Potential Applications of Carbon Dots in Development of Latent Fingerprint: a Critical Review

Harsimar preet kaur[1], Surender Singh Sehrawat[2], Gurleenkaur[3]

[1]M.Sc- Forensic Science and Toxicology, Chandigarh University, Punjab,India

[2]Assistant Professor, Deptt. of Forensic Science and Toxicology ,Chandigarh University, Punjab, India.

[3]Research Scholar, Deptt. of Forensic Science and Toxicology, Chandigarh University, Punjab,India

Abstract: Nanotechnology is brightest future of science and rapidly emerging in every filed of science such as Medicine, Physics, Chemistry, Pharmacy, molecular medicine and even in forensic science. This field already developed various nanomaterials for with biomedical and analytical fields and forensic fingerprinting. Carbon dots are such developed materials which have great biocompatibility, fluorescence properties, inertness, photo-bleaching resistance, low toxicity withcosteffectiveandenvironmentalfriendlyandhaspotentialapplicationinlatentfingerprint development.Carbondotscanbesynthesizedbyeasyprocesseswithchemicalusingcitricacid L-glutathione,thiourea,eggwhites,coffeegrounds,egg whites, applejuice,aspirin,andeven from chocolate. Various color of carbon dot can be produced by specific chemical reactions. The majority are red, green, blue and yellow color emission type under different excitation light frequencies and used in both method as spray and powder form. Carbon dots method are rapid and easy to perform, latent print can be developed from water soaked evidence and can be preserved for very long time. Latent prints can be developed form porous, non-porous and semi-porous substrates, which have potential to show primary, secondary and tertiary details forfingerprintevenafteraprolongageingupto60days.Developedprintcanbeseenbynaked eye and photographed by digital camera under UV light. Hence. Carbon dots have wide application and potential to develop any kind of latent prints and can be used in daily routing of crime scenesearch.

Keywords: Nanotechnology, Forensic Science, Nanomaterial, Carbon Dots, Latent fingerprints, Development

INTRODUCTION

Nanotechnology is emerging and rapidly growing fields in forensic science, that have already done a great contribution to the number of fields including physical, chemical, mate rial , biomedical and forensic sciences. In forensic sciences, some critical trace pieces of evidence are a nanoscale size and not easily visible which need to be detected and analyzed.(1) A latent fingerprint is one of such shreds of evidence found at the crime scene, is unique, permanent and universal. Fingerprint can be affected by environmental conditions and deteriorate with time, if not lifted within some time. Fingerprints are corroborative evidence that helps in accessing identify of individuals.

Threetypesoffingerprintscanbepresentonthecrimesceneincluding   latent,patentandvisible prints,wherelatentprintsarethemostcommontype.Visibleprintsincludebloodyfingerprints that form print due to stain with some colored materials and can be easily identified. Plastic prints are made by pressing fingers in fresh paint, wax, soap, also known as 3D impressions and can be easily seen and are photographed. Latent prints are invisible to the naked eye(2) fingerprints are originated form eccrine and sebaceous gland. Eccrineglandpresentonpalmsandsoles,secretesweat,mostlycomposedofwater(99%)with a very low amount of chloride, phosphate and sulfates as inorganic salt and protein andsugars as organic component. Sebaceous glands present all over the body and secrete oily matter sebum. Therefore, latent print left by fingers, because secretions of eccrine and sebaceous gland, on touching of any substrate. (3)(4)

Old methods:

Since now, a method like physical and chemical methods including Powdermethod, Fluorescent dye staining, Cyanoacrylate /Iodine fuming, Ninhydrin, silver nitrate also vacuum metal deposition method(5), have been already developed for fingerprint development. Among them, Fluorescent materials carbon dots are nowadays widely applied inorganic nanoparticles in the identification of latent fingerprints.(5)

New Technology:

Nanotechnology   devised   various   type   of   inorganic   nanomaterials   like semiconductor,magneticnanoparticle,Aunanoparticle,andquantumdotsforlatentfingerprint development.Fluorescent nanomaterials have gained significant interest in conventional fluorescent dye probes in recent years as potential competitors and have grown very rapidly due to the substantial need for fluorescent probes in chemical sensing, biological

tracking, and other related fields. Fluorescent nanomaterials have a quantum scale effect and the special effects of nanomaterials relative to conventional fluorescent dyes, which can solve many of the latter's drawbacks, such as low stability, poor fluorescence strength, and rapid photobleaching. Fluorescent nanomaterials have therefore been extensively used in physical , biological, and chemistry as well as other similar areas. Semiconductor quantum dots have been the object of interest for many types of nanoparticles due to their unusual electronic and luminescent properties.(17)

