Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

A facile fabrication of conjugated fluorescent nanoparticles and micro-scale patterned encryption via high resolution ink-jet printing

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1. Measurement of fluorescence quantum yield

The fluorescence quantum yields were measured by a spectrometer connected with an integration sphere (Fluoro Max-4, Quanta-Φ). The excitation light was 380 nm, and 5 mg/mL SDS solution was used as a blank sample. According to the formula, Quantum yield (QY)=Number of emitted fluorescence quantum/Number of absorbed light quantum. Here QY=Ea-Ec/Lc-La. La is the integrated area of the excitation spectrum of the samples; Lc is the integrated area of the excitation spectrum of the blank sample; Ea is the integrated area of the emission spectrum of the samples; Ec is the integrated area of the emission spectrum of the blank sample. For S1 (PFO), S2-S8, and F8BT, the fluorescence quantum yields of these samples were measured to be 0.38, 0.39, 0.31, 0.30, 0.40, 0.31, 0.33, 0.30, 0.11, respectively. And the results are shown in Table 1. This is similar to the quantum yield of conjugated polymer dots reported in the previous literature（Small 2014, 10(21), 4270－4275）._

Table 1 The fluorescence quantum yields of S1 (PFO), S2-S8, and F8BT

Sample	Excitation Wavelength: 380 nm		Emission Wavelength/nm		Area				QY
	Start Wavelength	End Wavelength	Start Wavelength	End Wavelength	La	Lc	Ea	Ec	
S1	375	385	410	660	298214.82	973644.84	287174.56	29830.49	0.38
S2	375	385	410	660	281621.7	850604.17	250226.31	26904.83	0.39
S3	375	385	410	660	224902.63	850604.17	222654.1	27499.45	0.31
S4	375	385	410	660	235002.55	850604.17	212203.36	26904.83	0.3
S5	375	385	410	660	376986.05	973644.84	267799.07	29830.49	0.40
S6	375	385	410	660	214102.49	850604.17	227644.24	27499.45	0.31
S7	375	385	410	660	286870.38	973644.84	258922.98	29830.49	0.33
S8	375	385	410	660	427403.68	973644.84	195674.68	29830.49	0.30
F8BT	445	455	550	650	207691.21	775255.08	58915.49	-5019.25	0.11

2. Characterization of fluorescent printing ink viscosity and surface tension

We use the parameters of sample S5 as the parameters of the fluorescent printing ink. We used a digital viscometer (NDJ-9S) and a surface tensiometers (MDTC-EQ-M08-01 KRUSS) to measure the fluorescent particle microemulsion, and its viscosity and surface tension were 0.96 mpa·s and 36.42 mN/m, respectively. The viscosity of the ink affects its flow in the cartridge and the shape of the droplets after passing through the nozzle. High viscosity ink may cause nozzle clogging. The low-viscosity ink may cause damped oscillations in the jet, resulting in inhomogeneous droplet size. We adjust the emulsion parameters and choose to add polyethylene glycol which is colorless, soluble in water, and highly viscous. The viscosity coefficient of polyethylene glycol is 86.52 mpa·s at room temperature. Polyethylene glycol and fluorescent particle emulsion are evenly mixed in volume ratios of 3/5, 4/5, 1/1, 9/8, and 5/4. The viscosities of the five samples are 1.07 mpa·s, 2.04 mpa·s, 10.20 mpa·s, 12.24 mpa·s, and 14.22 mpa·s measured with a digital viscometer, as shown in Figure 1a. The surface tensions of the five samples are 40.33 mN/m, 42.79 mN/m, 44.96 mN/m, 46.94 mN/m, and 47.33 mN/m measured with a surface tension meter, as shown in Figure 1b. The ink meets the requirements of precision electronic circuit printers and can realize pattern printing. When the volume ratio of polyethylene glycol to fluorescent particle emulsion is 1/1, the viscosity coefficient is 10.20 mpa·s, and the surface tension is 44.96 mN/m, the reciprocal of the Ohnesorge number, Z is calculated to be 3.67, which meets the requirements of inkjet printers for stable printing.

