

Supporting Information

Multi-Functional Organosilane-Polymerized Carbon Dots Inverse Opals

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1. Preparation and characterization of organosilane-polymerized carbon dots inverse opals (SiCDIOs)

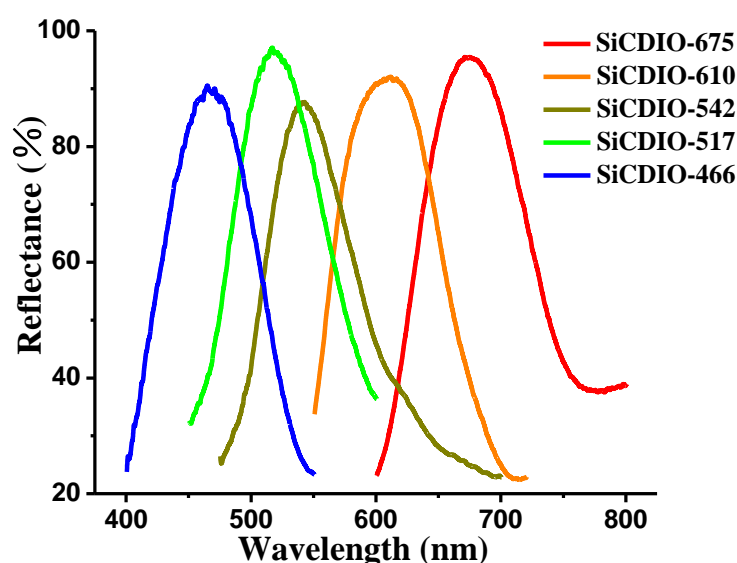


Figure S1. The reflectance spectra of SiCDIOs with bandgaps of 675, 610, 542, 517 and 466 nm.

The width of the reflectance peaks were narrow and reflectance intensity of samples were up to 90%, indicating a good photonic crystal (PC) structure. SiCDIOs with different bandgaps could be obtained from PC template with PS (polystyrene) spheres of different diameters. In details, the bandgaps of samples were 675, 610, 542, 517 and 466 nm respectively.

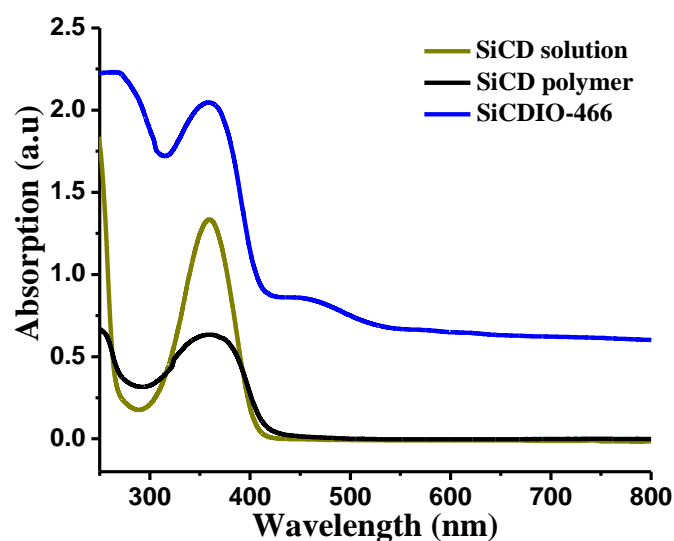


Figure S2. UV-Vis spectra of SiCD solution, SiCD polymer and SiCDIO-466 respectively.

All the samples had a strong absorption at wavelength of 358 nm no matter what forms they existed.

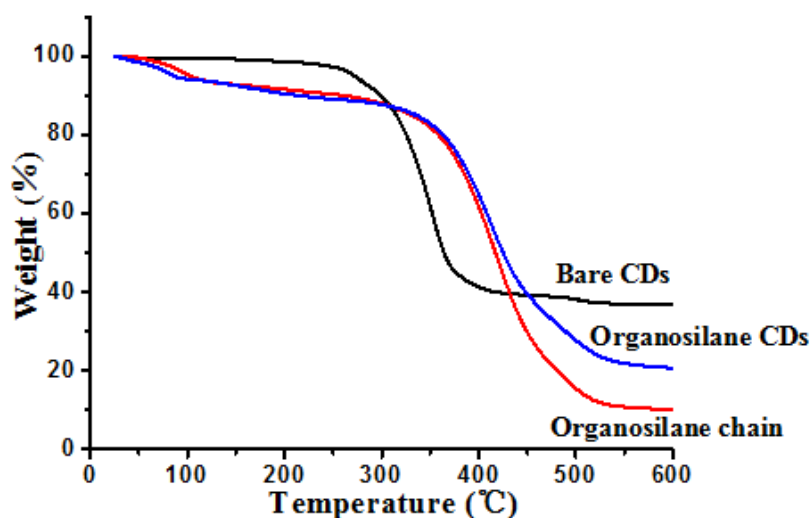


Figure S3. TGA of different materials, such as bare CDs, organosilane chain and organosilane CDs. TGA was conducted from 25 to 600 °C at the heating rate of 10 °C min⁻¹ with N₂ as a protecting atmosphere.

From TGA result, the remaining mass fraction of organosilane CDs, bare CDs and organosilane chain at 500 °C are 21.81%, 37.29% and 10.81% respectively. It is calculated that the weight content ratio of graphene quantum dots in organosilane CDs is 41.54%. And the weight content ratio of organosilane-chain in organosilane CDs is 58.46%.