Earlier quantum dots made from heavy metals were used which are nanometer-scale semiconductors, which exhibits the property of fluorescence and the type of color emitted light depends on the difference in energy state between ground level and higher energy state. Due to the toxic nature of quantum dots, they are now replaced by carbon dots. In 2004, carbon dots were observed (8) when purifying single-walled carbon nanotubes. (1).

Carbon dots are fastest growing nanomaterials having fluorescence activity and applications in biomedical and analytical fields refers to like optoelectronics(light emitting devise), bio imaging, drug delivery, photocatalyst and water purification.(6) Because of their special properties , such as low toxicity, tunable pollutants, low cost , good biocompatibility and high photo stability, they have wide applications in latent fingerprint detection.(4) Carbon dot biocompatibility and water solubility are related to the existence of water loving groups on the CD surface. (5).

Synthesis of various carbon dots :
Carbon dots have SP2 hybridized conjugation with carboxyl, hydroxyl and aldehyde groups. In SP2 hybridization, one 'S' and two 'P'-orbitals hybridize to form three equivalent sp2 hybrid orbitals with trigonal planar geometry. (7)They are synthesized by top-down and bottom-up methods. Top-down method involves the breakage of SP2 fluorescence carbon structures into small pieces with the help of laser ablation, arc discharge, and hydrothermal, chemical exfoliations. In the bottom-up method with the help of hydrothermal, microwave-assisted chemical and physical techniques, CDs are formed as bulk materials.(6).

Solid-state labeling markers are more preferred than aqueous solutions because the aqueous solutions lack portability and difficult to preserve and their property to diffuse decreases the resolution of latent fingerprints during detection while soli d-state doe s not show diffusion and can show better and clear fingerprints as they adhere to human skin oil that is present on objects surfaces.(19) But as fluorescent labelling markers, they can't be applied directly due to assemblage of pure CDs due to quenching (aggregation-induced luminescence quenching). The phenomenon is called quenching, when the molecules at higher energy are deactivated and the fluorescence ceases. (8).

Synthesizing of carbon dots can be done easily and is a hydrothermal process (microwave-assisted method). They can be synthesized from lemon juice (citric acid), egg whites, coffee grounds, egg whites, apple juice, aspirin, and even chocolate.(1)

