Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Writing chemical patterns using electrospun fibers as nanoscale inkpots for directed assembly of colloidal nanocrystals

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Synthesis of Silver Nanocubes

Chemicals: Ethylene glycol (anhydrous 99.8%, EG), silver trifluoroacetate (CF_3COOAg), polyvinylpyrrolidone (MW: 360,000), hydrochloric acid 37% (HCl), sodium hydrosulfide (NaHS), were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Silver nanocubes were synthesized by a modified polyol method,[1] briefly 15 mL of EG was added to a 100 mL round-bottomed flask, the flask was closed and then it was heated in a silicon oil bath at 150℃. The reaction solution was continuously stirred using a magnetic stir bar. After 10 min, 180 μL of 3mM NaHS solution in EG was added. After 2 minutes, 500 μL of 3 mM HCl solution in EG and 3.8 mL of 20 mg/mL poly(vinyl pyrrolidone) were added. Finally after 3 min, 1.2 mL of 282 mM CF_3COOAg solution in EG was added. After 60 min, the reaction was stopped by placing the reaction flask in an ice-water bath. Resultant Ag nanocubes were purified by centrifugation (8000g, 20min) in order to remove the EG and the excess of poly(vinyl pyrrolidone), and further redispersed in water before sample characterization.

Preparation of Titanium Dioxide NCs

15 nm sized rutile-TiO_2 NCs (15%) in water were purchased from Nanostructured & Amorphous Materials, Inc. Company. TiO_2 NCs were centrifuged without adding any chemicals at 5000 rpm for 5 min to separate agglomerations and supernatant was filtered by using 0.20 μm sized PVDF filter. Filtered NCs were directly used.

Synthesis of Nanoplatelets

Chemicals: All chemicals were purchased from Sigma Aldrich as follows: Zinc acetate (99.99%), cadmium oxide (CdO, 99.99%), zinc acetate dihydrate (99.999%), cadmium acetate (anhydrous, 99.995%), 1-dodecanethiol (DDT, 98%) 1-octadecene (ODE, 90%), trioctylphosphine (TOP, 90% technical grade), oleic acid (OA, 90%), 1-octanethiol (≥98.5%), oleylamine (OLA, 70%), sodium myristate (≥99.0%), cadmium nitrate tetrahydrate (≥99.0%), selenium (99.99%), sulfur (99.998%), Mercaptosuccinic acid (97.0%), toluene (≥99.5%), n-hexane (≥97.0%), methanol (≥99.7%), ethanol (99.8%, absolute).

Preparation of the Cd-myristate: Cd-myristate was prepared according to the literature.[2,3]

Synthesis of 4 ML thick CdSe core NPLs:

The synthesis of CdSe core NPLs was carried out by using a synthesis protocol outlined in the literature[2,3] with some modifications. Octadecene (30 mL), cadmium myristate (340 mg), and selenium (20 mg) were loaded in 100 mL of three-necked flask and heated to 95 ˚C under vacuum for 75 min. Then, the flask was heated to 240 ˚C under argon gas. 100 mg of cadmium acetate was quickly added at 195 ˚C into the solution and the solution was kept at 240 ˚C for 9 min. Before cooling, 1 mL of OA was injected into the solution and then the temperature of the flask was cooled down quickly with cold water. As synthesized NCs were cleaned two times with ethanol and 4 ML thick CdSe core NPLs were dispersed in hexane.

Synthesis of CdSe/CdZnS core/shell NPLs:

CdSe/CdZnS core/shell NPLs were synthesized by using our recently published hot injection shell growth synthesis recipe with some modifications.[3] Zn-acetate (0.17 mmol), Cd-acetate (0.03 mmol), oleic acid (0.5 mL), 1-octadecene (5 mL) and predefined amount of 2-times cleaned CdSe core NPLs in hexane (the amount has been determined according to the absorbance value) were loaded in 4-necked flask. Reaction flask was degassed to remove solvent and other impurities. The solution was kept under mild stirring at room temperature for 60 min. Then, the temperature of the solution was increased to 85 ^{o}C and kept for 60 min at this temperature. After this time, the degassing was completed and the system temperature was increased to 300 ^{o}C under argon gas flow. At 90 ^{o}C, oleylamine (0.5 mL) was injected into the flask and the injection of 1 octanethiol-ODE mixture (70 µL of 1-octanethiol-4 mL of ODE) was initiated at 160 ^{o}C with 10 mL/h injection rate of syringe-pump keeping the temperature rise up to 235 ^{o}C. Then, the injection rate was decreased to 4 mL/h and the solution was kept at 300 °C for 60 min. The reaction was completed and the temperature of the solution was cooled down to room temperature by using cold-water. At 50 °C, 5 mL of hexane was injected and the solution was precipitated 2 times by excess amount of ethanol and then re-dispersed in hexane.

