Invisible photonic printing: computer designing graphics, UV printing and shown by a magnetic field

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Invisible photonic printing, an emerging printing technique, is particularly useful for steganography and watermarking for anti-counterfeiting purposes. However, many challenges exist in order to realize this technique. Herein, we describe a novel photonic printing strategy targeting to overcome these challenges and realize fast and convenient fabrication of invisible photonic prints with good tenability and reproducibility. With this novel photonic printing technique, a variety of graphics with brilliant colors can be perfectly hidden in a soft and waterproof photonic-paper. The showing and hiding of the latent photonic prints are instantaneous with magnet as the only required instrument. In addition, this strategy has excellent practicality and allows end-user control of the structural design utilizing simple software on a PC.

Recently, photonic printing technique based on fabrication and manipulation of photonic structures has received increasing attention across science and engineering disciplines because of its applications in photonic circuits1, on-chip photonic devices2,3, reflective display units4–7, outdoor signage and photonic sensors8–14. Various photonic printing strategies have been extensively investigated in order to realize the fast and convenient preparation of photonic prints with good tenability and reproducibility. Successful strategies include the self-assembly of colloidal crystals locally on a substrate15–18, and the change of photonic structure by tuning the refractive index (n), lattice spacing (d), and crystal orientation (h) in a specific region of the pre-made colloidal crystals or related composite materials19–28. Invisible photonic printing, an emerging photonic printing technique with tremendous advantages, is especially useful for steganography and watermarking for anti-counterfeiting purposes. However, it is still not easy to realize because of the many great challenges29. First, the mostly reported visible photonic printing creates photonic prints with a permanent contrast of reflection wavelength (Δλ≠0), while the invisible photonic printing requires the photonic prints with an initial zero contrast (Δλ = 0) and later a non-zero contrast (Δλ≠0) when the latent information is revealed. However, a large amount of responsive content on the print is required in order to obtain a large contrast under external stimuli. Consequently, this will lead to a large deviation from invisibility due to the gradually increased mismatch of refractive index or lattice constant30. Secondly, the obtained latent prints must have long-lasting stability, excellent reversibility and the ability of being quickly released with a convenient and non-toxic means such as heating or magnetic field.

Recently, we have been engaged in ongoing efforts aimed at the development of novel photonic materials with special functions28,31,32. For example, we reported the fabrication of a novel photonic wordpad from fast magnetically induced self-assembly of superparamagnetic colloids, which is fixed inside a polyacrylamide glycol gel matrix through an instant radical polymerization28. Herein, we demonstrate a novel photonic printing strategy targeting to overcome the above challenges and realize fast and convenient fabrication of invisible photonic prints with good tenability and reproducibility. A variety of graphics with brilliant colors can be perfectly hidden in a soft and waterproof photonic-paper (P-paper) utilizing this novel technique. When the functionalized P-paper is put into a vertical magnetic field, only the prints with magnetic-responsive photonic activities are expected to be changed. The pre-hidden patterns will be revealed due to vastly different reflection wavelength contrast between the background and the print. From the perspective of practical printing technique, this strategy is of great interest due to its superior features, including the ability to (1) generate invisible patterns with magnetic showing effect, (2) obtain end-user control of structural design utilizing simple software on a PC, and (3) allow fast, convenient and scalable production at low-costs. Moreover, the adaptation of the P-paper for invisible photonic printing...
using common office laser printers would provide a new strategy for pattern-on-demand invisible photonic prints. This will find great applications in both scientific investigations and daily life, ranging from authentic identification systems to information storage medium.

**Results**

The fabrication strategy of the invisible photonic prints is outlined in Figure 1. Large-area, shape-controllable and low-cost P-paper (Figure 1a) was fabricated according to literature procedure. The P-paper is a three-phase material system consisting of carbon-encapsulated super-paramagnetic colloidal nanoparticles (CNPs), glycol and commercially available polydimethylsiloxane (PDMS) with physical and chemical stability. The pre-made carbon-encapsulated super-paramagnetic colloidal nanoparticles have magnetite/carbon core/shell structure with negatively charged groups (carboxyl) on the surface (Supporting information).