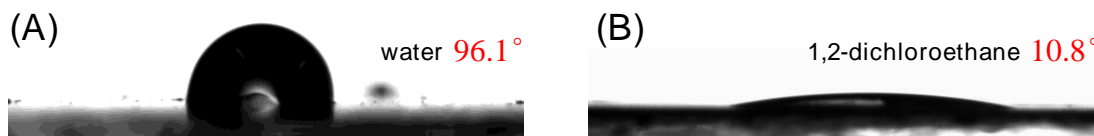


Figure S4. Contact angles (CAs) of (A) water and (B) 1,2-dichloroethane on the surface of SiCDIOs.

The CAs of water/1, 2-dichloroethane on the surface of sample were $96.1^{\circ}/10.8^{\circ}$ respectively. The sample showed a hydrophobic and lipophilic surface owing to existing of organosilane on the sample's surface.



Figure S5. (A) Optical images of SiCDIOs with different bandgaps, such as 675, 610, 542, 517 and 466 nm respectively from left to right. (B-D) The fluorescent images of corresponding samples that being excited at laser of (B) 375, (C) 480 and (D) 560 nm respectively.

The SiCDIOs with different bandgaps showed distinct fluorescent colors under various excitation lasers. The sample presented fluorescent colors of blue, green and red when being excited at laser of 375, 480 and 560 nm respectively.

2. The modulation effect of SiCDIOs' bandgap on fluorescence enhancement

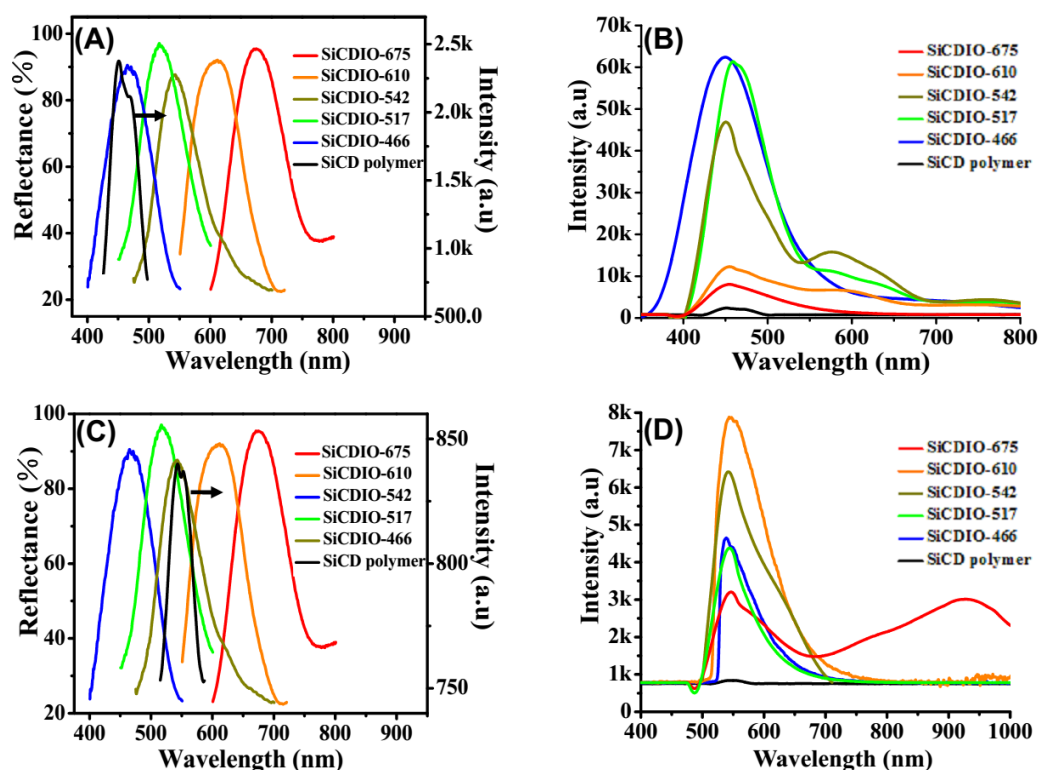


Figure S6. (A, C) The combination of reflectance spectra of SiCDIOs and emission spectra of SiCD polymer. The black lines were emission spectra of SiCD polymer that being excited at laser of 375 and 480 nm respectively. The other lines were reflectance spectra of SiCDIOs with different bandgaps. (B, D) The emission spectra of SiCD polymer and SiCDIOs with different bandgaps that being excited at laser of 375 and 480 nm respectively.

