Carbon dots based invisible ink for anti-counterfeiting and bribe trapping applications

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Invisible ink, also known as security ink, is a substance which is invisible but can later be made visible by some means. Around 217-218 century BC, it was used as one of the methods of secret communications. The ink can be made visible by different methods such as heating the ink or application of appropriate chemicals, or visible under ultraviolet light. Inks that can be made visible by chemical reactions or by heating may not be re-useable. However, invisible ink made of fluorescent materials can be made visible under visible light and is re-usable. Here, we discuss the usage of invisible ink and the carbon dots as the integral component of the invisible ink.

One of the important uses of invisible ink is to combat counterfeiting. Counterfeiting is a growing and challenging problem for various sectors. A variety of anti-counterfeiting technologies/materials have been developed that can be triggered by heat, light or magnetic field, etc. Among these, luminescent materials offer advantages in easy handling and is used most widely in counterfeiting.

Similarly, invisible ink based on luminescent materials can be used in corruption cases. Although fluorescent dyes, starch powder, phenolphthalein powder, etc. are being used for forensic analysis, the later one has remained most popular in India in corruption cases. An alkaline (colourless sodium carbonate solution) hand wash of phenolphthalein powder applied on currency note or confidential paper or on official document produces pink color. Unionized molecules of phenolphthalein are colourless while ionized molecules give pink or red colour depending on its quantity. However, the colour of the solution persists for few months and becomes colourless at the time of trial in the court and defense often tries to take the advantage of the situation. A mixture of phenolphthalein and hydroquinone (100:2) can be used as the resulting pink color does not fade substantially even after 4 years and can be seen by naked eye. Now-a-days, the forensic experts collect hand washed samples and conclude the presence of phenolphthalein using analytical methods such as UV-vis spectroscopy, FTIR spectroscopy, high-performance liquid chromatography (HPLC), and gas chromatography–mass spectrometry (GC-MS).[1] Though the problem can be addressed by adding a small quantity of hydroquinone, Na_2CO_3, or KOH, environment-friendly-persistent fluorescent materials are of high demand as they can also be used in corruption cases.

In order to trap the accused, chemical like phenolphthalein powder applied currency notes are used. When the accused touches the notes, a trace of the chemical is transferred onto his hands or fingers. When washed with a sodium carbonate solution, it becomes immediately pink ensuring the contact with currency notes. Marker pens with fluorescent ink are often used to invisibly mark valuable household items and can be traced later in case of burglary. They are also widely used as a crime countermeasure. Invisible ink used for computer inkjet printers is highly beneficial as information can be printed without cluttering up the visible contents.

Carbon dots (CDs) have emerged as a new class of luminescent material and attracted the attention of Researchers because of unique optical properties such as excitation-dependent emission, high photostability, cost-effective production. One of the key advantages associated with CDs is that they are not luminescent in solid form. However, they are luminescent in solution. It has also been exploited for sensing and optoelectronic devices. Recently, researchers have developed CDs targeting towards cell imaging and most importantly, for anti-counterfeiting applications. Another advantage associated with CDs is that a transmission electron microscope (TEM) is required to visualize them as they cannot be seen through our naked eyes. A typical TEM image of CDs is shown in Figure 1. The requirement of TEM can be considered as disadvantage. However, when an ink is prepared using the CDs, the colour is emitted upon the exposure of UV light that can be seen through naked eye. The CDs presented in Figure 1 is synthesized by the hydrothermal carbonization of citric acid and ethylene imine polymer at 110 °C for a reaction time of 2 h. Typical photoluminescence spectra of CDs are shown in Figure 2. Moreover, these CDs show good photostability.