Microwave Synthesis of Carbon Quantum Dots
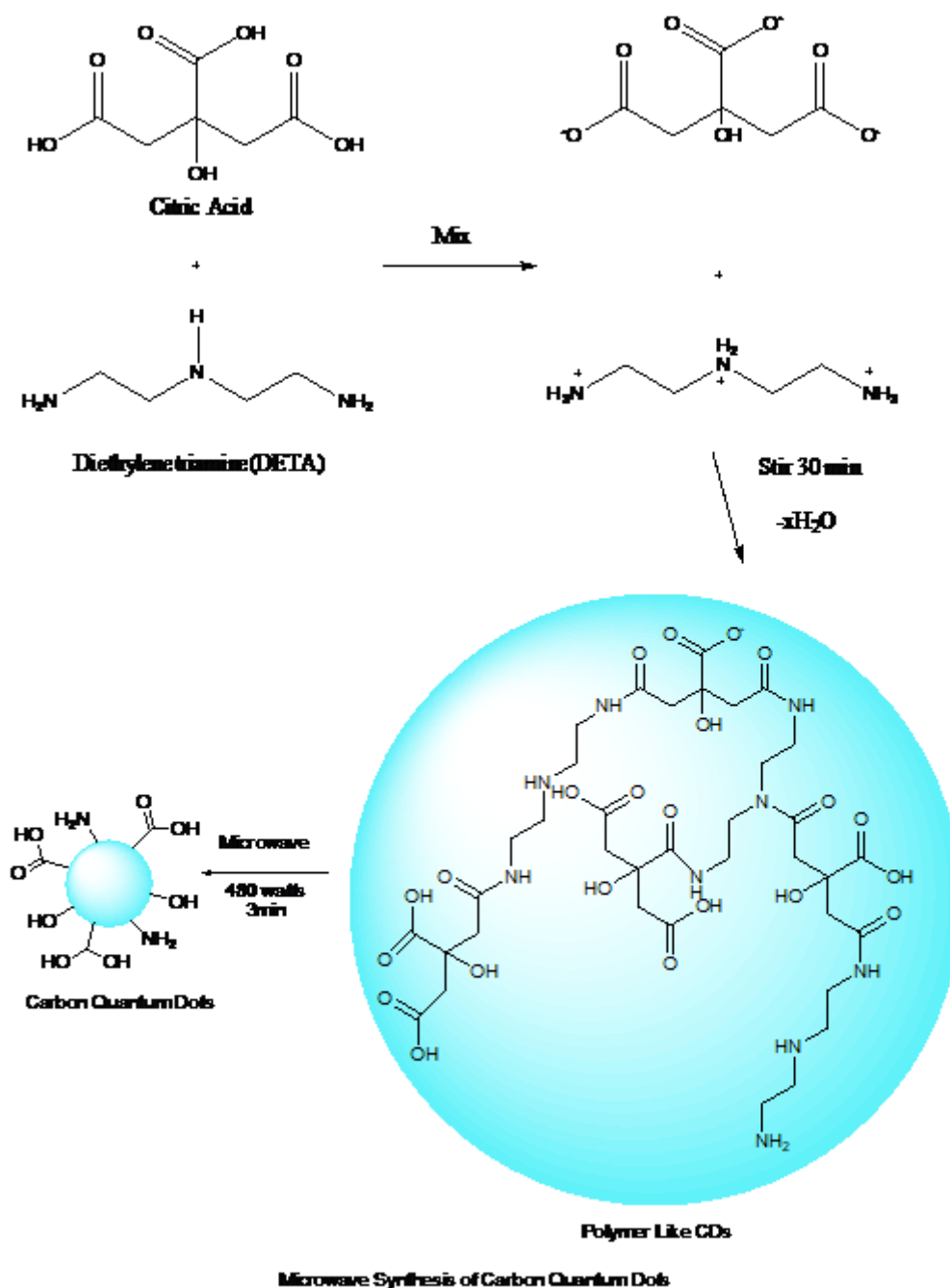
(1)

Some method for synthetization

1. Common method: mix citric acid with diethylenetriamine in water, then stirred at room temperature and microwaved. The property of fluorescence can be increased if citric acid is mixed with an amino group-containing small molecule. According to the study, increasing the presence of amino groups more will be the fluorescence emissions of CDs. After the mixture is microwaved, purification is performed, because the mixture is not only the carbon dots and needs to be purified. Column chromatography is used for the purification of the crude mixture of Carbon dots obtained.(1)

2. Reagents required for the preparation are DL-Malic acid, ethylenediamine, tris-HCl buffer solutions with different pH values. Citric acid and N-acetyl-L-cysteine as N and S

dopant synthesize B-CDs . Blue-emission CDs (P-B-CDs) are synthesized from ethyleneimine polymer and citric acid.(5)(20)

o-phenylenediamine and N, N-dimethyl formamide synthesize yellow emission CDs.(2)

3. P-phenylenediamine with phosphorous acid synthesize R-CDs which can be used as a spray for latent fingerprint identification (5)

4. Time-based CDs are synthesized by varying the time intervals under the microwave, the fluorescence of CDs increases with time and may be related to its quantum yield. It is prepared by adding 5gm of citric acid to Polyethyleneimine and saline Phosphate buffered, and kept for continuous stirring for 10 minutes and heated in the microwave for 30 minutes at 180 W(7)

5. Carbon-dots can also be prepared by Sucrose. 0.5gm of Sucrose is added to 2ml of Polyethylene glycol (acts as a stabilizer) with 30 ml of water and 1 ml conc. H_2SO_4 which is added dropwise, the mixture then microwaved.(learned from practical work by teacher)

Characterization of carbon dots:

After formation, analysis has to be performed to assure that resultant product is achieved or not, which is known as characterization. Characterization of carbon dots can be done by using techniques like Infrared Spectroscopy (IR), UV-visible spectroscopy (UV-Vis), Nuclear Magnetic Resonance spectroscopy (NMR) and Transmission Electron Microscopy (TEM), Fourier transform infrared spectra and X-Ray Photoelectron spectra (XPS). (9)(21)

The primary method of analyzing the Carbon dots is obtaining UV spectra (describes the optical characteristics of carbon dots) as carbon showing maximum absorption below 380 nm(1). In the ultraviolet field, CDs have heavy absorption, which can also stretch to a visible region (17) .

