

Supporting Information

Transformative 2-Dimensional Layered Nanocrystals

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Methods

Synthesis of TiS₂ nanodiscs. Titanium (IV) chloride (160 μ l, 1.5 mmol) was mixed with oleylamine (3 g, 11.2 mmol) in a round-bottom flask under argon atmosphere and the mixture was heated at 300 °C. Subsequently, carbon disulfide (0.3 ml, 1.2 mmol) was injected into the flask at the same temperature. After 1 hr, reaction mixture was treated with hexane (2 ml) and methanol (3 ml) to isolate black TiS₂ nanodiscs (80 mg).

Synthesis of Cu₂S toroid nanocrystals: TiS₂ nanodiscs (57 mg, 0.53 mmol) were mixed with copper (II) chloride (CuCl₂) (0.53, 1.06, 2.12 mmol) in a round-bottom flask containing oleylamine (3 g, 11.2 mmol). The reaction mixture was heated to 200 °C for 30 min and then was cooled to room temperature. During the course of the reaction, the initial black-colored solution gradually became dark brown. Then hexane (2 ml) and methanol (3 ml) were used to precipitate brown Cu₂S (70 mg). Intermediate structures containing TiS₂-Cu₂S were obtained by varying the relative molar ratio of Cu ion and TiS₂ nanodiscs or varying the reaction temperature as described in the main text.

Synthesis of TiS₂-Ag₂S hetero-structure nanocrystals. TiS₂ nanodiscs (10 mg, 0.08 mmol) were dispersed in trioctylphosphine (5 g, 11.2 mmol) and silver nitrate (AgNO₃) (135 mg, 0.8 mmol) was added. Then, the mixture was heated to 70 °C and maintained for 1 h under the argon atmosphere with vigorous stirring. The solution was cooled to room temperature and the product was washed and precipitated by centrifugation at 3000 rpm for 15 min.

Synthesis of TiS₂-MnS hetero-structure nanocrystals. TiS₂ nanodiscs (10 mg, 0.08 mmol) were dispersed in oleylamine (5 g, 18.6 mmol) and manganese (II) chloride (MnCl₂) (100 mg, 0.8 mmol) was added in a round-bottom flask. The reaction mixture was heated to 100 °C for 3 h and then was cooled to room temperature. During the course of the reaction, the initial

black-colored solution gradually became purple. The solution was cooled to room temperature and the product was washed and precipitated by centrifugation at 3000 rpm for 15 min.

Synthesis of CdS nanocrystals. TiS_2 nanodiscs (10 mg, 0.08 mmol) were dispersed in oleylamine (5 g, 18.6 mmol) and cadmium (II) chloride (CdCl_2) (146 mg, 0.8 mmol) was added in a round-bottom flask. The reaction mixture was heated to 80 °C for 5 h and then was cooled to room temperature. During the course of the reaction, the initial black-colored solution gradually became green. The solution was cooled to room temperature and the product was washed and precipitated by centrifugation at 3000 rpm for 15 min.

Characterizations

TEM analyses were performed using a JEM 2100 at 200 kV and JEM-ARM1300S at 1250 kV. TEM samples were prepared by dropping nanocrystals suspended in a toluene solution onto a carbon-coated molybdenum grid or ultra thin copper grid. EELS analysis was performed using a post-column energy filter (Gatan HV-GIF2000). Power X-ray diffraction measurements were conducted using a Rigaku D/MAX-RB equipped with a graphite-monochromated $\text{Cu}_{\text{K}\alpha}$ radiation source (40 kV, 120 mA).

Elemental mapping of toroidal Cu_2S nanocrystal.

Electron energy loss spectroscopy (EELS) analysis of toroid nanocrystal shows copper and sulfur atoms are the constitutive elements.

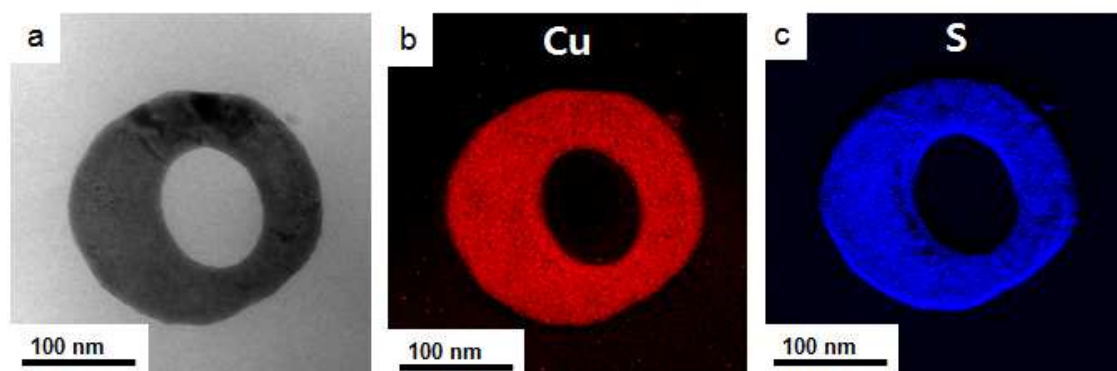


Figure S1. a) Zero-loss filtered TEM image. b) Copper and (c) sulfur signals are color-coded as red and blue.