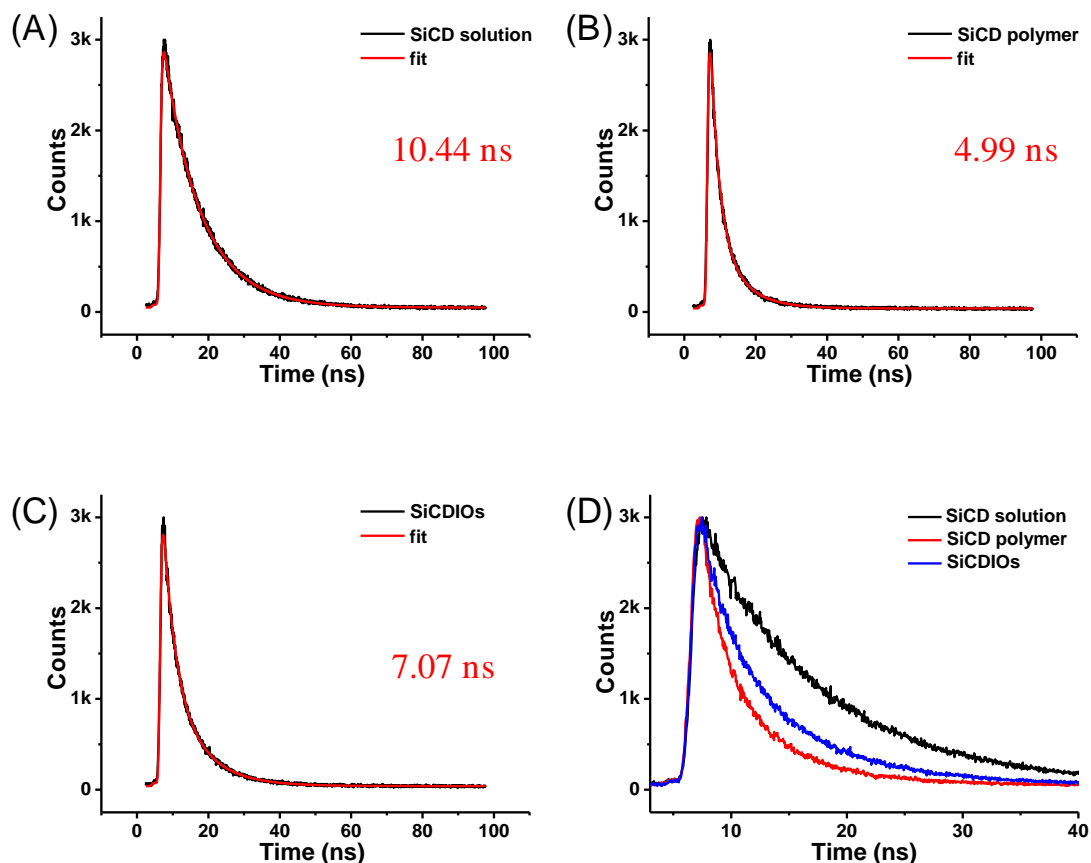


Figure S7. (A, B, C) Luminescence decays (375 nm excitation) of (A) SiCD solution (dissolved in ethanol with $V_{\text{CDs}}:V_{\text{ethanol}}=1:3$), (B) SiCD polymer and (C) SiCDIOs. (D) Total spectra.

The Luminescence decay of SiCD polymer (4.99 ns) was less than SiCD solution (10.44 ns) owing to fluorescence quenching caused by aggregation. However, SiCDIOs (7.07 ns) could effectively enhance the luminescence decay compared to SiCD polymer due to the introduction of PC structure.

Table 1. Fluorescence intensity and enhancement factor of samples under laser of 375, 480 and 560 nm respectively. SiCDIO-675, -675 and -466 mean the SiCDIOs with bandgap overlapping neither emission spectra of SiCD polymer nor the red/or blue edge of it when being excited at laesr of 375, 480 and 560 nm respectively.

		SiCD polymer	SiCDIO-675	SiCDIO-610	SiCDIO-542	SiCDIO-517	SiCDIO-466
375 nm	fluorescence intensity (a.u)	2352	7918	12221	46590	60934	62540
	compare to SiCD polymer	1	3.37	5.20	19.81	25.91	26.59
	compare to SiCDIO-675	0.30	1	1.54	5.88	7.70	7.90
480 nm	fluorescence intensity (a.u)	841	3180	7881	6413	4327	4649
	compare to SiCD polymer	1	3.78	9.37	7.63	5.15	5.53
	compare to SiCDIO-675	0.26	1	2.48	2.02	1.36	1.46
560 nm	fluorescence intensity (a.u)	600	15921	14374	8703	7916	6483
	compare to SiCD polymer	1	26.54	23.96	14.51	13.19	10.81
	compare to SiCDIO-466	0.09	2.46	2.22	1.34	1.22	1

3. Construction of anti-fake pattern by structured Si template

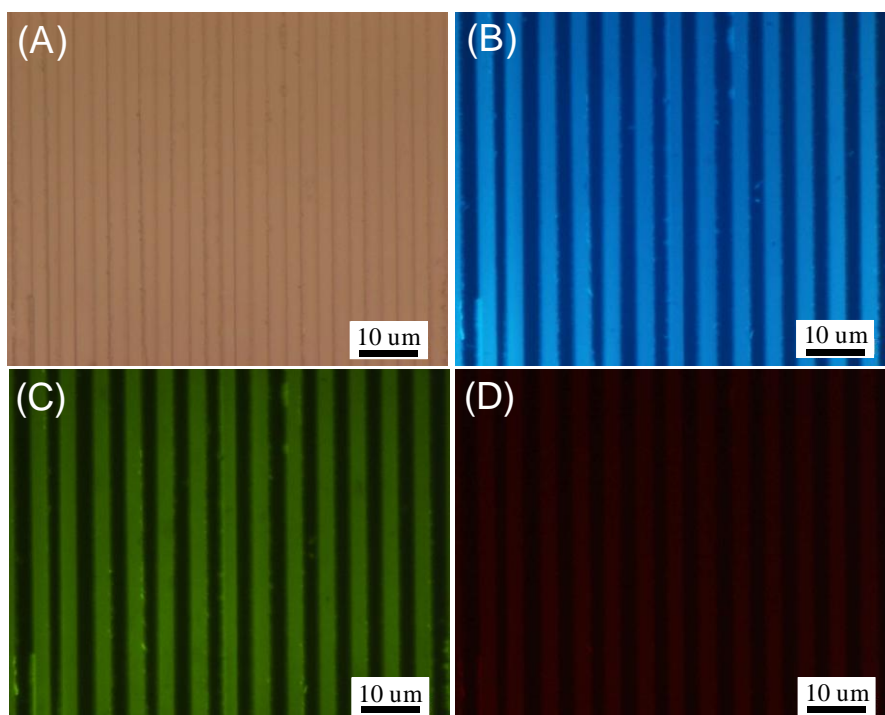


Figure S8. (A) Optical image of patterned SiCD polymer on a cover glass and (B-D) corresponding fluorescent images that being excited at laser of (B) 375, (C) 480 and (D) 560 nm respectively.