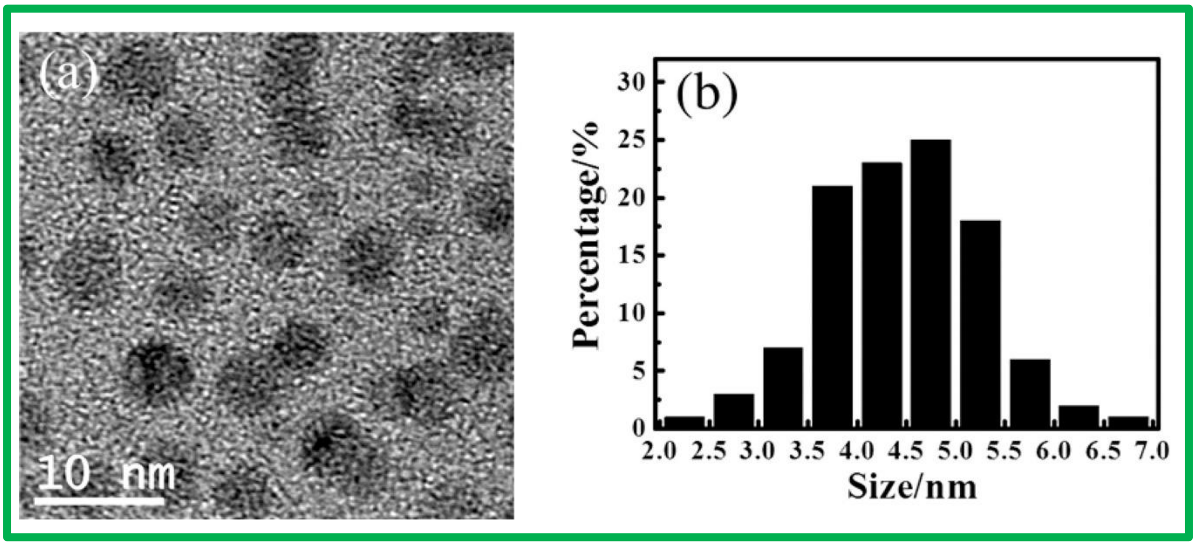

Figure 1. (a) A typical TEM image and (b) particle size distribution of CDs. The average size is 5.0 nm. Reprinted with permission from “J.-Y. Li, Y. Liu, Q.-W. Shu, J.-M. Liang, F. Zhang, X. –P. Chen, X. –Y. Deng, M. T. Swihart, and K. –J. Tan, Langmuir 33, 1043 (2017). Copyright 2017 American Chemical Society."

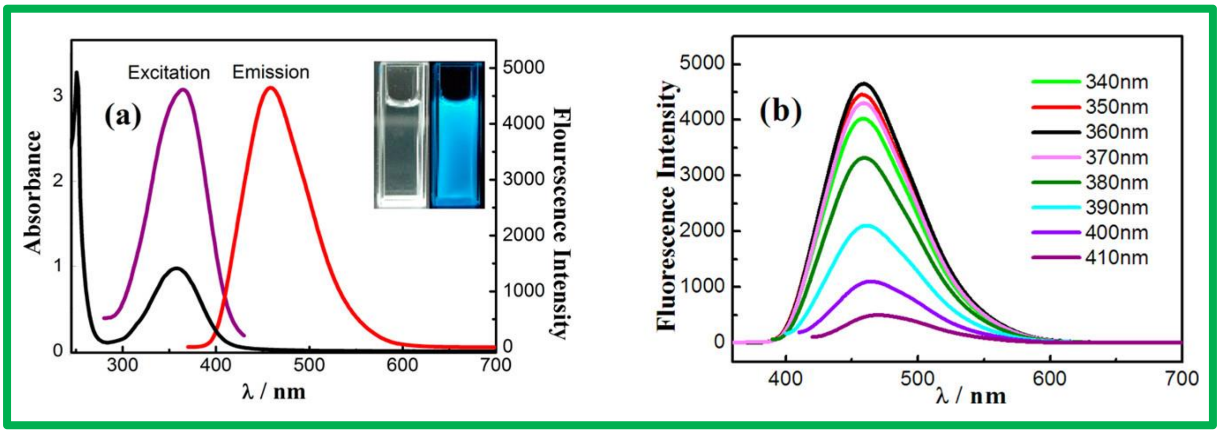

Figure 2. (a) UV–vis absorption (black line), excitation, and emission spectra of CDs dispersed in water. Inset: photographs of the CD solution under daylight and UV illumination. (b) Emission spectra of the CDs excited at different wavelengths. Reprinted with permission from “J.-Y. Li, Y. Liu, Q.-W. Shu, J.-M. Liang, F. Zhang, X. –P. Chen, X. –Y. Deng, M. T. Swihart, and K. –J. Tan, Langmuir 33, 1043 (2017). Copyright 2017 American Chemical Society."