Ligand exchange recipe for NPLs:

60 mg of 11-Mercaptoundecanoic acid and 50 mg of KOH were sonicated 3 minutes and dissolved in 4 mL of methanol. Then, this solution was poured into 4 mL of dilute solution of synthesized CdSe/CdZnS core/shell NPLs in hexane. NPL containing solution was stirred overnight at room temperature to effectively provide ligand exchange from organic phase to water phase. Hexane accumulated on the upper side of the tube was discarded by pipette and the remaining part of solution was centrifuged at 10000 rpm to extract excess amount of precursor from the solution. After centrifugation, precipitated ligand exchanged NPLs were dissolved in 0.1 M KOH in DI water.

CdSe/ZnS Core/Shell Quantum Dots Synthesis

Red-emitting CdSe/ZnS core/shell QDs were synthesized by modifying previously reported synthesis recipe.[4,5] Oleic acid (5 mL), Zn-acetate diyhdrate (1.68 mmol) and CdO (1 mmol) chemicals were mixed within a 4-necked flask equipped with a magnetic stirrer. The flask was heated to 140 °C and kept for 45 min at this temperature under vacuum. After, the flask was cooled to 50- 60 °C, 25 mL octadecene was injected into the solution under Ar gas flow. After ODE was introduced, the temperature of the solution was increased to 90 °C under vacuum, and then heated to 300 °C under Ar-gas flow. The prepared TOP-Se precursor (1M and 0.2 mL), was quickly injected into the flask while being stirred and kept at this temperature for 80 s. After slow addition of 1-dodecanethiol (300 μL) into the solution, the system was kept at 300 °C for 20 min. To finalize the reaction, TOP-S (2M, 1 mL) was injected into the system and kept for 10 min. Finally, the solution was cooled down to room temperature using water bath. 5 mL hexane was added at 50 °C into the flask and the solution was centrifuged at 5000 rpm. The precipitate was discarded and supernatant was precipitated with 5000 rpm for 10 min by adding ethanol. Finally, the precipitate was dispersed in hexane.

Ligand Exchange Procedure from Organic to Water Phase

Phase transfer from organic phase to water phase has been carried out by using ligand-exchange protocol which is a modified recipe from the literature[6] by using 3-mercaptosuccinic acid (MSA) as follows:

The CdSe/ZnS QDs samples were cleaned successively with excess acetone and methanol. Cleaned QDs were dispersed in 10 mL of fresh hexane and the concentration of the sample was set to 30 mg/mL. 40 mL of DI water and 15 mL of NH_4OH solution were mixed with CdSe/ZnS QDs followed by stirring the solution at room temperature for 3 hours. This is followed by the addition of 750 mg of MSA to the mixture and the solution was kept overnight to enable effective ligand-exchange with MSA on the surface of the NCs. Then, the solution was precipitated and cleaned with ethanol as 4:1 v:v (ethanol: mixture). The precipitate was dissolved in DI-water and used for the immobilization.

Characterization

Photoluminescence and absorption characterizations of the QDs were performed by using Cary Eclipse fluorescence spectrophotometer and UV-Visible spectrophotometer of Shimadzu 1800 and Thermo Genesys 10S spectrometer, respectively. Scanning electron microscopy images were taken FEI Nova NanoLab 600i SEM/FIB device. Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) data were collected by using Tecnai G2 F30 at 300 kV. QY of the samples was determined by using absolute QY measurement system. The methodology of QY measurements can be found in Mello et al.[7] The system is composed of a spectrometer (Ocean Optics Maya 2000), an integrating sphere (Hamamatsu) and a monochromator integrated Xenon lamp. The excitation wavelength was set to 400 nm for these measurements.

Table S1: Optical properties of synthesized CdSe/CdZnS core/HI shell NPLs before and after ligand-exchange.

	Peak emission Wavelength (nm)	**FWHM (nm)**	**PLQY (%)**	**first excitonic peak (nm)**	**2nd excitonic peak (nm)**
Before exchange in hexane	637.0	21.76	91	630.2	571.2
After exchange in water	637.8	21.75	89	630.3	571.9

