

Cationic dye-diatomite composites: Novel dusting powders for developing latent fingerprints



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ABSTRACT

Most fingerprints left at crime scenes are latent and require treatment to render them visible. Powder method, the most widely used procedure for developing latent fingerprints, is based on the visual contrast between background surface and powder-covered fingerprint region, thus dusting powders with excellent performance are urgently needed. Four cationic dye-diatomite composite powders with different colors have been prepared relying on the adsorption between cationic dye molecule and diatomite. Compared with synthetic silica matrix, the employment of natural diatomite greatly reduces the amount of dye usage, which is simple, green and low-cost. The cationic dye-diatomite composite powders are successfully used as novel dusting powders for developing latent fingerprints on various substrates including glass slides, notebook paper, PVC sheets, ceramic tile, water bottle label, stainless steel coin, tea caddy, compact disc and packing box. High-quality patterns of fingerprints with second level features can be obtained within a short period of time. This work shows that the cationic dye-diatomite composite powders have high sensitivity, high selectivity and good contrast and are promising for practical use in forensic science.

1. Introduction

Patterns of friction ridge skins on human fingers have three levels of features. First-level feature refers to pattern type (arch, loop, or whorl), overall flow of ridges, and position of core and delta. Second-level feature refers to types (ridge endings, bifurcations, dots, etc.) and relative positions of minutiae within the pattern. Third-level feature refers to minute details of each friction ridge (edge shapes, and sizes), shapes and locations of sweat pores. These features are unique to each individual and immutable throughout a person's lifetime [1–3]. Thus fingerprints, impressions left by the friction ridge skins, have been recognized as one of the most valid physical evidences for identification purpose in the field of forensic science since the late 19th century [4–6]. Except in certain limited cases like suspect's fingers contaminated by dust, blood or paint, the majority of fingerprints left at crime scenes are not readily visible to the naked eye (termed latent fingerprints) and need to be developed to enhance their visualization [7–11]. Taking advantage of advanced techniques such as nanotechnology, spectroscopy and immunoassay, some emerging methods for developing latent fingerprints have been extensively studied in recent years [12–16]. However, powder method has always been the most frequently used procedure in crime scene investigation due to wide

applicability and high efficiency. The effectiveness of this method depends mainly on visual contrast between background surface and fingerprint region that has been covered with dusting powder. Accordingly, preparation of colored or fluorescent powders for developing latent fingerprints has become a hot issue. Furthermore, dusting powders with low toxicity, high detection sensitivity and long shelf life are urgently required [17–20].

In general, adhesive force between dusting powder and fingerprint residue that is mainly composed of eccrine sweat and sebaceous secretion derives from two aspects—pressure deficit and electrostatic attraction [21–23]. According to the literature, silica particles usually have good adhesion to fingerprint residue and it is easy to incorporate colored or luminescent constituents into them, making them desirable matrix materials for preparing dusting powders [24–26]. The first two systematic studies on silica-based composite powders for developing latent fingerprints appeared in 2008 [27,28]. Theaker et al. have synthesized a series of dye-doped silica powders through hydrolysis of silane coupling agents with a certain amount of dyes in liquid phase [27]. But the problem is that solvent can infiltrate and remove dye molecules during the growth of these particles. To overcome this drawback, a high level of dye usage is inevitable. Liu et al. have successfully trapped Eu^{3+} metal ions and sensitizer complex in silica to produce fluorescent

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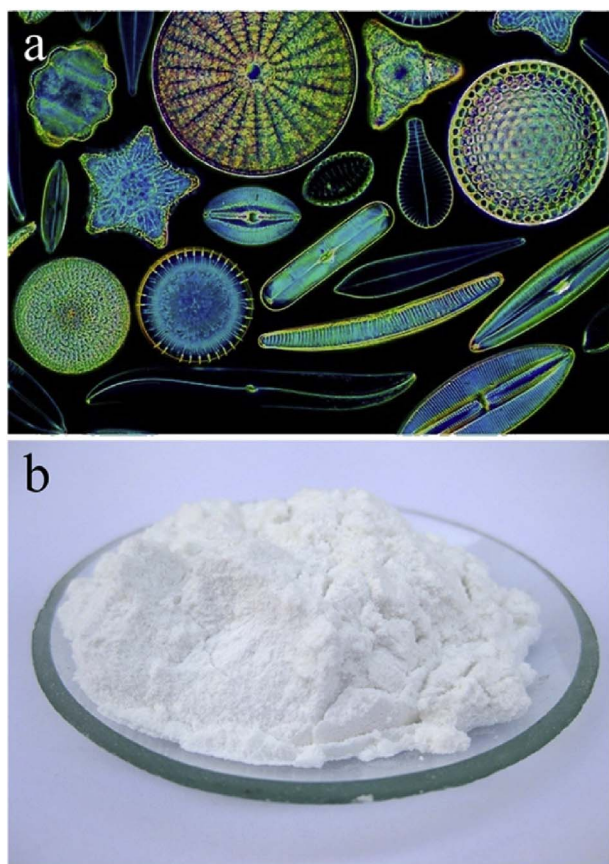


Fig. 1. (a) Photograph of various diatoms taken by dark field microscope; (b) Photograph of diatomite taken by digital camera.

powder via sol-gel method [28]. However, the fabrication process is time-consuming because formation of xerogel lasts for nearly a month. Therefore, for the following studies, it is quite important to select suitable precursors and optimize preparation conditions.

