$	0.01
$[(CdS)_{0.1}]$-$Y_{1.8}$	$Cd_{0.1}S_{0.1}H_{0.2}Na_{66.8}Al_{67}Si_{125}O_{384}$	0.11
$[(CdS)_{1}]$-$Y_{1.8}$	$Cd_{1.2}S_{1.0}H_{2.0}Na_{64.6}Al_{67}Si_{125}O_{384}$	1.3
$[(CdS)_{6}]$-$Y_{1.8}$	$Cd_{5.8}S_{5.6}H_{11.2}Na_{55.4}Al_{67}Si_{125}O_{384}$	6.1
$[(CdS)_{12}]$-$Y_{1.8}$	$Cd_{11.6}S_{11.1}H_{22.2}Na_{43.8}Al_{67}Si_{125}O_{384}$	11.7
$[(CdS)_{34}]$-$Y_{1.8}$	$Cd_{33.5}S_{33.0}H_{66.0}Na_{0.0}Al_{67}Si_{125}O_{384}$	29.5
$[(CdS)_{0.01}]$-$Y_{2.5}$	$Cd_{0.01}S_{0.01}H_{0.02}Na_{53.98}Al_{54}Si_{138}O_{384}$	0.01
$[(CdS)_{0.1}]$-$Y_{2.5}$	$Cd_{0.1}S_{0.1}H_{0.2}Na_{53.8}Al_{54}Si_{138}O_{384}$	0.11
$[(CdS)_{1}]$-$Y_{2.5}$	$Cd_{1.3}S_{1.2}H_{2.4}Na_{51.4}Al_{54}Si_{138}O_{384}$	1.4
$[(CdS)_{6}]$-$Y_{2.5}$	$Cd_{6.1}S_{6.0}H_{12.0}Na_{41.8}Al_{54}Si_{138}O_{384}$	6.6
$[(CdS)_{12}]$-$Y_{2.5}$	$Cd_{12.4}S_{12.2}H_{24.4}Na_{29.2}Al_{54}Si_{138}O_{384}$	12.8
$[(CdS)_{30}]$-$Y_{2.5}$	$Cd_{27.0}S_{26.8}H_{53.6}Na_{0.0}Al_{54}Si_{138}O_{384}$	25.2
$[(CdS)_{0.01}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{0.01}S_{0.01}H_{0.02}Na_{59.78}TEA_{7.2}Al_{67}Si_{125}O_{384}$	0.01
$[(CdS)_{0.1}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{0.1}S_{0.1}H_{0.2}Na_{59.6}TEA_{7.2}Al_{67}Si_{125}O_{384}$	0.11
$[(CdS)_{1}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{1.2}S_{1.1}H_{2.2}Na_{57.4}TEA_{7.2}Al_{67}Si_{125}O_{384}$	1.2
$[(CdS)_{6}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{6.3}S_{6.1}H_{12.2}Na_{47.2}TeA_{7.2}Al_{67}Si_{125}O_{384}$	6.3
$[(CdS)_{12}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{12.1}S_{12.0}H_{24.0}Na_{35.6}TEA_{7.2}Al_{67}Si_{125}O_{384}$	11.6
$[(CdS)_{30}(TEA)_{sup}]$-$Y_{1.8}$	$Cd_{29.4}S_{29.2}H_{58.4}Na_{1.0}TEA_{7.2}Al_{67}Si_{125}O_{384}$	25.4
$[(CdS)_{0.01}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{0.01}S_{0.01}H_{0.02}Na_{47.08}TEA_{6.9}Al_{54}Si_{138}O_{384}$	0.01
$[(CdS)_{0.1}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{0.1}S_{0.1}H_{0.2}Na_{46.9}TEA_{6.9}Al_{54}Si_{138}O_{384}$	0.11
$[(CdS)_{1}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{1.1}S_{1.0}H_{2.0}Na_{44.9}TEA_{6.9}Al_{54}Si_{138}O_{384}$	1.1
$[(CdS)_{6}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{6.0}S_{5.8}H_{11.6}Na_{35.1}TEA_{6.9}Al_{54}Si_{138}O_{384}$	6.1
$[(CdS)_{12}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{11.7}S_{11.5}H_{23.0}Na_{23.7}TEA_{6.9}Al_{54}Si_{138}O_{384}$	11.5
$[(CdS)_{30}(TEA)_{sup}]$-$Y_{2.5}$	$Cd_{22.5}S_{22.4}H_{44.8}Na_{2.1}TEA_{6.9}Al_{54}Si_{138}O_{384}$	20.7
$[Na_{f}]$-Y_{2}	$Na_{62.6}Al_{62.6}Si_{129.4}O_{384}$	
$[Na_{f}]$-Y_{4}	$Na_{64.6}Al_{64.6}Si_{127.4}O_{384}$	
$[Na_{f}]$-Y_{8}	$Na_{70.2}Al_{70.2}Si_{121.8}O_{384}$	
$[Na_{f}]$-Y_{28}	$Na_{75.4}Al_{75.4}Si_{116.6}O_{384}$	
$[(CdS)_{34}]$-$Y^{0.08\mu}$	$Cd_{33.5}S_{33.0}H_{66.0}Na_{0.0}Al_{67}Si_{125}O_{384}$	29.5
$[(CdS)_{31}]$-$Y^{2\mu}$	$Cd_{31.3}S_{28.4}H_{56.8}Al_{62.6}Si_{129.4}O_{384}$	27.8
$[(CdS)_{32}]$-$Y^{4\mu}$	$Cd_{32.3}S_{29.0}H_{58.0}Al_{64.6}Si_{127.4}O_{384}$	28.4
$[(CdS)_{35}]$-$Y^{8\mu}$	$Cd_{35.1}S_{34.6}H_{69.2}Al_{70.2}Si_{121.8}O_{384}$	30.5
$[(CdS)_{38}]$-$Y^{28\mu}$	$Cd_{37.7}S_{33.3}H_{66.6}Al_{75.4}Si_{116.6}O_{384}$	31.5



SI 3. ^{13}C NMR of ODC-[Na(TMA)$_{sup}$(TMA)$_{sod}$]-Y$_{1.8}$



SI 4. ^{13}C NMR of ODC-[$(CdS)_{30}$$(TEA)_{sup}$]-$Y_{1.8}$, [$(CdS)_{30}$$(TEA)_{sup}$]-$Y_{1.8}$, ODC-[$Cd_{30}$$(TEA)_{sup}$]-$Y_{1.8}$, and [$Cd_{30}$$(TEA)_{sup}$]-$Y_{1.8}$ (A) ODC-[$(CdS)_{23}$$(TEA)_{sup}$]-$Y_{2.5}$, [$(CdS)_{23}$$(TEA)_{sup}$]-$Y_{2.5}$, ODC-[$Cd_{23}$$(TEA)_{sup}$]-$Y_{2.5}$, and [$Cd_{23}$$(TEA)_{sup}$]-$Y_{2.5}$ (B)



SI 5. UV-vis spectrum of bulk CdS