G-CDs shows an absorption peak at 327nm and an emission peak at 520nm(2).

Application of carbon dots (CDs) in latent fingerprint detection

The carbon dot can be prepared with easy process and have outstanding biocompatibility ,cost effective, environment friendly and luminescent properties. These shows possible applications in development of latent fingerprint.(10)Carbon dots have widespread application in the visualization of the fingerprints. The small size and high reactivity make them useful for developing latent prints. These properties allows CDs to bind with ridge of fingerprints.(11) Aging of fingerprints is major problem for latent print detection, because there is loss of organic and inorganic ion, water and other residues which make detection really unproductive (12) but wide applicability of nanomaterial carbon dot overcome this problem of aging.

Earlier it was reported by Wang and his co-workers, that latent fingerprints can be collected using carbon dots made from pig intestines.(13) They also found out that carbon dots imbedded in polyvinyl alcohol (PVA) due to long term stability of films give a highly detailed image of the fingerprint. Now, recently it has been seen that citric acid which acts as a source of carbon with diethylenetriamine gives good results. Carbon dots are mixed in liquid polyvinyl alcohol (PVA) and are cast on the fingerprints and the casted film is allowed

to dry. After dried, fingerprints can be visualized with UV flashlight within a frequency around 395-400 nm.(1)

The latent fingerprint was developed with B-CDs, Y-CDs, P-B-CDs, and G-CDs are compared. Method Y-CD shows no outline where P-B-CD shows a general outline with vague lines, less clear image with low fluorescence with nearly no use in practical life. Print image develop with B-CDs, shows perfect and smooth outline of fingerprint with low fluorescence intensity and robust background interaction. The emission peak of B-CDs decreases as the excitation wavelength increased from 360nm-460nm. The B-CDs were affected by the background color of the surface, whereas the G-CDs were independent of the background interference, a wide range of wavelengths can be used. (2)

G-CDs method exhibits clear ridges and furrows with reasonable distinction against background distraction on transparent tape and foil paper. Prints on coverslips shows weak fluorescence and fragility to external friction showed, good results where on the sealed bag, ridges were understandable with weaker intensity of fluorescence and had an obvious fingerprint profile. Developed prints observed in the darkroom by exciting it with a frequency of 365 nm UV range. After variety of experiment, Best result obtained, as the pH reaches to 9 with a maximum immersion for 30 min at room temperature, because G-CDs take prolong time to develop. G-CDs can preserve evidence for 60 days. But with week fluorescence and features can observed at 60th day that shows practical capability. Object like knife and ax, soaked in water can be developed with G-CDs solution and exhibits clear profile with consistency of ridges, minutiae features and strong contrast, some unclear ridges due to diffusion of residue of fingerprint in water, leads to effective development and remains for long term.(2)

SiO2@ C-dot powder method is valuable tool for development of latent printFingerprint formed on non-porous, semi-porous surfaces and porous surfaces with SiO2@ C-dots shows improved visualisation and well-defined ridges on different surfaces without background hindrance and with enhanced contrast and sensitivity below 365 nm UV-light. SiO2@ C-dots method is rapid and easy to use, only in 30s result can be achieved.(14)

N,S-SFCD method shows stable fluorescence intensity in pH range 6-9 and incubation time 1 min. Methods like nebulization and ultrasonic produce optimum quality of imaging where whole fingerprint with secondary & tertiary level details can be seen. All these make N,S-SFCD useful for real world application. Latent print can be developed on various non-porous and porous substrate. Bright fluorescent images with clear finger print detain seen in non-porous substrate where high background noise and poor resolution seen for porous substrates. N,S-SFCD can be used as powder and aqueous/spraying method. Moreover, powder method have higher applicability on porous substrate and provide contrast against various colored substrate. The developed prints seen as blue, green, yellow, or red on excitation in the UV, 420, 440, and 460 nm wavelength regions (22), clear pattern of ridges can be observed with naked eyes. This method can preserve prints for a long time like 30 days but prolong preservation cause loss of structures in aging. (14)(15).