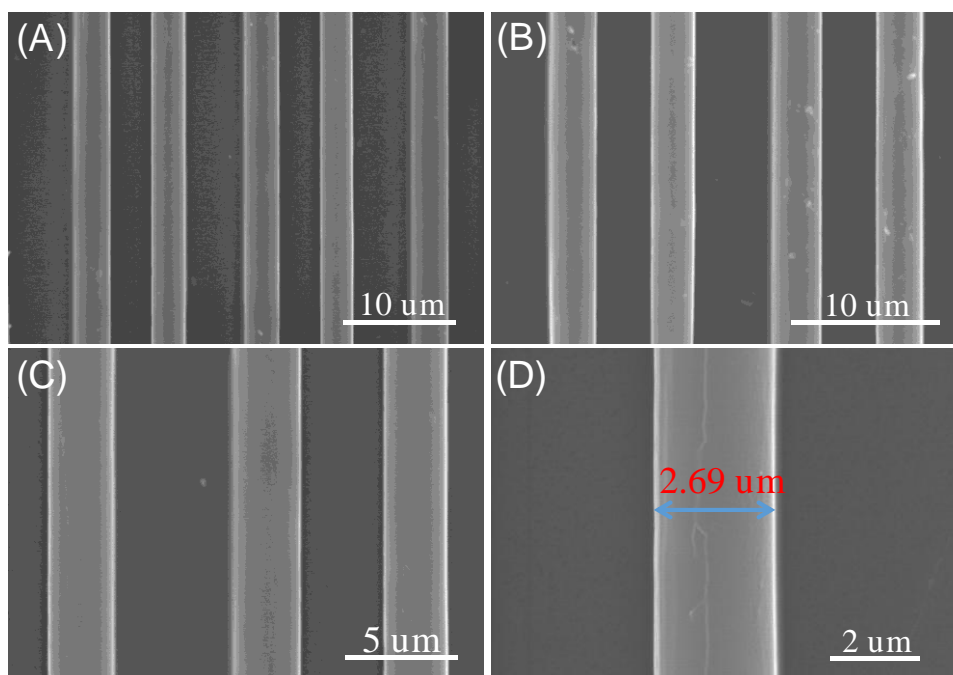


Figure S9. (A-D) SEM images of patterned SiCD polymer on a cover glass.

Dropping a ethanol solution of SiCDs ($V_{\text{CDs}}:V_{\text{ethanol}}=1:3$) to the structured Si template with raised micrometer lines and followed the “sandwich” method mentioned in the text except PC template replaced by a cover glass to verify mechanism for the formation of anti-fake pattern of SiCDIOs. Fine micrometer lines with 2.69 μm were observed on the cover glass, thus proved that raised micrometer lines on the structured Si template really provided a space for aggregation of SiCD solution.