In a typical preparation process (Figure 2a), a certain amount of CNPs are dispersed in glycol solvent to form a homogeneous solution under ultrasonication, and subsequently mixed with PDMS precursor Part-A (Sylgard184 elastomer base) and PDMS precursor Part-B (Sylgard184 curing agent) using mechanical stirring. The viscous mixture was poured into a container with a specific shape (2.0 cm × 2.0 cm × 1 cm) and cured at 60 °C for 2 hours to produce a dark brown polymer matrix. It should be noted that the size of the P-paper only depends on the dimensions of the container and the amount of the liquid precursor. Therefore, fabrication of the P-paper on a larger scale is completely feasible with a larger container and more precursors. After the curing reaction, the glycol solution containing the CNPs can form very stable emulsion-like droplets at micron size throughout the solidified PDMS matrix (Figure 2a, 2b and Figure S7a, S7b). Without an applied external magnetic field, the CNPs in the glycol micro-droplets are randomly dispersed and display a brown color, which is the intrinsic color of the CNPs (Figure 1a). However, under an external magnetic field, the CNP networks in the UV-irradiated surface region will lead to the leakage of glycol solution. As such, the required liquid medium, in which the dynamic assembly of CNPs occurred, no longer existed. This ultimately led to the loss of the magnetic-responsive photonic activity of the P-paper. Therefore, the exposed regions will permanently lose the magnetic-responsive feature after UV-irradiation, while the shielded regions will remain the original dynamic nature.

The optical microscopy images (Figure 2c–2h) clearly demonstrate that the cross-section of the surface layer of the UV-irradiated region no longer produced a color change under the induction of a vertical magnetic field. In contrast, the shielded regions can still strongly diffract brilliant optical color and the magnetic-responsive photonic activity is maintained. These images clearly illustrate that UV-irradiation can effectively destroy the magnetic-responsive photonic activity of the exposed region. The SEM images demonstrate an obvious change between the irradiated region (Figure S8a, b) and the shielded region (Figure S8c, d). After UV-irradiation, the PDMS polymer matrix in the exposed region was clearly wrinkled and tended to rupture. However, the PDMS polymer matrix in the shielded region was relatively smooth with no obvious cracks. In addition, the SEM image (Figure 2d) reveals many holes in the UV-irradiated surface regions and the microstructures of the PDMS were dramatically different from those unexposed PDMS (Figure 2c). The P-paper after UV-irradiation was further characterized by Fourier transform infrared spectrum (FTIR) to obtain additional information on the chemical transformation. The FTIR spectra (Figure S9) of the surface layer of the P-paper with different UV-irradiation time clearly indicate a noticeable decrease in the –CH3 signals with increasing exposure time. Simultaneously, the shape of Si–O bond absorption peak was changed, indicating the structure transformation from CH3–Si–O– fragments to –O–Si–O– network.

All the above results are fully consistent with our hypothesis that UV-irradiation will induce chain scissions of the PDMS polymer chains and rupture of the PDMS networks. As a result, the glycol solution leaked out from the glycol micro-droplets. As such, the required liquid medium, in which the dynamic assembly of CNPs occurred, no longer existed. This ultimately led to the loss of the magnetic-responsive photonic activity of the exposed region of the P-paper. To further confirm our hypothesis, two control experiments were carried out. In the first control experiment, all the conditions are the same as above except 0.5 g PDMS was used. The liquid...
mixture will not be cured after curing at 60°C for 2 hours because it contains less PDMS. After 30 minutes UV-irradiation, the viscous mixture still underwent an instant color change under a vertical magnetic field (Figure S10). This shows that UV irradiation of PDMS will not generate any new chemicals to influence the dynamic assembly of CNPs in the glycol solution. In the second control experiment, a blank P-paper was completely covered by a common transparent slide and was UV-irradiated for 30 minutes. After the UV-irradiation, the P-paper still displayed brilliant color the same as that from the fresh P-paper (Figure S11). This indicates that the UV-irradiation-generated heat can not induce the loss of the magnetic-responsive photonic activity in the surface layer (Figure 2e–2h), and leads to a visible image (Figure 3c). This is an important finding and also the key to the work, because it provides an operable printing strategy that meets the requirements of reflection wavelength in hiding and showing mode, respectively. In addition, no new responsive content is introduced, and the change in surface morphology of the P-paper is negligible from a macro perspective. This results in a close to zero reflection wavelength contrast (Δλ) between the background and latent prints (Figure 4).