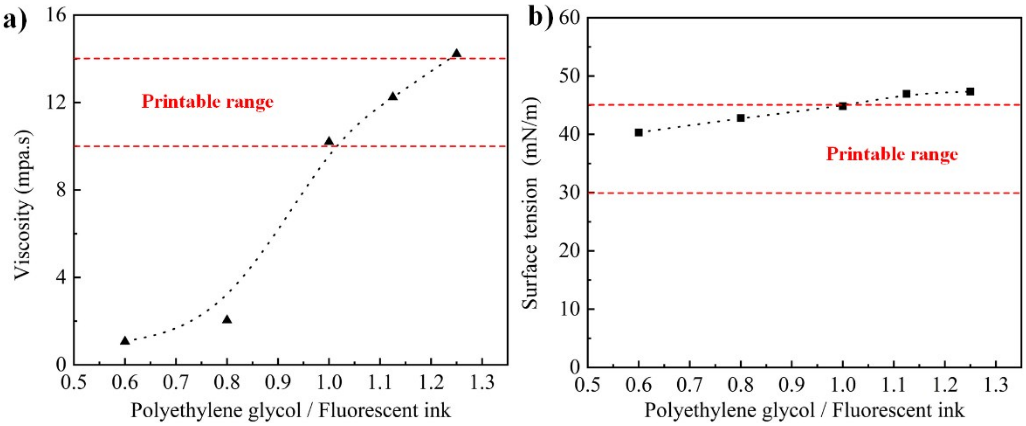

Figure 1 a) The relationship between the ratio and viscosity of printing ink. b) The relationship between the ratio and surface tension of printing ink

3. Stability analysis of fluorescent printing ink

We must consider the stability of the ink during the printing experiment to ensure that the ink will not cause sedimentation, delamination and other problems when placed in the ink cartridge for a long time. We test the particle size change of the fluorescent printing ink over a period of time with a nano particle size and zeta potential analyzer. Set the test interval to two days, as shown in Figure 2. From the figure, we can see that there is almost no change in particle size within 9 days. The prepared ink sample system should be stable without problems such as sedimentation and delamination. It has the potential to be extended to practical applications.

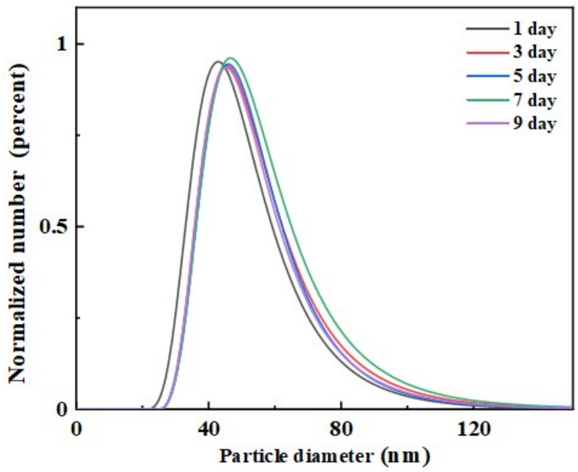

Figure 2 Change of ink particle size

4. Fluorescence spectrum analysis of fluorescent printing ink

We respectively detect the fluorescence spectra of polyethylene glycol, PS@PFO@F8BT fluorescent particle emulsion and fluorescent printing ink, as shown in Figure 3. The figure shows that polyethylene glycol has no fluorescence. The fluorescence intensity of fluorescent printing ink is decreased compared to PS@PFO@F8BT fluorescent nanoparticle emulsion, and the trend of fluorescence spectrum is almost unchanged. Polyethylene glycol did not change the fluorescent properties of the ink.

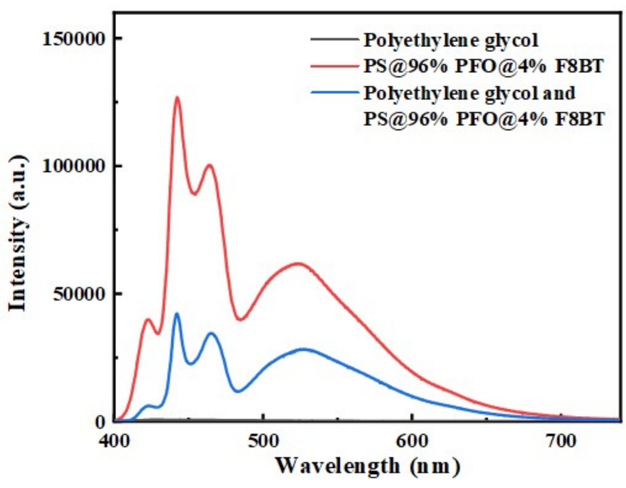

Figure 3 Contrast of fluorescence spectra between print ink and fluorescent particle emulsion