CDs in anti-counterfeiting and anti-corruption cases

Case 1: It has been shown that highly fluorescent CDs can be synthesized using a domestic induction coil heater.[3] An aqueous solution of citric acid and ethylenediamine diamine was heated at 100 °C for 12 to 15 min to produce CDs with an average size of less than 5 nm. The CDs emit blue light with a quantum yield of 73.5% under UV light.[3]

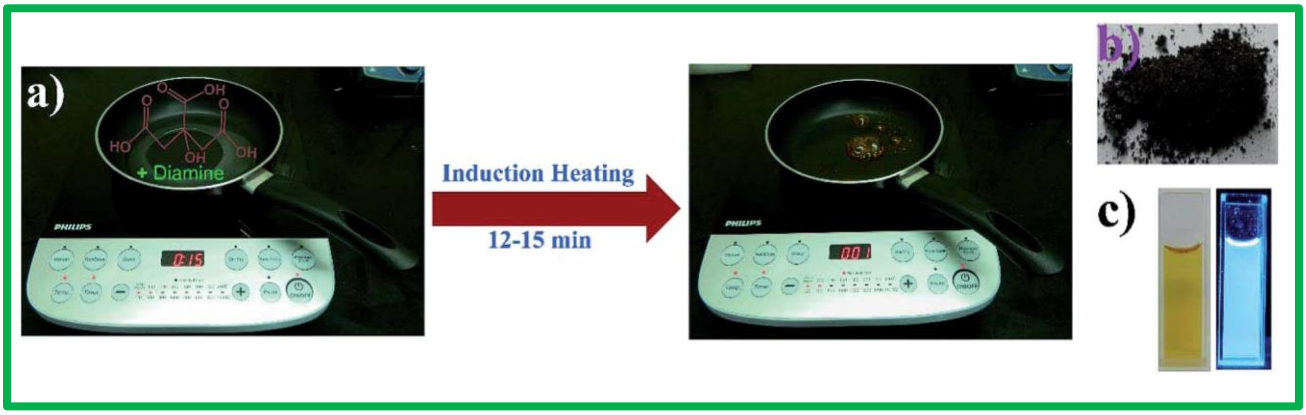

Figure 3. (a) Method for synthesizing CDs using a domestic induction heater plate, (b) dried CDs, and (c) dispersion CDs under day light and UV light. Reprinted with permission from M. P. Ska and A. Chattopadhyay, RSC Adv., 2014, 4, 31994–31999 (2014). M. P. Ska and A. Chattopadhyay, RSC Adv., 2014, 4, 31994–31999 (2014). Copyright 2014 Royal Society of Chemistry."

Figure 4. (a) A ball point pen refill filled with CDs under daylight and UV light. (b) Sketches drawn on 20 rupee note using the refill that are observable under UV light. (c) Sketch and its appearance under UV light following washing with water and then by detergent solution. (d) Gram scale CDs. Reprinted with permission from M. P. Ska and A. Chattopadhyay, RSC

Adv., 2014, 4, 31994–31999 (2014). M. P. Ska and A. Chattopadhyay, RSC Adv., 2014, 4, 31994–31999 (2014). Copyright 2014 Royal Society of Chemistry."

The group of Chattopadhyay has prepared a gel by mixing CDs with chitosan biopolymer and filled a refill of an ordinary ball-point pen with CD gel.[3] Images of the refill under day light and UV light are shown in Fig. 4a. The sketches of different sizes and shapes on Indian currency note are drawn and the images are recorded under the UV light as shown in Fig. 4b. Importantly, the sketches are clearly visible even after washing with water and detergent solution as evident from Figure 4c. The method described by Chattopadhyay group can produce in large scale as evident from Figure 4d. Overall, it has been demonstrated that CDs can be used for UV-active marking for anti-counterfeiting and anti-corruption cases.

Case 2: Barun et al have synthesized N-doped carbon dots (N-CDs) via hydrothermal treatment of citric acid, ethylene diamine, and HCl solution.[4] Quantum yield of the encapsulated N-CDs in a polyvinyl alcohol (PVA) matrix is 91%. Like the previous case, the N-CDs can also be used in anti-counterfeiting as well as corruption cases. As synthesized, aqueous solution of N-CDs can directly be used as invisible ink on 1000 yen Japanese currency as shown in Figure 5 for anti-counterfeiting demonstration.