**Discussion**

To test the effectiveness of this novel invisible photonic printing strategy, various patterns were hidden in the P-paper (Figure 3). As shown in Figure 3b, these patterns were invisible at first due to the negligible reflection wavelength contrast (Δλ) between the background and latent prints (Figure 4). However, various brilliant patterns were visualized immediately when these printed P-papers were exposed to a vertical magnetic field (Figure 3c). The optical diffraction color depends on the average particle size of the CNPs included in the P-papers (Figure S1). In addition, the exchange between invisible-form and visible-form are highly reversible (schematic video-Supporting Information Available). This directly demonstrates the

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**Figure 2** | (a) Schematic illustration the fabrication route of the blank P-paper, (b) Schematic illustrations of the mechanism of preparing the invisible photonic prints, (c, d) Scanning-electron micrographs of P-paper, (c): unirradiated region; (d): irradiated region, (e-h) Obtained optical microscopy images of a cross-section of the printed P-paper under a vertically aligned external magnetic field. The depth of the destruction layer by UV-irradiation is approximately 350 μm deep.

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**Figure 3** | (a) Photographs of slides with printed-graphics designed on a computer, (b) Photographs of latent graphics on P-papers and (c) Photographs of graphics revealed by a magnetic field.
Synthesis of monodisperse carbon-encapsulated superparamagnetic colloidal nanoparticles with different average particle size. In a typical synthesis, ferrocene (0.30 g) was dissolved in acetone (30 ml). After intense sonication for 30 min, hydrogen peroxide (1.00, 1.50, and 2.00 ml) was slowly added into the above mixture solution, which then was vigorously stirred for 30 min with a magnetic stirring apparatus. After that, the precursor solution was transferred to the Teflon lined stainless autoclave with a total volume of 50.0 ml and then heated to and maintained at 210°C. After 72 h, the carbon-capped superparamagnetic colloidal nanoparticles were obtained respectively as shown in the Figure S1. Synthesized superparamagnetic colloidal nanoparticles were initially dispersed in acetone. Then the superparamagnetic colloidal nanoparticles were collected by magnetic separation, and re-dispersed in glycol solution (10 mg/ml) respectively for further use.

Fabrication of P-paper. According to previous report31, 0.5 ml above homogeneous sample solution containing the carbon-capped superparamagnetic colloidal nanoparticles was mixed with 2.0 g PDMS precursor Part-A (Sylgard184 elastomer base) and 0.4 g PDMS precursor Part-B (Sylgard184 curing agent) respectively. After intense mechanical agitation for 5 min, the viscous mixture (take 1 ml) was transferred to a cubic container (2.0 cm × 2.0 cm × 1 cm), crosslinked 2 hours at 60°C to get an approximately 2000 μm thick P-paper (Figure 2a).

Fabrication of invisible photonic prints. A two-step process was used to prepare the invisible photonic prints. First, graphics designed on a PC were printed on a transparent slide with common office laser printer. Then, as a photomask, the printed slides were sealed to the surface of the prepared P-paper under the UV-irradiation for 30 minutes and peeled off after the irradiation. The entire preparation process is illustrated in Figure 1. An NdFeB permanent magnet with center magnetic field 0.05 T was used to generate a magnetic field, which was attached to the back of the treated P-paper to reveal the latent photonic prints.

Methods

Synthesis of monodisperse carbon-encapsulated superparamagnetic colloidal nanoparticles with average particle size (a) 200 nm, (b) 140 nm and (c) 125 nm.