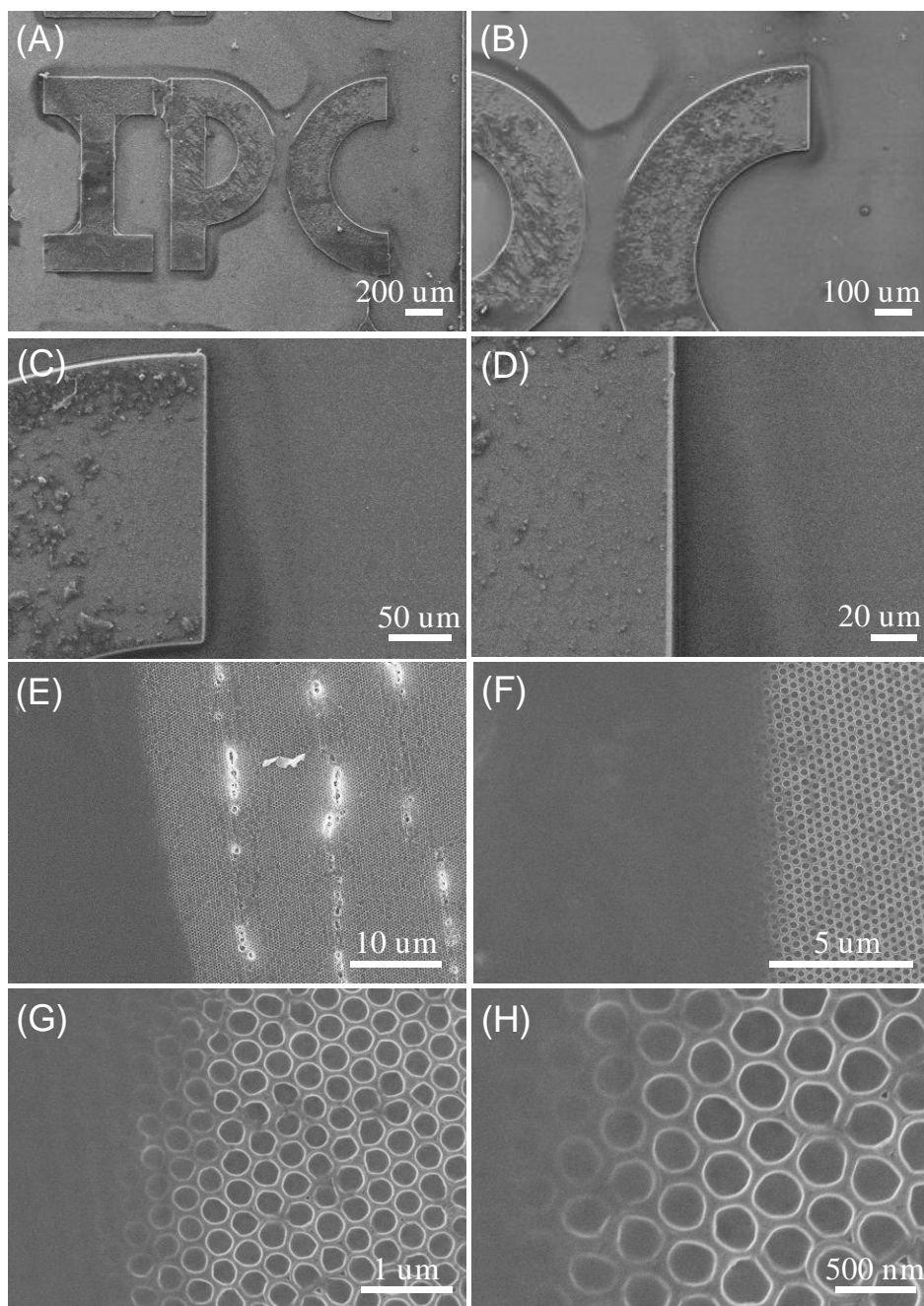


Figure S10. (A-H) SEM images of “IPC” pattern fabricated from structured Si template and corresponding boundary of pattern. (C, D) SEM images of magnified area of “C” pattern in (B). (E-H) SEM images of magnified area of boundary of “C” pattern in (D).

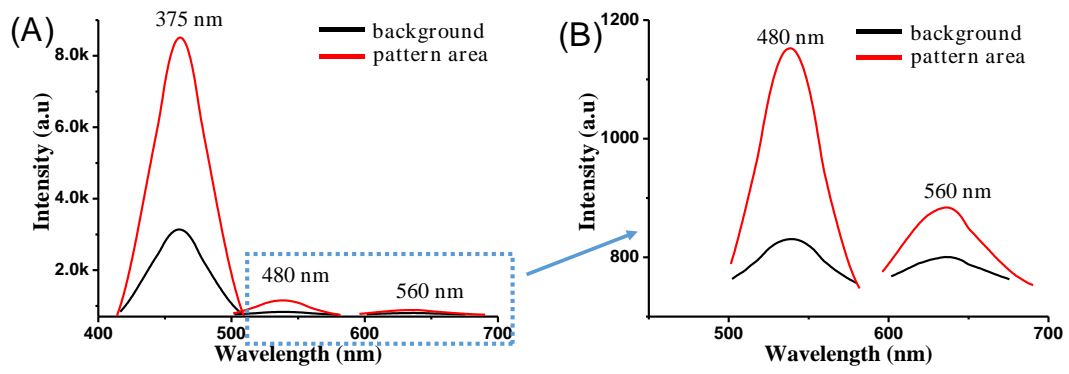


Figure S11. (A) Comparison of fluorescence intensity (being excited at laser of 375, 480 and 560 nm respectively) between backgroud and pattern area, which fabricated from structured Si template. (B) The enlargement area of (A).

Obviously, the fluorescence intensity of pattern area was stronger, regardless of the wavelength of excitation laser.

4. Formation of anti-fake pattern from blueshift of SiCDIOs' bandgap at high temperature

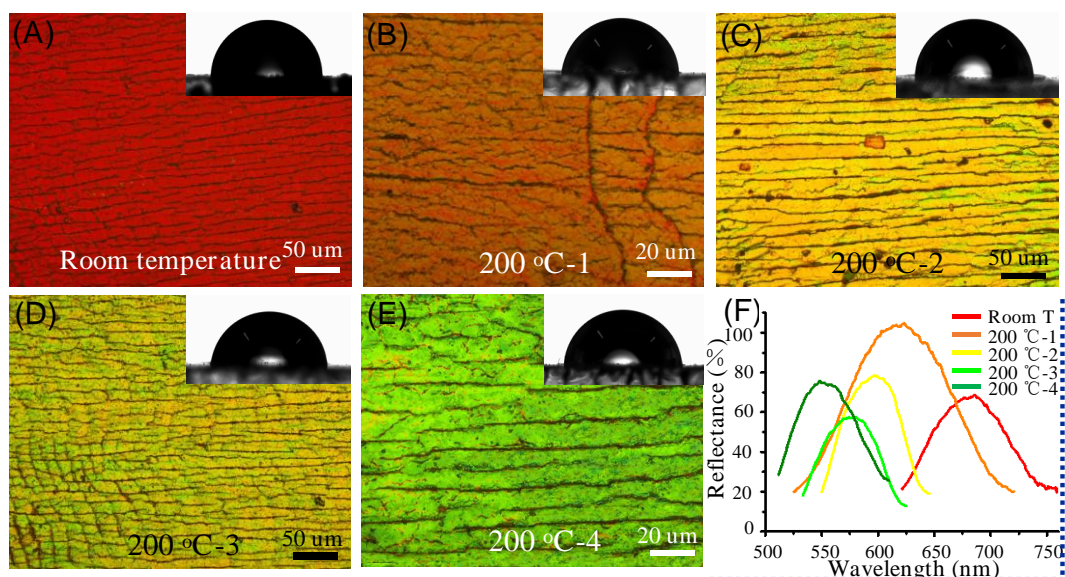


Figure S12 (A) Optical image of SiCDIOs in room temperature. (B-E) Optical images of SiCDIOs in 200 °C for (B) 1, (C) 2, (D) 3 and (E) 4 min respectively. The inserted were water CAs on the corresponding sample. (F) Reflectance spectra of SiCDIOs before and after thermal treatment (200 °C) of 1, 2, 3 and 4 min respectively.