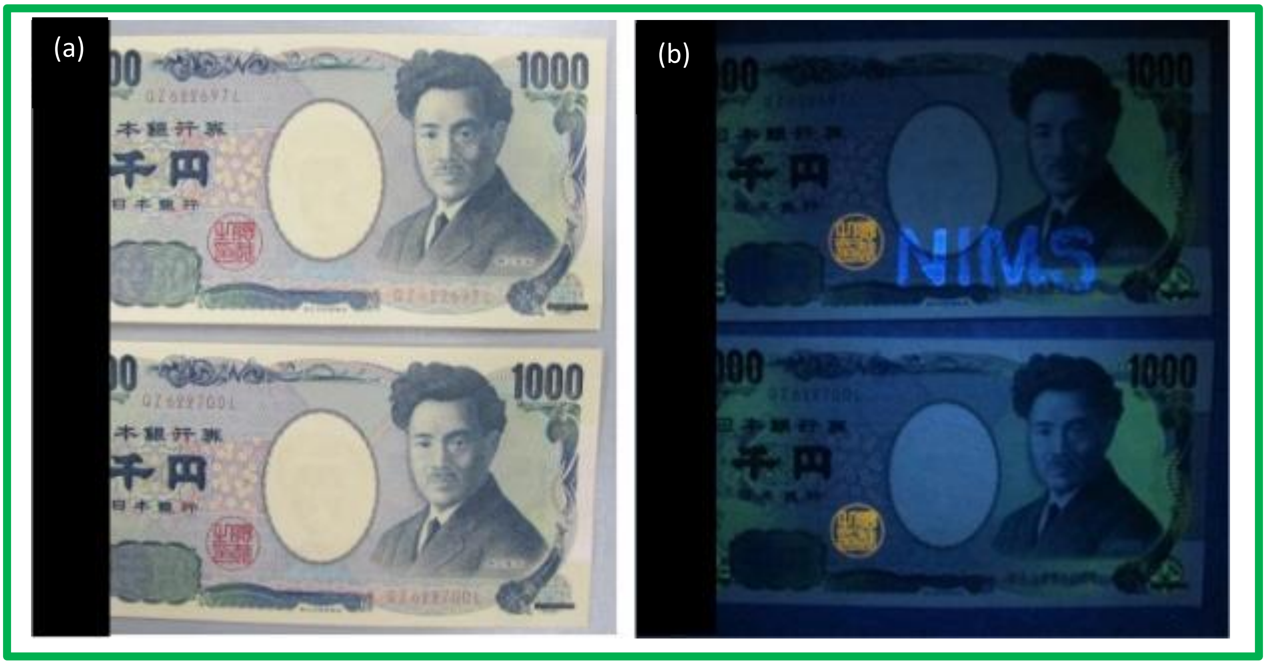

Figure 5. Photographs of a two 1000 yen notes (a) under visible and (b) UV light. (a) One is marked with N-CD ink and the other is unmarked, (b) the same under UV light. Reprinted

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Case 3: Jiang et al have demonstrated a triple mode emission (photoluminescence (PL), upconversion PL (UCPL) and afterglow (RTP)) ink with CDs in the field of advanced anti-counterfeiting.[5] The CDs have been synthesized by heating m-phenylenediamine in an ethanol solution at 180 ^{0}C for 12 h in an autoclave. The preparation of colourless film with CDs and PVA is prepared as summarized in Figure 6. It is interesting to note that film of blue and cyan colours can be generated from the colourless film by exciting with a UV lamp (365 nm) and an NIR femtosecond pulse laser (800 nm), respectively. When the film is illuminated with a UV light and then turned off, a green afterglow is observed with the naked eye.