TEM images of Time dependent chemical transformation of TiS_2 nanodiscs upon reaction with Cu ion at 200 °C.

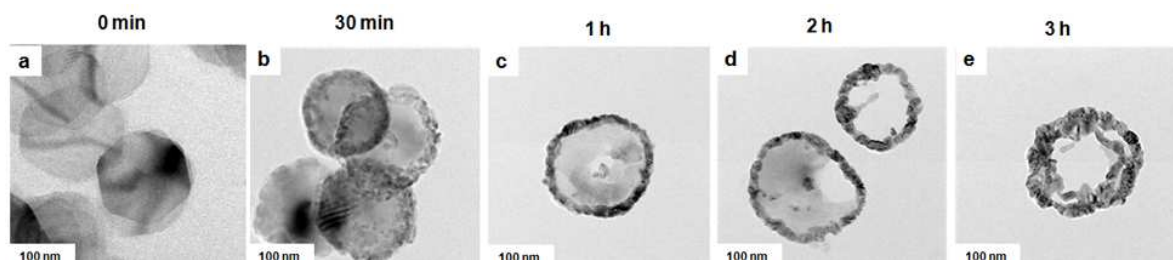


Figure S2. The molar ratio of reactant Cu ion to template (TiS_2) is two. Aliquots were collected during the reaction for TEM analysis at several time points. (a) 0 min. (b) 30 min. (c) 1 h. d) 2 h. (e) 3 h.

X-ray diffraction patterns of $\text{TiS}_2\text{-Ag}_2\text{S}$ and $\text{TiS}_2\text{-MnS}$ toroidal hetero-nanocrystals and CdS toroidal nanocrystals.

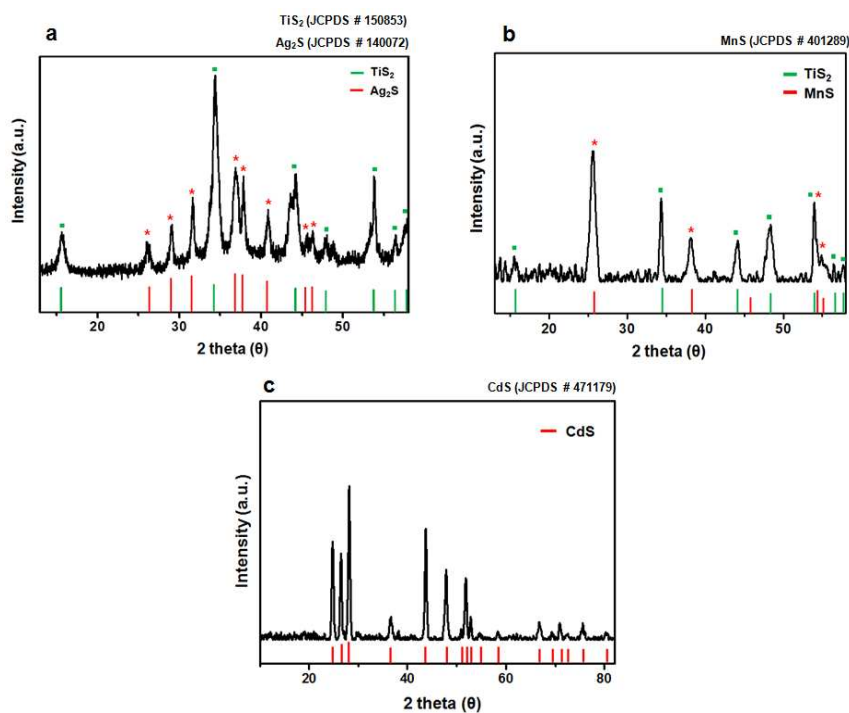


Figure S3. XRD patterns of (a) $\text{TiS}_2\text{-Ag}_2\text{S}$ and (b) $\text{TiS}_2\text{-MnS}$ toroidal hetero-nanocrystals and (c) CdS toroidal nanocrystals obtained from the reactions between TiS_2 nanodisc and Ag ion, Mn ion and Cd ion.