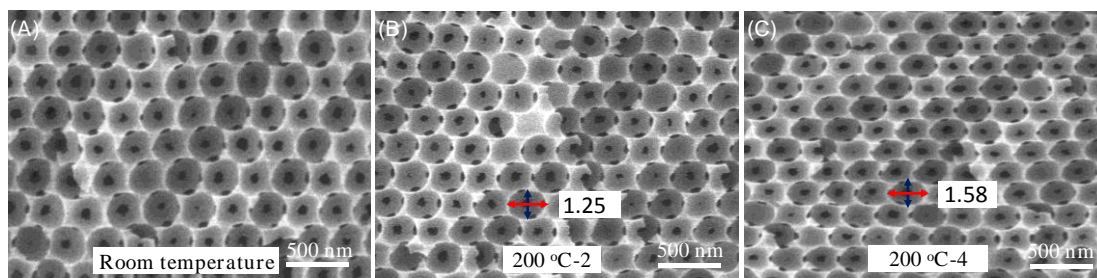


Figure S13. (A-C) Side-view SEM images of SiCDIOs (A) before and after thermal treatment (200 °C) for (B) 2 and (C) 4 min respectively.

The ratios of the length to width of anisotropy pore were 1.25 and 1.58 for the thermal treatment (200 °C) of 2 and 4 min respectively, indicating a gradual directional shrinkage of the polymerization network at high temperature.

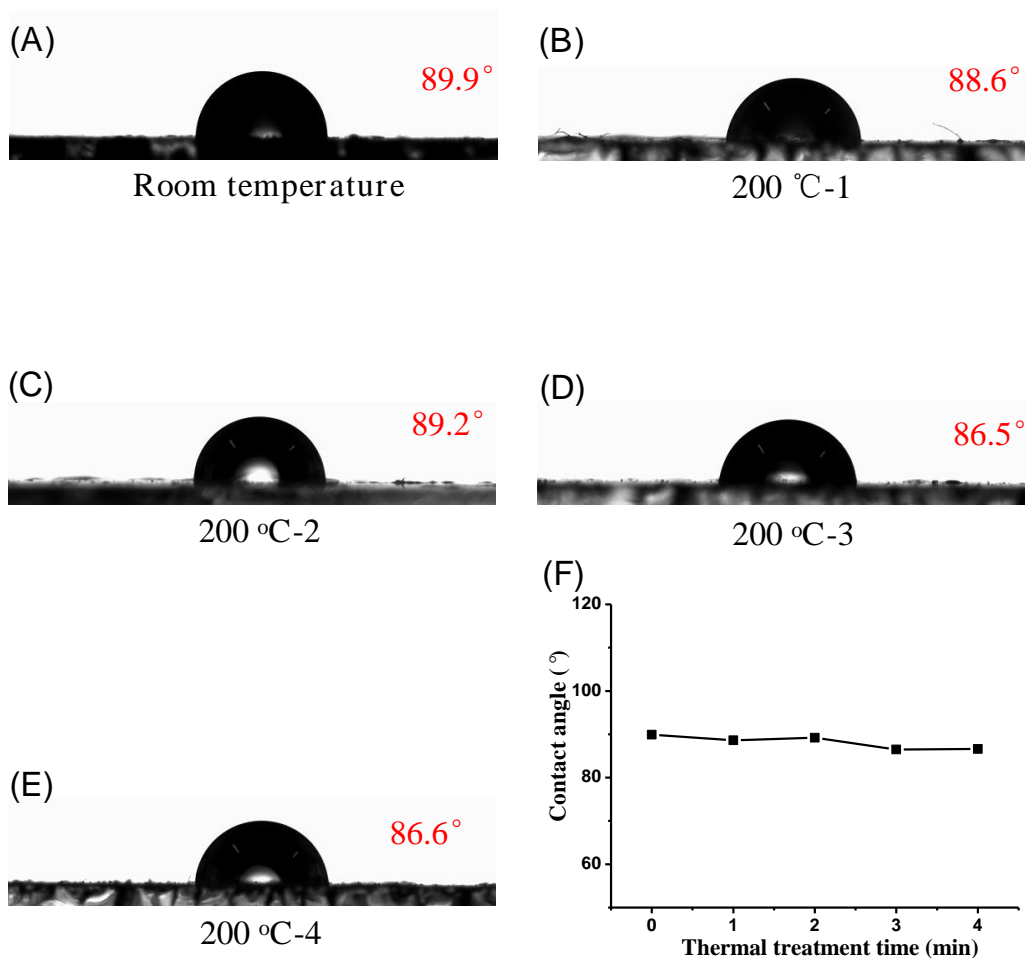


Figure S14. (A-E) Water CAs on the surface of SiCDIOs with thermal treatment (200 °C) of (A) 0, (B) 1, (C) 2, (D) 3 and (E) 4 min respectively. (F) The change of water CAs according to different thermal treatment times.