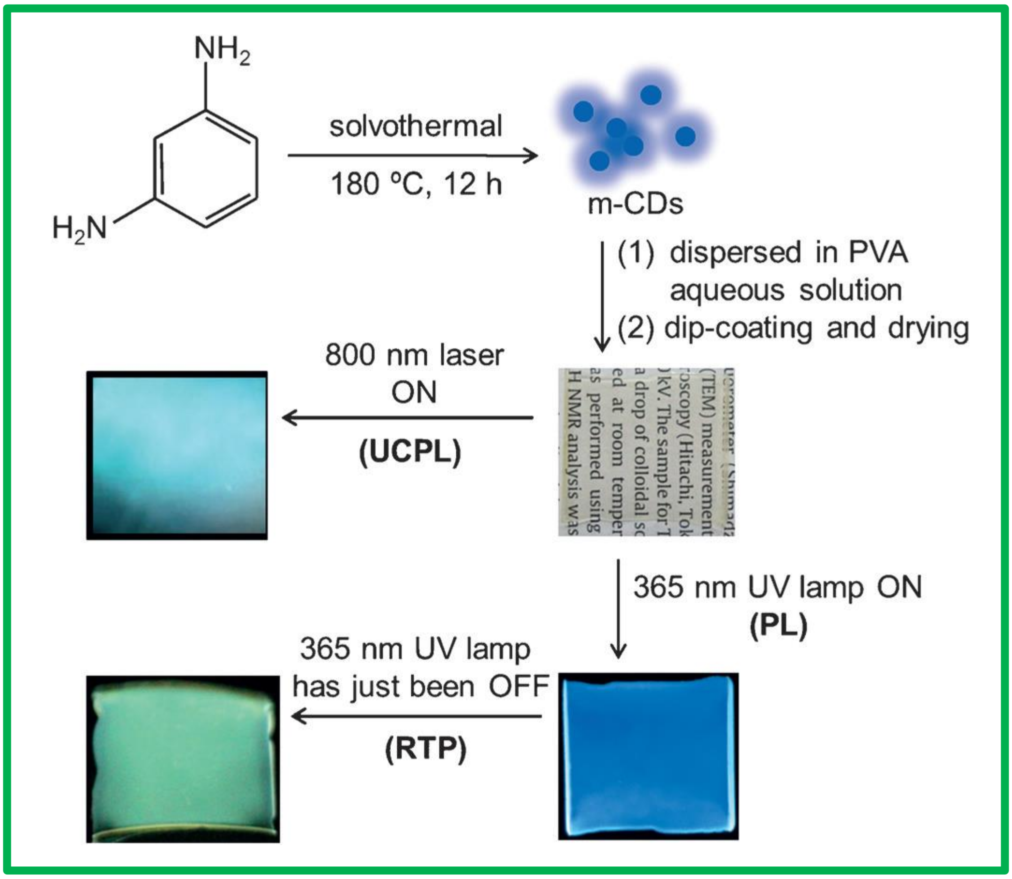

Figure 6. Preparation of CDs and a film of CDs-PVA composite. Emission of CDs-PVA composite film under a 365 nm of UV light (PL mode), after the UV light is turned off (RTP mode), and under 800 nm NIR femtosecond laser (UCPL mode). Reprinted with permission from K. Jiang, L. Zhang, J. Lu, C. Xu, C. Cai, H. Lin, Angew Chem. 128, 7347 (2016). Copyright 2016 Wiley."