Fingerprints on surfaces showed consistent images of outline ridges without background staining and distortion, of outstanding visibility and contrast under 365 nm light, Carbon polymer Dots (CPDs)-starch powder produced.(23) The multiple background substrates

exhibits, fluorescence images with satisfactory contrast between backgrounds with easily identifiable details of the fingerprint .Low emission carbon polymer dots in powder form have high contrast and low background interference for fluorescence image (24). Latent fingerprint older as 30 day can be clearly detected and observed, structures not destructed as aging increases. (16)

Photography:

- Canon 5DII digital camera or gel imager was used to take images of developed latent fingerprints. In G-CDs.
- The LFPs produced were captured under UV 365 nm light with a Canon EOS 500D digital camera.(23)
- The Chemi Scope 2850 luminescence imaging system (Clinx Science Ins., Shanghai) collected all the fluorescent images, which had band-pass philtres of various wavelengths, such as UV excitation (365 nm), green excitation (550 ± 24 nm), and red excitation (610 ± 40 nm).(24)

CONCLUSION:

With the evolution of nanomaterials, minute chip materials are used in forensic nanotechnology instead of bulky instruments. Such nanomaterials speed up the investigation process with high reliability. In the present review devised nanomaterial has advanced properties that make it suitable for use in forensic fingerprinting which develops latent fingerprints in any condition, irrespective of nature and color substrate. Experimentations performed by various scientists indicating that carbon dots have the potential to develop latent fingerprints and can be used further for investigation, crime scene search, and research & development.

Conflict of interest : The reviewers note that no conflict of interest exists In respect to this paper's publication.

REFERENCES

[1] Molinero,A.A.,Enright,M., & Cossairt , B (n.d). Preparation and Characterization of Carbon Quantum Dots And Their Application to Fingerprint Imaging

[2] Zhao,D.,Ma,W.,&Xiao,X.(2018).TheRecognitionofsweatlatentfingeqirintswithgreen- emitting carbon dots. *Nanomaterials,*8(8), 612

[3] Hazarika, P ., & Russell, D. A. (2012). Advances in fingerprint analysis. Angewandte chemie-International Edition , 51(15), 3524-3531. https://doi.org/10.1002/anie.201104313

[4] Wang, C., Zhou, J ., Lulu, L., & Song, Q. (2018 a). Rapid Visualization of Latent Fingerprints with Color-Tunable Solid Fluorescent Carbon Dots. *Particle & Particle Systems Characterization, 35(3),* 1700387

[5] Chen, J., Wei, J.-S., Zhang, P., Niu, X.-Q., Zhao, W., Zhu, Z.-Y., . . . Xiong, H.-M. (2017).Red-emissive carbon dots for fingerprints detection by spray method:

coffee ring effect and unquenched fluorescence in drying process. *ACS Applied Materials & Inteifaces,9(22),* 18429 -18433.

[6]   Sagbas, S., & Sahiner, N. (20 I 9). Carbon dots: preparation, properties, and application. In *Nanocarbon and its Composites* (pp. 651- 676).Elsevier.

[7]   Bahadur,R., Kumawat, M. K., Thakur, M., & Srivastava, R. (2019). Multi - fluorescent cationic carbon dots for solid-state fingerprinting. Journal of Luminescence, 208,428—436.

[8]   Wang, H.-J., Hou, W.-Y., Yu, **T.-T.,** Chen, H.-L., & Zhang, Q.-Q. (2019). Facilemicrowave synthesis of carbon dots powder with enhanced solid-state fluorescence and its applications in rapid fingerprints detection and white-light-emitting diodes. *Dyes and Pigments, 170,*107623.

[9]   Wang, T., Che n, G., Li, L., & Wu, Y. (20 19). Highly fluorescent green carbon **dots** as a fluorescent probe for detecting mineral wa te r ph. *Sensors (Switzerland), 19(17)* https://doi.org/ I0.3390/s1917380 I

[10]   Lim, S. Y., Shen, W., & Gao, Z. (2015). Carbon quantum dots and the ir app lic ations. *Chemical Society Reviews, 44(1),* 362-38 I.