The water CAs were 89.9°, 88.6°, 89.2°, 86.5° and 86.6° for the sample treated in 200 °C for 0, 1, 2, 3 and 4 min respectively, which indicated the sample's surface couldn't be damaged and only the polymerization network of SiCDs underwent condensation at high temperature.

5. The durability of SiCDIOs in organic solvent

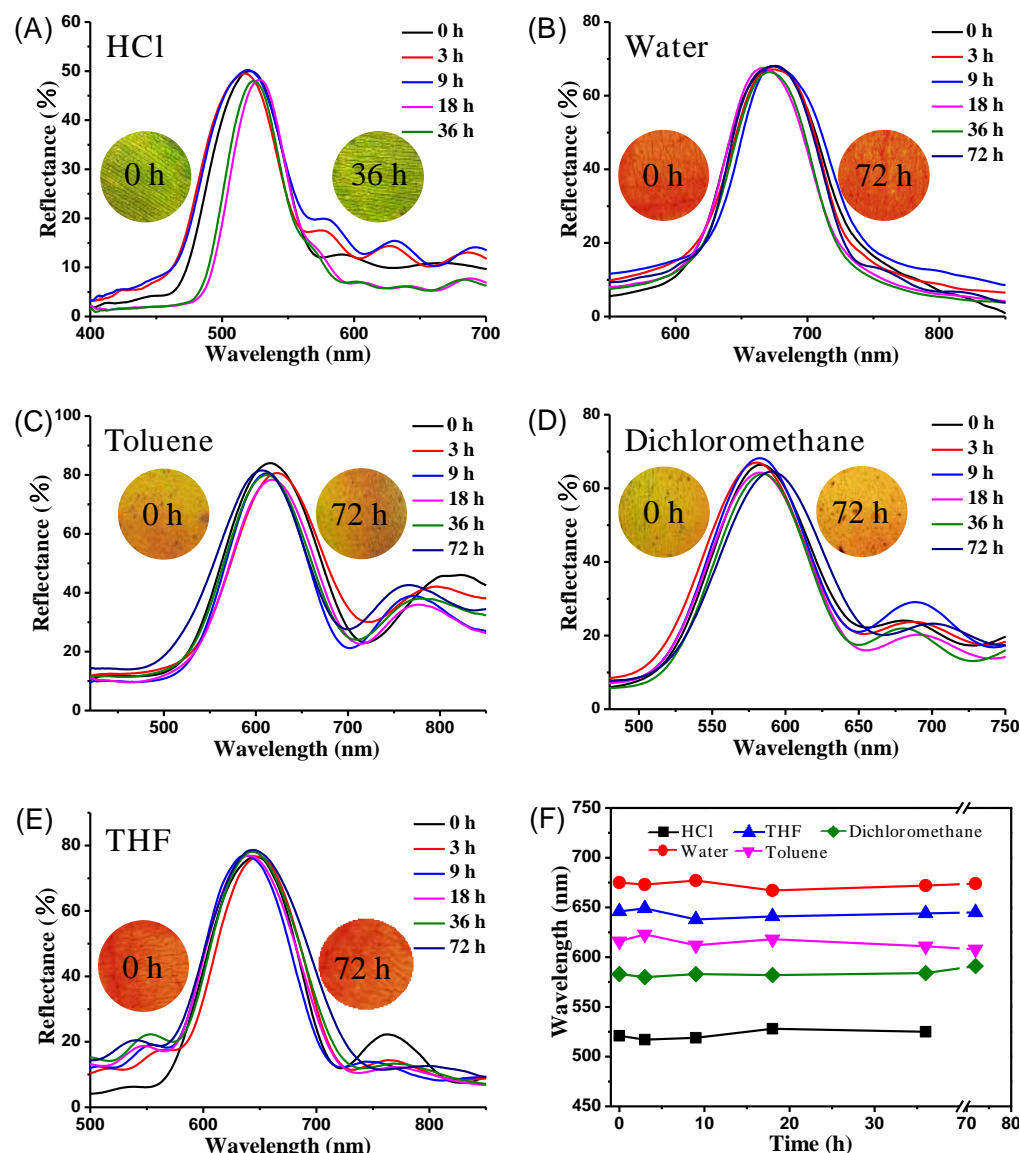


Figure S15. (A-E) Reflectance spectra of as-prepared SiCDIOs after being immersed in (A) HCl (0.24 mol/L), (B) water, (C) toluene, (D) dichloromethane and (E) THF for 0, 3, 9, 18, 36 and 72 h (expect HCl). The inserted were optical images of the sample before and after immersion. (F) The change of SiCDIOs' bandgap after being immersed in diverse solvents for different times. The bandgap of sample kept almost unchanged before and after being immersed in above solvents, demonstrating a good durability towards these solvents.