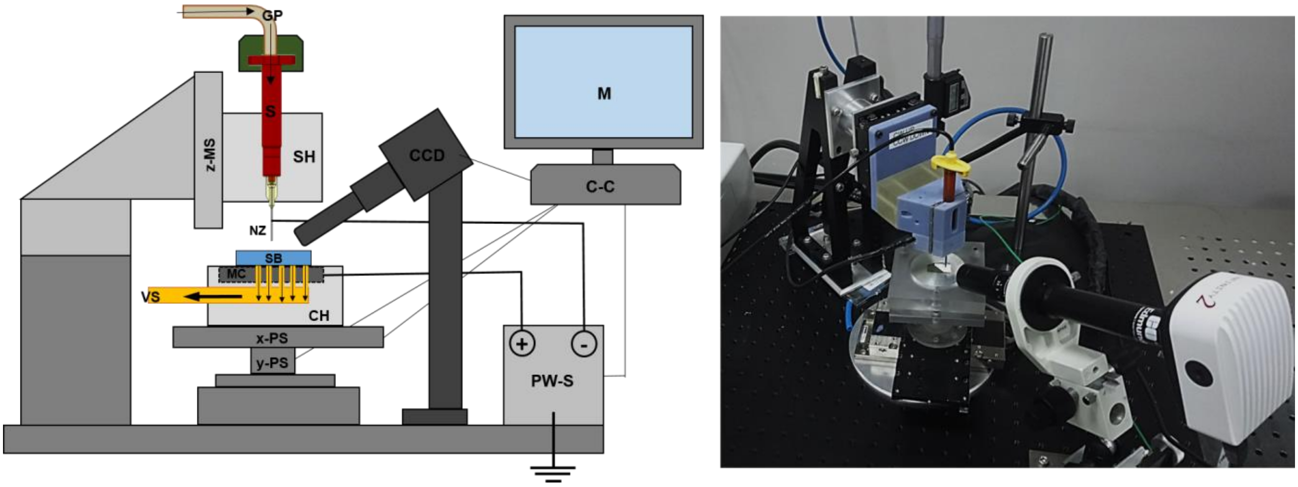

Fig. S1 Schematic (left) and photograph (right) of the setup for the near field electrospinning. PW-S: power source (0-1500 V), y-PS: magnetic stage working in y axis, x-PS: magnetic stage working in x axis, z-MS: manual stage for controlling working distance in z axis, MC: metallic collector integrated in flexi glass block, CH: flexi glass block for holding metal collector, SB: working substrate, VS: vacuum suction system to prevent movement of the substrate, NZ: 30G blunt end needle, S: syringe that contains polymer ink, SH: syringe holder, GP: controllable gas pressure system for feeding ink to needle, CCD: CCD camera for imaging writing process, C-C: computer integrated control system for controlling piezo stages and power source, M: monitor.