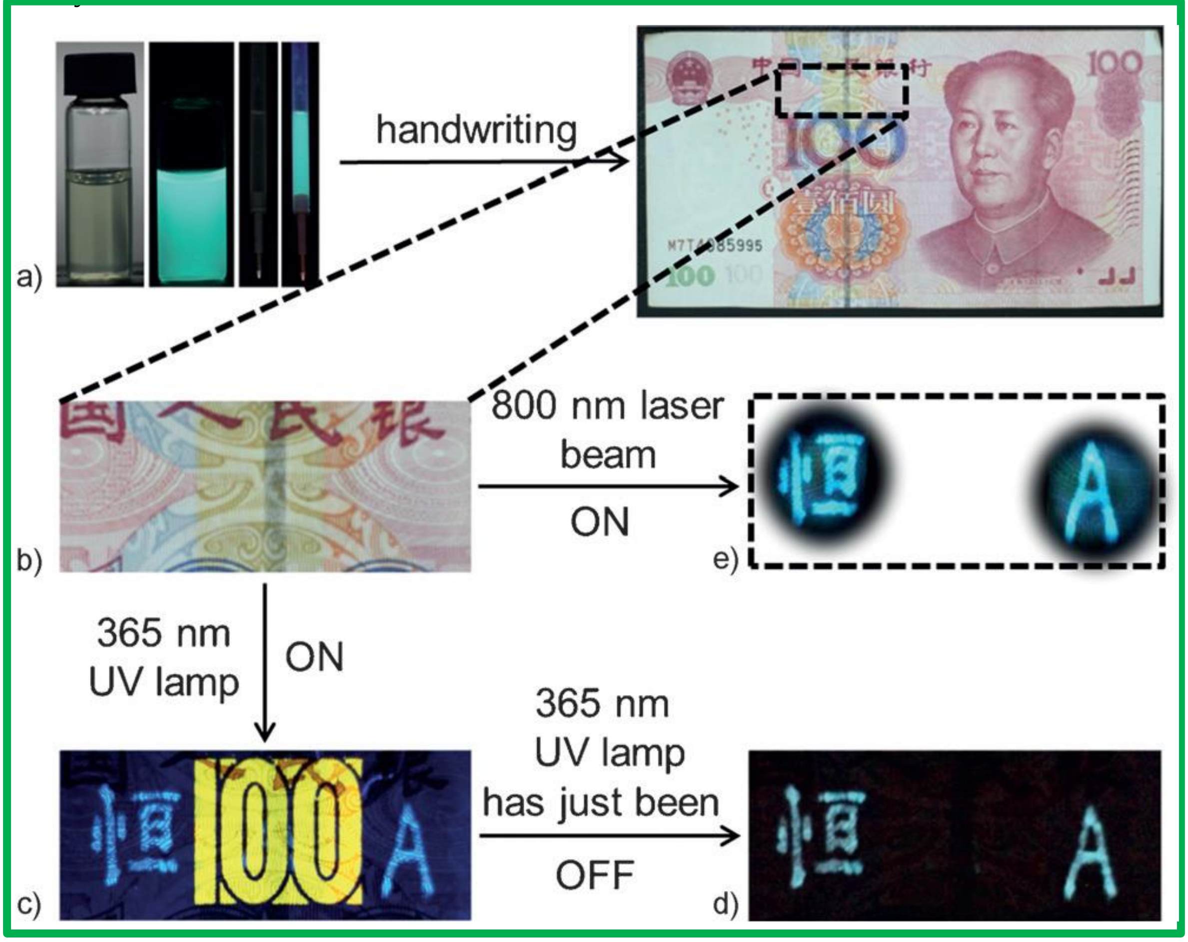

Figure 7. Photographs of (a) CDs-PVA dispersion in daylight and under a 365 nm UV light, (b) handwritten characters in CDs-PVA ink on a RMB note, and (c-e) performance of the triple-mode anti-counterfeiting ink upon excitation with a 365 nm UV light, after the UV light is turned OFF, and excitation with a 800 nm femtosecond laser, respectively. Reprinted with permission from K. Jiang, L. Zhang, J. Lu, C. Xu, C. Cai, H. Lin, Angew Chem. 128, 7347 (2016). Copyright 2016 Wiley."

As shown in Figure 7(a), CDs-PVA aqueous dispersion is nearly colourless. However, it emits bright cyan light when excited with UV light.[5] A gel pen refill can be filled with the CDs-PVA dispersion as in the previous cases and used directly as an ink. To demonstrate the application in anti-counterfeiting cases, Jiang et al have taken a banknote (RMB) and written an English character "A" and Chinese character "heng" on it using the gel pen. Though the characters were not visible under day light, bright blue characters (PL mode) along with the yellow number "100" (existing anti-counterfeiting mark) were visible under a 365 nm UV light. The yellow number "100" disappeared but the characters ("A" and "heng") were observed as a blue-green color after the UV lamp was turned off (RTP mode). Cyan colored characters were observed (UCPL mode) when excited with a femtosecond laser (800 nm). These unique triple-mode emission features of the CDs-PVA composite film are highly beneficial for anti-counterfeiting applications.

Case 4. There are natural resources such as wasted coffee powder, orange juice, watermelon peel, grass, etc. that can act as one of the ingredients for the synthesis of CDs.[6,7] Some of the reports deal with the anti-counterfeiting applications of these CDs as well.[7,8]

Conclusions

Overall, CDs can be used for a variety of applications including anti-counterfeiting as well as anti-corruption cases. The advantages associated with CDs are the low-cost synthesis, photostability, unique optical properties, etc.

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