[11]   Rawtani, D., Tharmavaram, M., Pandey, G, & Hussain, C. M. (2019). Functionalized Nanomaterial for Forensic Sample Analysis. *TrAC Trends in Analytical Chemistry ,* I15661

[12]   Wang,J.,Ma,Q.,Liu,H.,Wang,Y.,Shen,H.,Hu,X.,...Tan,W.(2017).Time-gatedimaging of latent fingerprints and specific visualization of protein secretions viamolecular recognition. *Analytical Chemistry, 89(23),* I 2764-12770.

[13]   Wang,C.-F.,Cheng,R.,Ji,W.-Q.,Ma,K.,Ling,L.,&Chen,S.(2018).Recognitionoflatent fingerprints and ink-free printing derived from interfacial segregation of carbon dots.*ACS AppliedMaterials&Interfaces,10(45),*39205-39213

[14]   Peng, D., Liu, X., Huang , M., Wang, D., & Liu, R. (2018). A novel monodisperse SiO2@C- dot for the rapid and facile identification of latent fingermarks using self-quenching resistantsolid-state fluorescence. *Dalton Transactions, 47(16),* 5823-5830 . https://doi.org/10.1039/c8dt00579f

[15]   Wang, C., Zhou, J ., Lulu, L., & Song, Q. (2018 b). Rapid Visualization of Latent Fingerprints with Color-Tunable Solid Fluorescent Carbon Dots. *Particle and Particle Systems Characterization,35(3),*1-8.https://doi.org/IO.1002/ppsc.201700387

[16]   Li, F., Wang, X., Liu, W., Wang, L., & Wang, G. (201 8). One -step solvothermal synthesis of red emissive carbonized polymer dots for latent fingerprint imaging. *Optical Materials,*86(September),79-86.https://doi.org/l0.1016/j.optmat.2018.09.040

[17]   Zuo, Jun et al. "Preparation And Application Of Fluorescent Carbon Dots". Journal Of Nanomaterials, vol 2015, 2015, pp. 1-13. Hindawi Limited, doi:10.1155/2015/787862. Accessed 28 Oct 2020.

[18]   X. Xu, R. Ray, Y. Gu et al., "Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments," Journal of the American Chemical Society, vol. 126, no. 40, pp. 12736–12737, 2004.

[19]   Yuechen Zhai, Fangzhong Shen, Xutao Zhang, Pengtao Jing, Di Li, Xudong Yang, Ding Zhou, Xiaowei Xu, Songnan Qu. "Synthesis of green emissive carbon

dots@montmorillonite composites and their application for fabrication of light-emitting diodes and latent fingerprints markers" , Journal of Colloid and Interface Science, 2019

[20] Archana Charanpahari, Nidhi Gupta, Vidyasagar Devthade, Sachin Ghugal, Jatin Bhatt. "Chapter 179-1 Ecofriendly Nanomaterials for Sustainable Photocatalytic Decontamination of Organics and Bacteria" , Springer Science and Business Media LLC, 2018

[21] Jiazhuang Guo, He Li, Luting Ling, Ge Li, Rui Cheng, Xuan Lu, An-Quan Xie, Qing Li, CaiFeng Wang, Su Chen. "Green Synthesis of Carbon Dots toward Anti-Counterfeiting" , ACS Sustainable Chemistry & Engineering, 2019

[22] Chan Wang, Jingdan Zhou, Lu Lulu, Qijun Song. "Rapid Visualization of Latent Fingerprints with Color-Tunable Solid Fluorescent Carbon Dots" , Particle & Particle Systems Characterization, 2018

[23] Feng Li, Xi Wang, Wen Liu, Luqi Wang, Guiyan Wang. "One-step solvothermal synthesis of red emissive carbonized polymer dots for latent fingerprint imaging" , Optical Materials, 2018

[24] Meng Wang, Ming Li, Aoyang Yu, Jian Wu, Chuanbin Mao. "Rare Earth Fluorescent Nanomaterials for Enhanced Development of Latent Fingerprints" , ACS Applied Materials & Interfaces, 2015