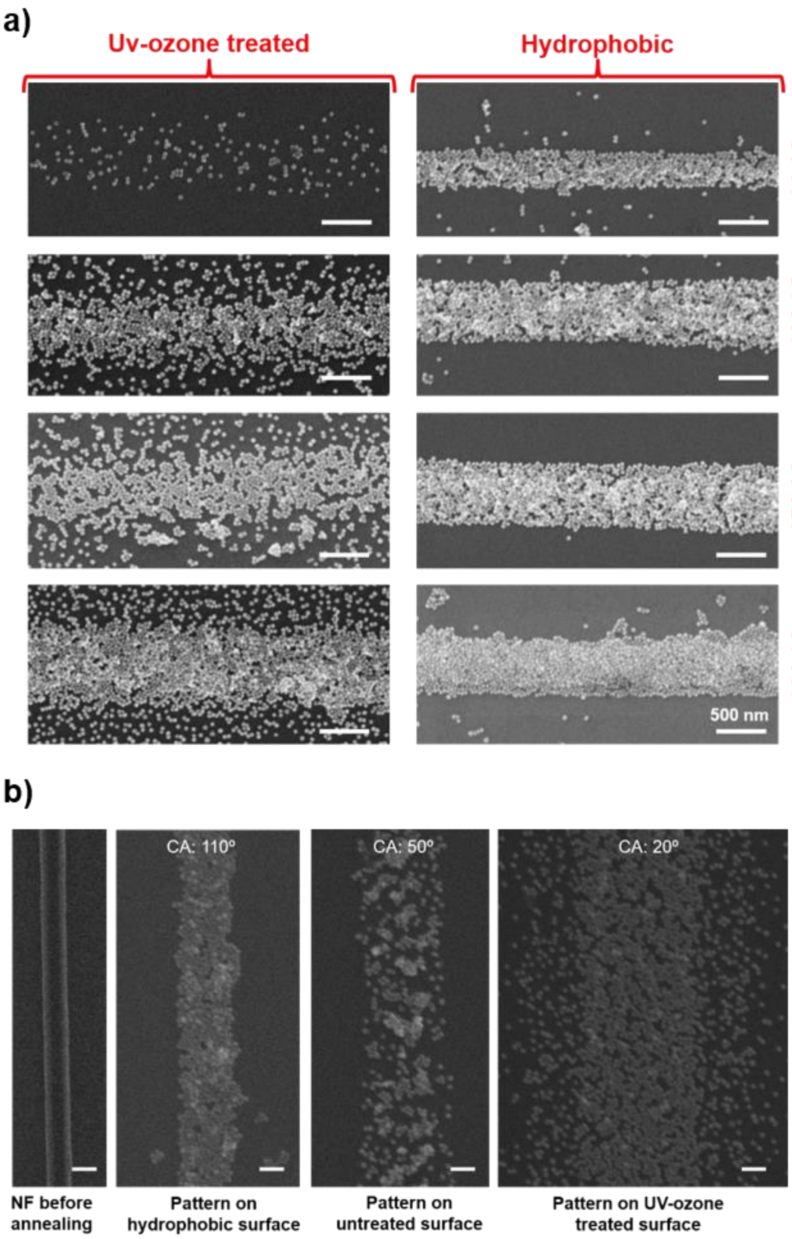

Fig. S2 SEM images of the patterned PEG nanoribbons following immobilization of 40 nm Au NCs. a) UV-ozone treated (left column) and hydrophobized (right column) substrate prepared at different grafting temperatures. Scale bar is 500 nm. b) from left to right: PEO NF inkpot before annealing, and patterns fabricated from the NF on hydrophobic, untreated (bare) and UV-ozone cleaned substrates, respectively. The contact angles of the substrates are given at the top of the images. Scale bar is 200 nm.

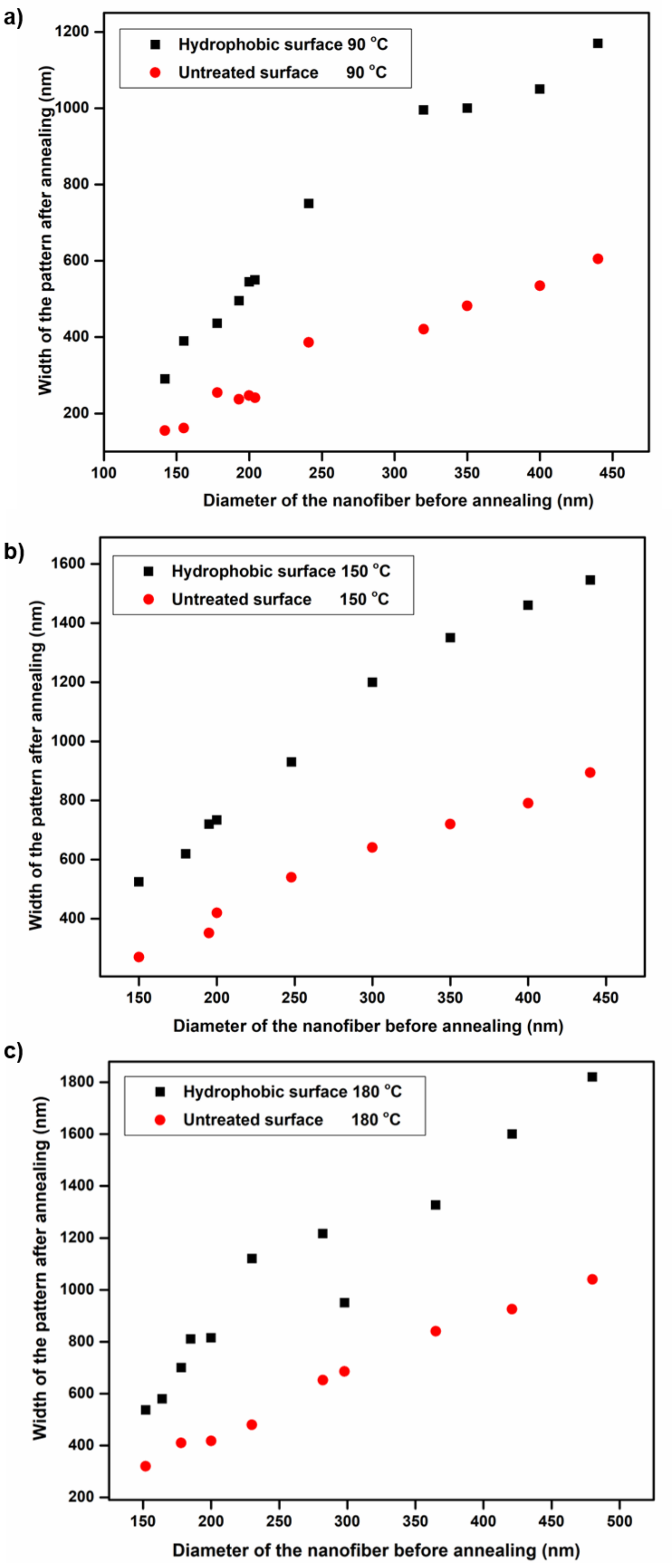

Fig. S3 Variation of the width of the patterns as a function of the diameter of the NF prepared at grafting temperatures of a) 90 ºC, b) 150 ºC, c) 180 ºC.