5. Anti-counterfeiting and Ultra-micro printing

We can not only increase the number of QR code grids to 37*37 to increase the amount of information storage, as shown in Figure 4a. Moreover, it is also possible to add a logo picture in the center of the QR code without affecting the recognition of the QR code to further enhance its information encryption and anti-counterfeiting functions, as shown in Figure 4b. In addition, we can also use precision printers to achieve ultra-micro printing of different fonts, as shown in Figure 4c for the ultra-micro printing of three fonts. Through the upright microscope and ultraviolet light source, it can be observed that the minimum character height of ultra-micro printing is 0.6 mm, and each letter is composed of ink dots, as shown in Figure 4c.

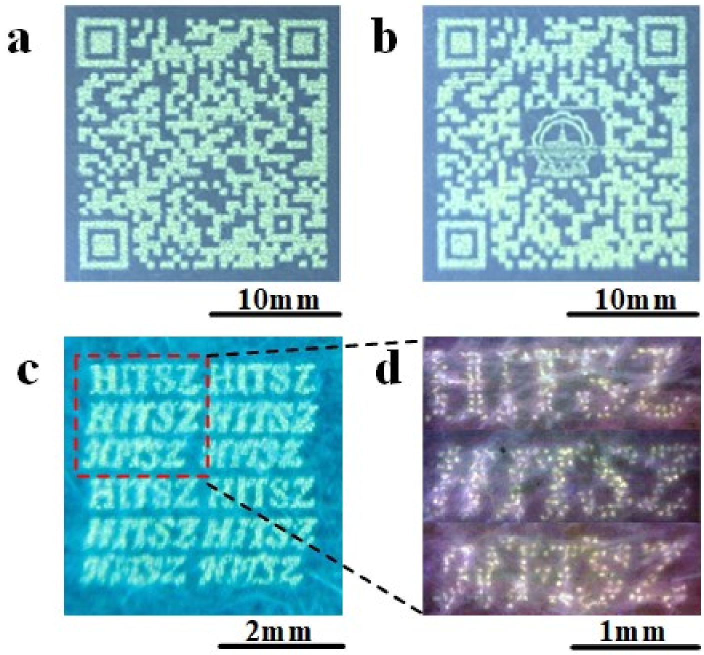

Figure 4 a) QR code with a grid number of 37*37; b) QR code with logo picture; c) the ultra-micro printing of three fonts; d) the ultra-micro printed characters in an upright microscope and ultraviolet light source

6. Weather resistance of QR code

We believe that invisible QR codes need to be recognized in actual applications for two months or more. We use a smartphone to recognize the QR code and use a stopwatch to record the time. As shown in Figure 5, when the storage time is from one month to twelve months, the average recognition time of each group of data gradually increases from 1.57 s to 2.45 s. The printed QR code can still be recognized within 2.5 s after one year.

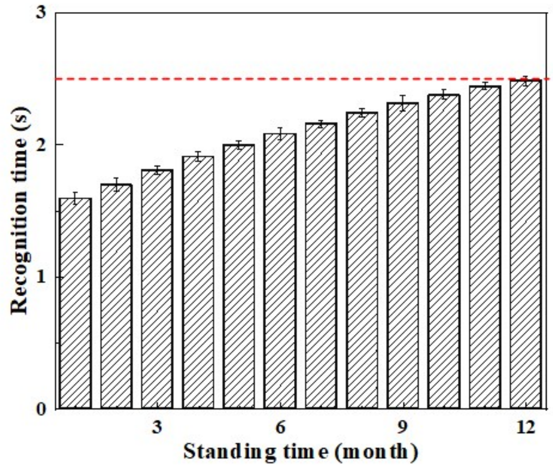

Figure 5 The change of QR code recognition time increases with the placing time