In a typical synthesis, ferrocene (0.30 g) was dissolved in acetone (30 ml). After intense sonication for 30 min, hydrogen peroxide (1.00, 1.50, and 2.00 ml) was slowly added into the above mixture solution, which then was vigorously stirred for 30 min with a magnetic stirring apparatus. After that, the precursor solution was transferred to the Teflon lined stainless autoclave with a total volume of 50.0 ml and then heated to and maintained at 210°C. After 72 h, the carbon-capped superparamagnetic colloidal nanoparticles were obtained respectively as shown in the Figure S1. Synthesized superparamagnetic colloidal nanoparticles were collected by magnetic separation, and re-dispersed in glycol solution (10 mg/ml) respectively for further use.

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1. Arsenault, A. et al. Towards the synthetic all-optical computer: science fiction or reality? J. Mater. Chem. 14, 781–794 (2004).
2. Ozin, G. A. & Yang, S. M. The race for the photonic chip: Colloidal crystal assembly in silicon wafers. Adv. Funct. Mater. 11, 95–104 (2001).
3. Ueno, K., Sakamoto, J., Takeoka, J., Takeoka, Y. & Watanabe, M. Electrochromism based on structural colour changes in a polyelectrolyte gel. J. Mater. Chem. 19, 4778–4783 (2009).
4. Ge, J. P., Hu, Y. X. & Yin, Y. D. Highly Tunable Superparamagnetic Colloidal Photonic Crystals. Angew. Chem. Int. Ed. 46, 7428–7431 (2007).
5. Ge, J. P. et al. Magnetochromatic Microspheres: Rotating Photonic Crystals. J. Am. Chem. Soc. 131, 15687–15694 (2009).
6. Aguirre, C. L., Reguera, E. & Stein, A. Tunable Colors in Opals and Inverse Opal Photonic Crystals. Adv. Funct. Mater. 20, 2565–2578 (2010).
7. Weissman, J. M., Sunkara, H. B., Tse, A. S. & Asher, S. A. Thermally Switchable Periodicities from Novel Mesopically Ordered Materials. Science 274, 959–960 (1996).
8. Holtz, J. H. & Asher, S. A. Polymerized Colloidal Crystal Hydrogel Films as Intelligent Chemical Sensing Materials. Nature 389, 829–832 (1997).
9. Kohler, J., Lotsch, B. V., Ozin, G. A. & Bein, T. Vapor-Sensitive Bragg Mirrors and Optical Isotherms from Mesoporous Nanoparticle Suspensions. ACS Nano 3, 1669–1676 (2009).
10. Zhao, Y. J. et al. Porous Bubbles for Label-Free Multiplex Detection of Tumor Markers. Adv. Mater. 21, 569–572 (2009).
11. Zhao, Y. J. et al. Multiplex Label-Free Detection of Biomolecules with an Imprinted Suspension Array. Angew. Chem. Int. Ed. 48, 7350–7352 (2009).
12. Li, M. Z. et al. Ultrasonic DNA Detection Using Photonic Crystals. Angew. Chem. Int. Ed. 47, 7258–7262 (2008).
15. Jiang, P., Smith, D. W., Ballato, J. M. & Foulger, S. H. Multicolor Pattern Generation in Photonic Bandgap Composites. Adv. Mater. 17, 179–184 (2005).

16. McGrath, J. G., Bock, R. D., Cathcart, J. M. & Lyon, L. A. Self-Assembly of “Paint-On” Colloidal Crystals Using Poly(styrene-co-N-isopropylacrylamide) Spheres. J. Mater. Chem. 19, 1584–1591 (2007).

17. Cui, L. Y. et al. Fabrication of large-area patterned photonic crystals by ink-jet printing. J. Mater. Chem. 19, 5499–5502 (2009).

18. Allard, D., Lange, B., Fleischhaker, F., Zentel, R. & Wulf, M. Opaline effect pigments by spray induced self-assembly on porous substrates. Soft Matter. 3, 121–131 (2005).

19. Kubo, S. et al. Control of the Optical Band Structure of Liquid Crystal Infiltrated Inverse Opal by a Photoinduced-Nematic Isotropic Phase Transition. J. Am. Chem. Soc. 124, 10950–10951 (2002).

20. Sato, O., Kubo, S. & Gu, Z. Z. Structural Color Films with Lotus Effects, Superhydrophilicity, and Tunable Stop-Bands. Acc. Chem. Res. 42, 1–10 (2009).