Table S2: The ratio of spreading and suppressing efficiency as a function of the annealing temperature.

Temp. (°C)	**Spreading Ratio ($d_{\text{pattern witdh on bare}}$/ d_{NF})**	**Spreading Ratio ($d_{\text{pattern witdh on FAS}}$ / d_{NF})**	**Suppression Ratio ($d_{\text{pattern witdh on bare}}$) / ($d_{\text{pattern witdh on FAS}}$ /)**
90	2.701 ± 0.301	1.293 ± 0.160	2.077 ± 0.219
120	2.905 ± 0.296	1.468 ± 0.169	2.001 ± 0.155
150	3.675 ± 0.178	2.011 ± 0.143	1.848 ± 0.113
180	3.764 ± 0.688	2.373 ± 0.535	1.653 ± 0.462

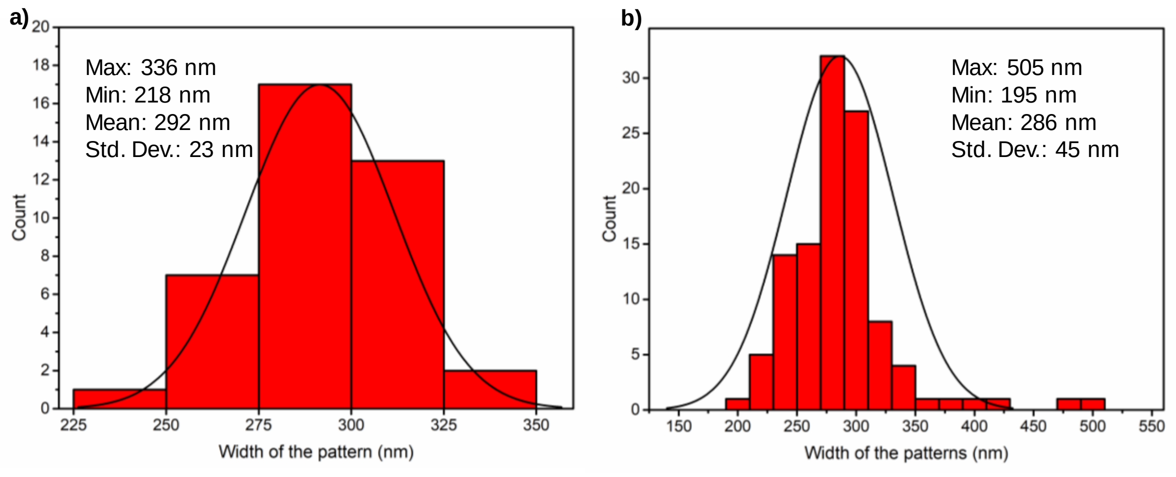

Fig. S4 The width distribution of the patterns fabricated using a NF inkpot with a diameter of ~200 nm at a grafting temperature of 120 °C. The images were taken following immobilization of 40 nm Au NCs on patterns consisting of end-grafted PEG layer. a) Analysis of a single linear pattern. 40 SEM images (50,000 × magnification) were taken along a single linear feature with a length of ~1 cm. The locations of SEM images were randomly chosen with a distance of ~250 µm. a) Analysis of an array of lines. SEM images (50000 × magnification) were taken from 50 different lines.

Surface-enhanced Raman spectroscopy (SERS) measurements on the patterns

SERS measurements were performed with a Witec alpha300 M+ model Raman spectrophotometer (Germany) equipped with a laser at a wavelength of 532 nm. Methylene Blue (Sigma-Aldrich) was dissolved in ethanol at a concentration of 10 µM. A drop with a volume of 3 µL was then deposited on the patterns generated on a Si substrate. Raman scattering measurements were performed after drying of the solvent using 50× objective with a spot size of 1 µm and an integration time of 0.05 s. The Raman spectra and intensities were obtained from Raman mappings over an area of 250 × 150 μm^2 (Fig. S5) with a step size of 0.5 µm.