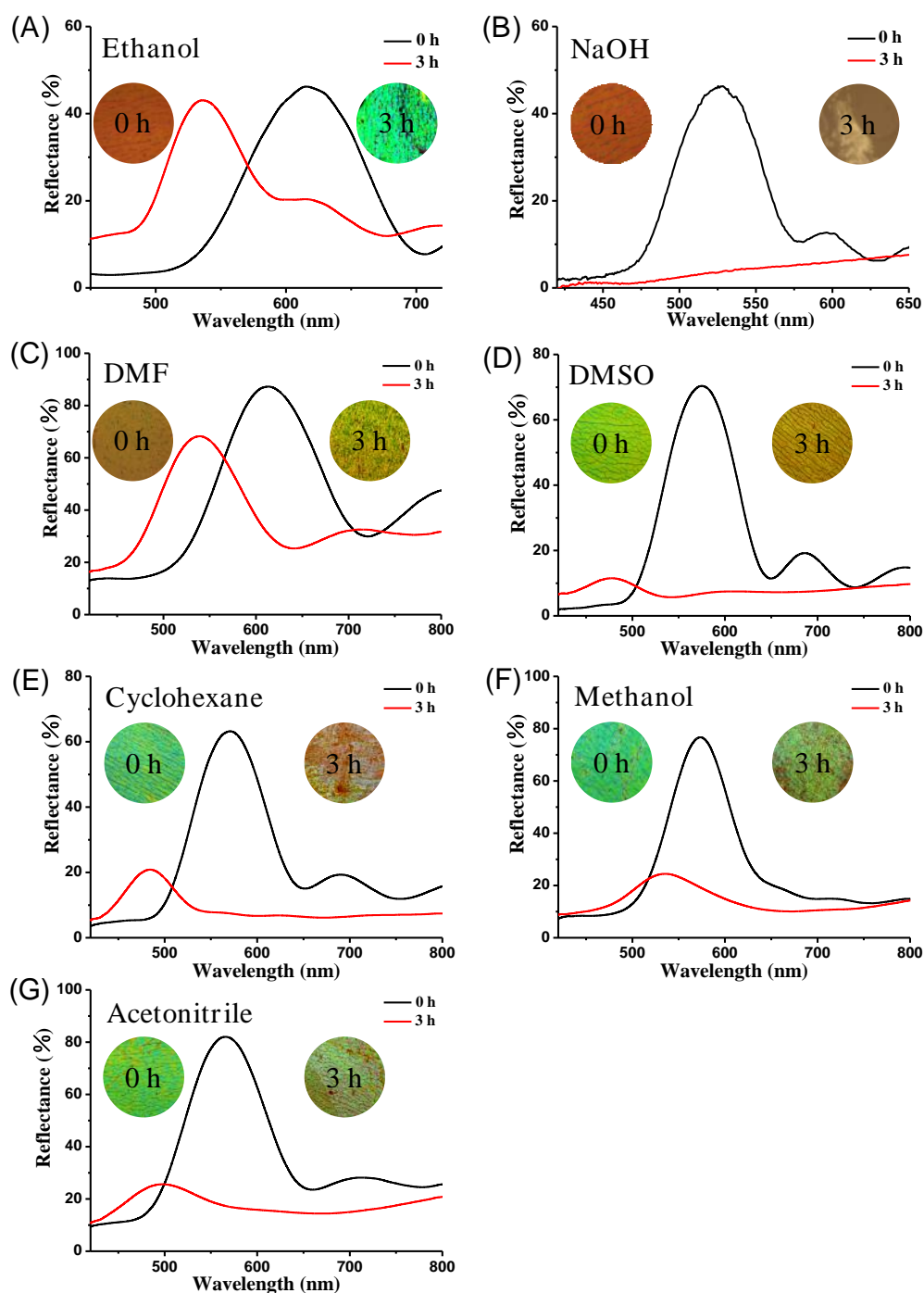


Figure S16. (A-G) Reflectance spectra of as-prepared SiCDIOs before and after being immersed in (A) ethanol, (B) NaOH (0.1 mol/L), (C) DMF, (D) DMSO, (E) cyclohexane, (F) methanol and (G) acetonitrile respectively for 3 h. The inserted are optical images of the sample before and after immersion.

Figure S15 and **16** presented the durability of as-prepared SiCDIOs after being immersed into different organic solvents, such as HCl (0.24 mol/L), water, THF, ethanol, NaOH (0.1 mol/L) and etc.¹ In details, the structure color of SiCDIOs kept almost green even being soaked in HCl for 36 h accompanied with little change of bandgap from 521 to 517, 519, 528 and 525 nm when being immersed for 3, 9, 18 and 36 h (Figure S15(A)). Notably, the reflectance intensity of the sample remained almost unchanged, which indicated a retention of favourable PC structure. Furthermore, the bandgaps of SiCDIOs keep almost unchanged when being immersed into different solvents such as HCl (0.24 mol/L), THF, toluene, water, and dichloromethane for some time. Typically, The bandgaps of SiCDIOs were 675, 673, 677, 667, 672 and 674 nm for being immersed in water; the bandgaps of the sample were 616, 623, 612, 618, 611 and 608 nm for being immersed into toluene; 583, 580, 583, 582, 584 and 591 nm for dichloromethane, and 646, 649, 638, 641, 644 and 645 nm for THF according to the time of 0, 3, 9, 18, 36 and 72 h, as shown in Figure S15(B-E). Similarly, no obvious transformation of bandgap and decrease of the reflectance intensity were observed after the sample being immersed in above solvents for 72 h. In contrast, the sample was easily destroyed by solvents such as ethanol, NaOH (0.1 mol/L) and etc, owing to a good solubility of SiCDs in ethanol and destructively property of alkali to SiO₂ in (Figure S16(A, B)). In details, The bandgap of SiCDIOs had a blueshift of 80, 75, 100, 85, 37 and 72 nm after being immersed in ethanol, DMF, DMSO, cyclohexane, methanol and acetonitrile respectively for 3 h. Especially, PC structure had been completely destroyed after being immersed in NaOH (0.1 mol) for 3 h.

¹ J. M. Zhou, H. L. Li, L. Ye, J. Liu, J. X. Wang, T. Zhao, L. Jiang and Y. L. Song, *J. Phys. Chem. C*, 2010, **114**, 22303-22308.