21. Tetreault, N., Miguez, H., Yang, S. M., Kitaev, V. & Ozin, G. A. Refractive Index Patterns in Silicon Inverted Colloidal Photonic Crystals. Adv. Mater. 15, 1167–1172 (2003).

22. Jiang, P., Smith, D. W., Ballato, J. M. & Foulger, S. H. Multicolor Pattern Generation in Photonic Bandgap Composites. Adv. Mater. 17, 179–184 (2005).

23. Ge, J. P., Goehl, J., He, L., Lu, Z. D. & Yin, Y. D. Rewritable Photonic Paper with Hygrosopic Salt Solution as Ink. Adv. Mater. 21, 4259–4264 (2009).

24. Kim, H. et al. Structural colour printing using a magnetically tunable and lithographically fixable photonic crystal. Nat. Photonics 3, 534–540 (2009).

25. Fudouzi, H. & Xia, Y. N. Photonic Papers and Inks: Color Writing with Colorless Materials. Adv. Mater. 15, 892–896 (2003).

26. Xuan, R. Y. & Ge, J. P. Photonic Printing through the Orientational Tuning of Photonic Structures and Its Application to Anticounterfeiting Labels. Langmuir 27, 5694–5699 (2011).

27. Matsubara, K., Watanabe, M. & Takeoka, Y. A Thermally Adjustable Multicolor Photochromic Hydrogel. Angew. Chem. Int. Ed. 46, 1688–1692 (2007).

28. Hu, H. B., Chen, Q. W., Wang, H., Li, R. & Zhong, W. Reusable photonic wordpad with water as ink prepared by radical polymerization. J. Mater. Chem. 21, 13062–13067 (2011).

29. Burgess, I. B. et al. Encoding Complex Wettability Patterns in Chemically Functionalized 3D Photonic Crystals. J. Am. Chem. Soc. 133, 12430–12432 (2011).

30. Xuan, R. Y. & Ge, J. P. Invisible photonic prints shown by water. J. Mater. Chem. 22, 367–372 (2012).

31. Hu, H. B., Chen, Q. W., Cheng, K. & Tang, J. Visually readable and highly stable self-display photonic humidity sensor. J. Mater. Chem. 22, 1021–1027 (2012).

32. Hu, H. B., Chen, Q. W., Tang, J., Hu, X. Y. & Zhou, X. H. Photonic anti-counterfeiting using structural colors derived from magnetic-responsive photonic crystals with double photonic bandgap heterostructures. J. Mater. Chem. 22, 11048–11053 (2012).

33. Ge, J. P. & Yin, Y. D. Magnetically Tunable Colloidal Photonic Structures in Alkanol Solutions. Adv. Mater. 20, 3485–3491 (2008).

34. Efimenko, K., Wallace, W. E. & Genzer, J. Surface Modification of Sylgard-184 Poly(dimethyl siloxane) Networks by Ultraviolet and Ultraviolet/Ozone Treatment. J. Colloid Interface Sci. 254, 306–315 (2002).

35. Ye, H. K., Gu, Z. Y. & Gracias, D. H. Kinetics of Ultraviolet and Plasma Surface Modification of Poly(dimethylsiloxane) Probed by Sum Frequency Vibrational Spectroscopy. Langmuir 22, 1863–1868 (2006).

36. Xue, C. Y., Zhang, W., Stella-Choo, W. H. & Yang, K. L. Simplest Method for Creating Micropatterned Nanostructures on PDMS with UV Light. Langmuir 27, 13410–13414 (2011).

37. Berdichevsky, Y., Khandurina, J., Guttman, A. & Lo, Y. H. UV/ozone modification of poly(dimethylsiloxane) microfluidic channels. Sensors and Actuators B 97, 402–408 (2004).

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H.B.H. and Q.W.C. conceived the research. Q.W.C. supervised the research. H.B.H. designed the experiments, analyzed and interpreted the results, and wrote the manuscript. C.L.C. contributed to its revision. Other authors also contributed extensively to the work presented in this paper.

Additional information
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