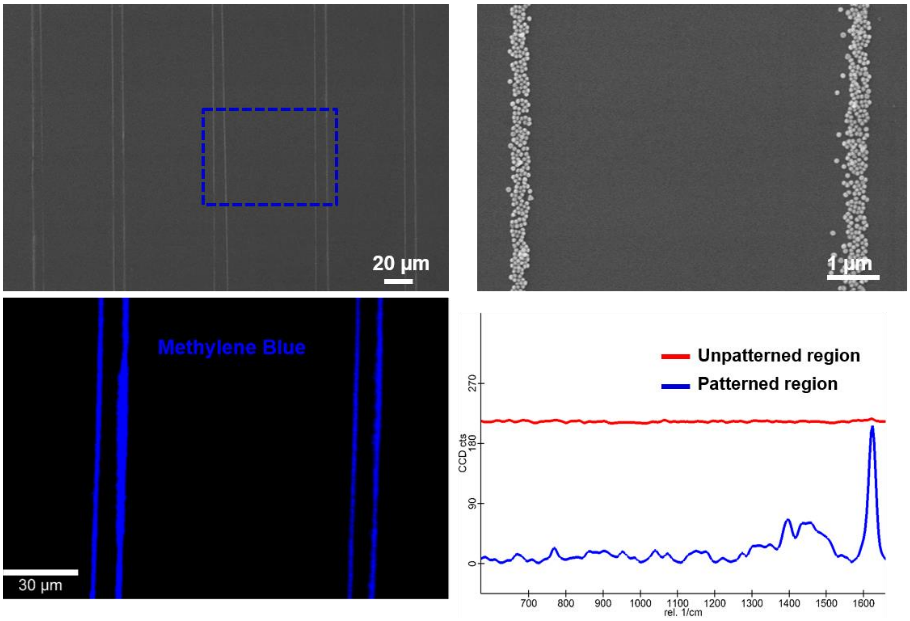

Fig. S5 Demonstration of SERS application on chemical nanopatterns with the immobilized Au NCs (80 nm). The top row shows the SEM images of the arrays of Au NCs. The bottom row shows the Raman mapping image and spectra obtained from the patterns and background regions.

Adhesive Tape Test

To test the adhesion strength of Au NCs assembled on nanopatterned PEG layers, we performed an adhesive tape test on hydrophilic and hydrophobic substrates. Highly adhesive carbon tape (Nisshin EM) was applied on the surface by ensuring full contact and then peeled off. This process was repeated 10 times. SEM images were taken from the same regions before and after the test (Fig. S6)

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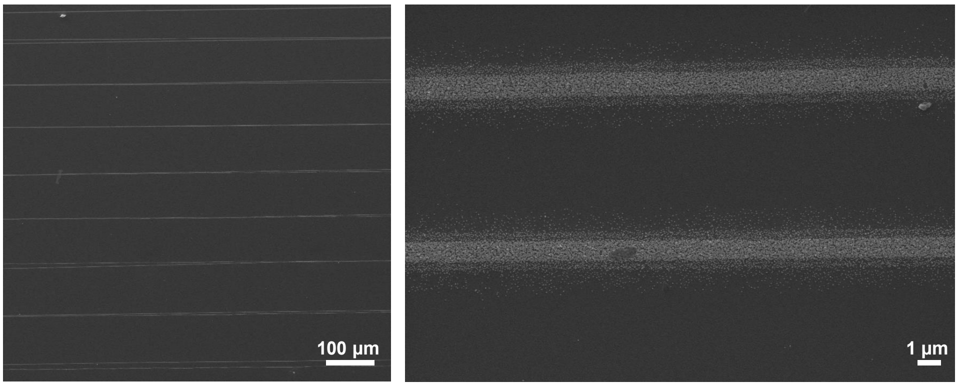
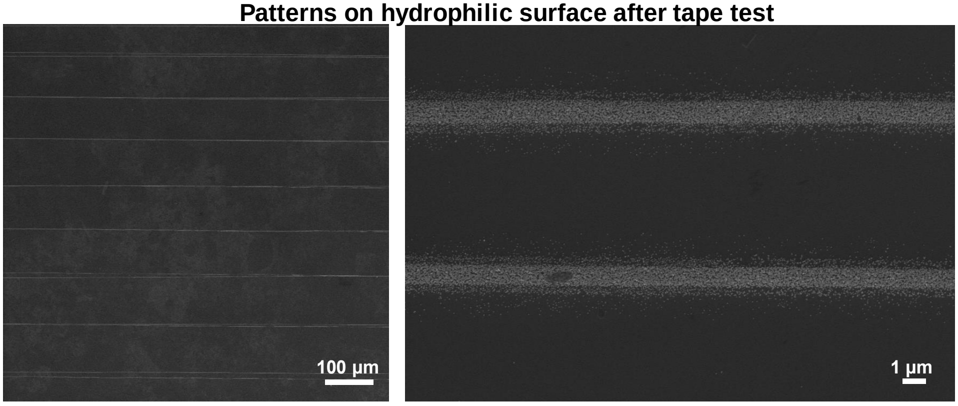
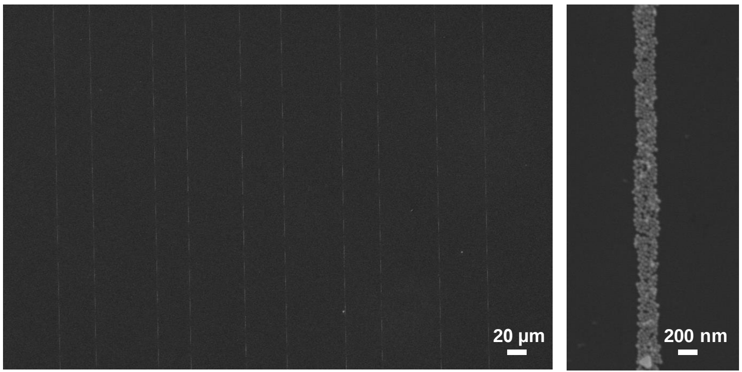
Patterns on hydrophilic surface before tape test



Patterns on hydrophilic surface after tape test



Patterns on hydrophobic surface before tape test



Patterns on hydrophobic surface after tape test

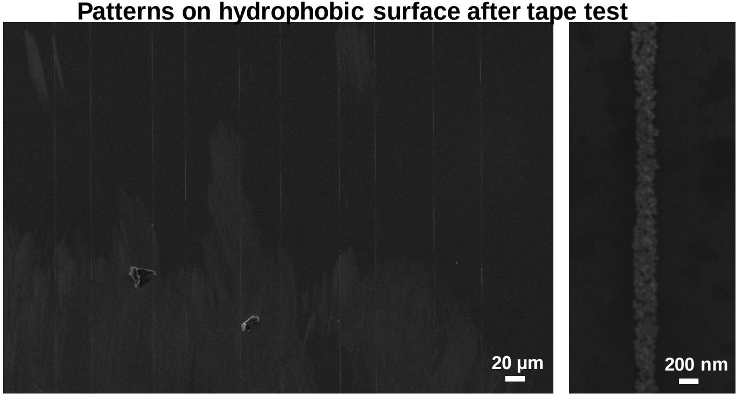


Fig. S6 SEM images of patterns on hydrophilic and hydrophobic substrates before and after the adhesive tape test.

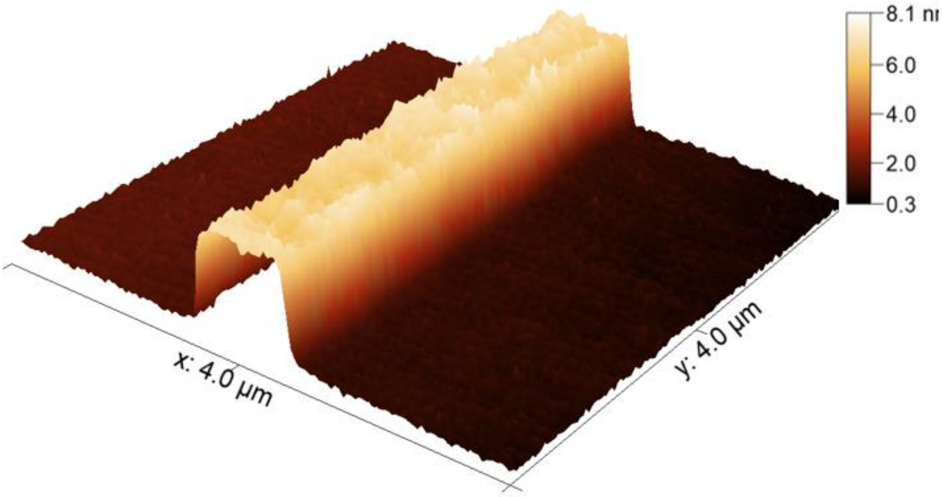


Fig. S7 AFM image of a nanoribbon consisting of end-grafted P2VP.

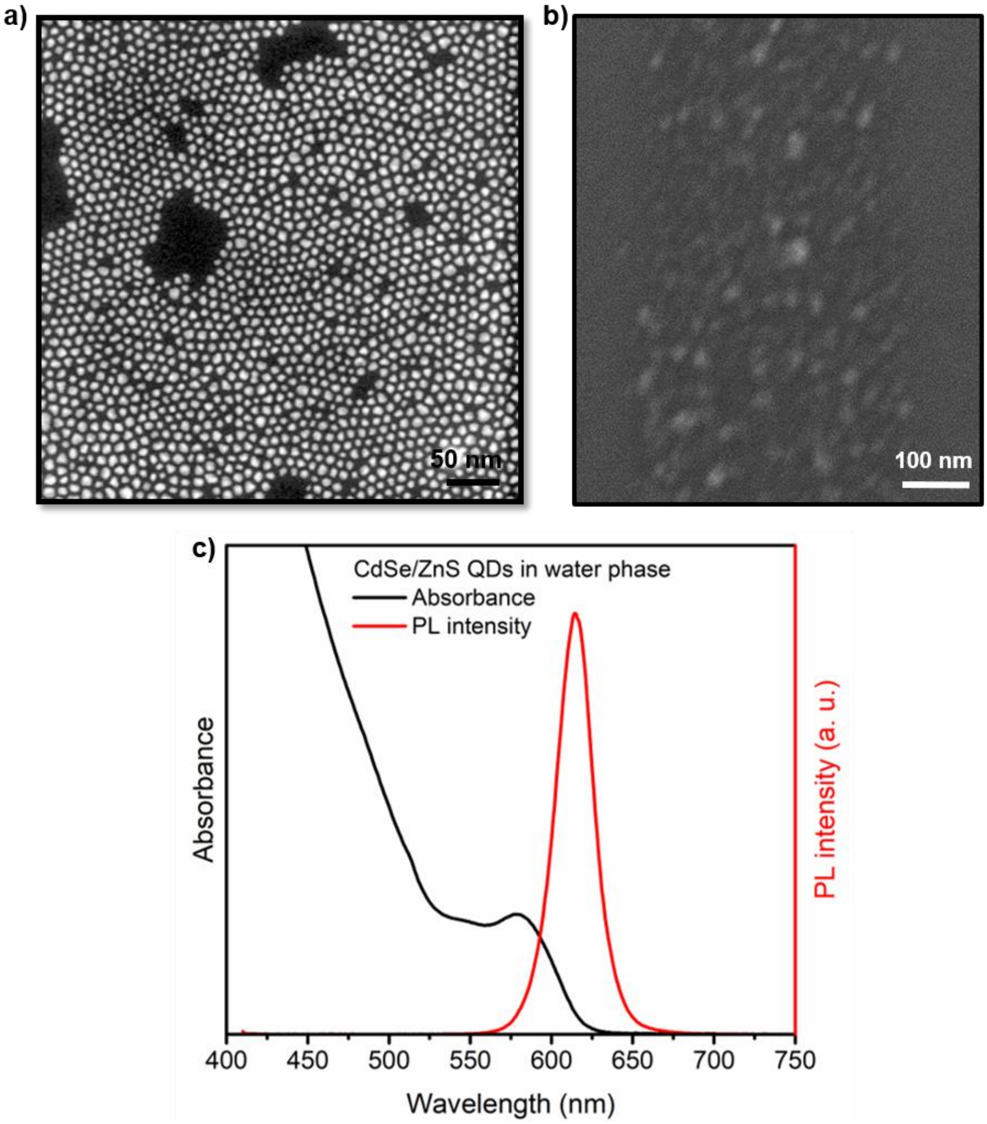


Fig. S8 CdSe/ZnS QDs. a) HAADF-STEM image of the CdSe/ZnS QDs, b) SEM image of a P2VP nanoribbon with immobilized CdSe/ZnS QDs, c) photoluminescence and absorption spectra of CdSe/ZnS QDs in water phase.

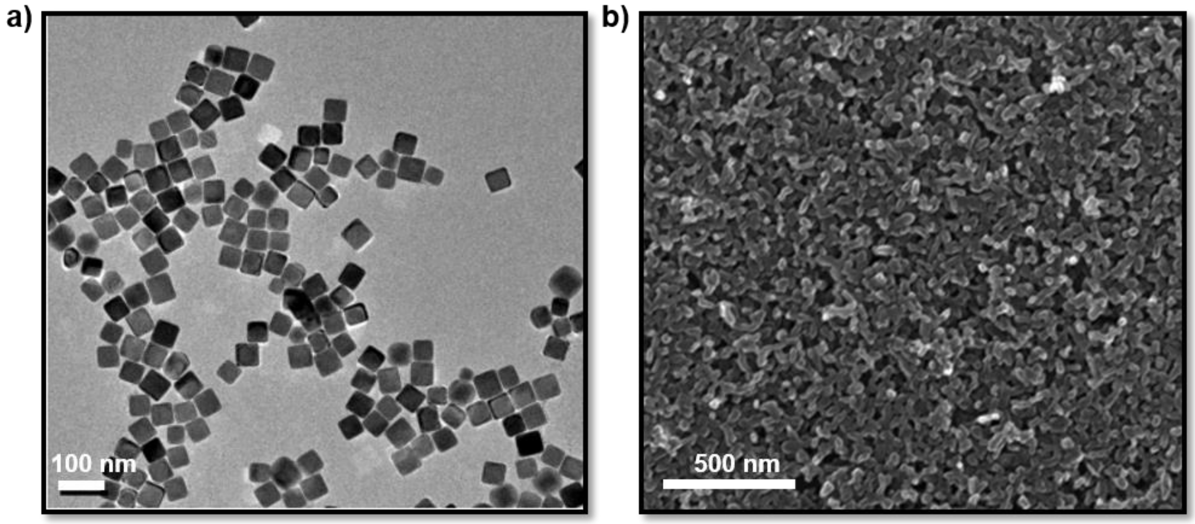


Fig. S9 a) TEM image of silver nanocubes, b) FIB image of TiO_2 nanoparticles.

References

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