Diatoms, as shown in Fig. 1(a), are a major group of unicellular algae [29–31]. Frustules of dead diatoms could transform into amorphous hydrous silica named diatomite. Diatomite powder as shown in Fig. 1(b) possesses lots of favorable properties, e.g., fine and uniform particle size, large surface area, high porosity, low specific gravity and good chemical stability. As a result, diatomite has been utilized as adsorbent, filtration medium, thermal insulation medium, mild abrasive, catalyst carriers, and agent in purification and extraction of DNA [32–34]. It is noteworthy that thousands of independent holes with submicron diameter naturally exist within a single particle of diatomite, which is difficult to obtain by means of chemical synthesis [35]. Meanwhile, numerous hydroxyl groups on diatomite surface are usually negatively charged in aqueous media [36]. Therefore, considering its unique microstructure and surface property, diatomite would exhibit high retention capacity for cationic dyes, and the adsorbed dye molecules can be physically and chemically protected from the external environment. From the above analysis, diatomite could be a perfect silica matrix to prepare novel dusting powders.

In the present study, for the first time the author reports application of cationic dye-diatomite composite powders for sensitive development of latent fingerprints. Through anchoring cationic dyes including methylene blue (MB), safranin T (ST), malachite green (MG) and crystal violet (CV) as guest molecules into pores of host diatomite by simple adsorption process, four types of cationic dye-diatomite composite powders with different colors have been severally prepared and utilized to develop latent fingerprints on various substrates by powder method. Since they exhibit strong adhesive force to fingerprint region rather

than substrate surface on which the latent fingerprints have been deposited, friction ridge details of developed fingerprints can be clearly identified and photographed under natural light. On the other hand, making full use of natural materials and minimizing usage of artificial dyes fully conform to the concept of green and sustainable chemistry.

2. Experiment

2.1. Materials and characterization

All chemical reagents in this work, including sucrose, hydrochloric acid, ethanol, methylene blue (MB), Safranin T (ST), malachite green (MG) and crystal violet (CV) were analytical grade and used without further purification. Deionized water (resistivity of 18.25 MΩ cm) produced by a lab water purifier (Molecular Instrument Shanghai Co., MolecularΣH₂O) was used as both solvent and cleaning water. Diatomite powder was purchased from Changbai Diatomite Co., Ltd. Metal oxides and organic impurities in raw diatomite were eliminated by chemical and thermal treatments, separately. The diatomite powder was immersed into 0.5 M HCl aqueous solution with magnetic stirring at 60 °C for 2 h, rinsed with deionized water, and calcined in air at 500 °C for 1 h. To remove tiny fragments, diatomite powder after purification was added to saturated sucrose solution; supernatant liquid after low speed centrifugation at 500 × g for 5 min was discarded. This separation procedure was repeated three times, and final sediment was thoroughly washed with deionized water and dried in a vacuum oven at 60 °C.

Fourier transform infrared spectrum (FT-IR) of diatomite powder within the range of 4000–400 cm⁻¹ was recorded at room temperature using a FT-IR spectrometer (Bruker, IFS-66V/S) by the standard KBr disk method. X-ray diffraction (XRD) pattern of diatomite powder was collected by a diffractometer (Rigaku, D/max 2550) with monochromatized CuKα (λ = 1.541874 Å) radiation source, operating at 50.0 kV and 200.0 mA. Surface morphology and elemental composition of diatomite particles were observed through field emission scanning electron microscope and energy-dispersive X-ray spectrometry (FE-SEM and EDX, JEOL, JSM-6700F) with an operation voltage of 15 kV. Ultraviolet-visible (UV-VIS) absorption spectra of aqueous solutions were tested by a UV-VIS spectrometer (Shimadzu, UV-3600).

2.2. Preparation of cationic dye-diatomite composite powders

All adsorption measurements were carried out under ambient conditions. Aqueous solutions of cationic dye (MB, ST, MG or CV) with concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 mg L⁻¹ were prepared as standard solutions. 100 mg diatomite powder was added into corresponding aqueous solution of cationic dye with an initial concentration of 2.5 mg L⁻¹, volume of 100 mL and pH of 8.0 by adding sodium hydroxide solution. The suspension was kept stirring for 1 h and centrifuged to obtain supernatant. Based on UV-VIS spectra of the standard solutions and the supernatant, adsorption amount of a specific cationic dye in diatomite (Q_d , mg g⁻¹) can be calculated according to the following equation:

$$Q_d = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i (mg L⁻¹) is the initial concentration, C_e (mg L⁻¹) is the equilibrium concentration, V (L) is the volume of solution, and m (g) is the mass of diatomite. Based on the above adsorption measurements, a green and simple batch method was carried out to prepare four kinds of cationic dye-diatomite composite powders at room temperature. Briefly, 5.0 g diatomite powder was dispersed into 50 mL deionized water. Cationic dye (MB, ST, MG or CV) with a mass of 1.2-fold Q_d was added to this suspension and it was then kept stirring for 1 h. After that, sediment collected by filtration was rinsed with a solution containing 5% ethanol and 95% deionized water to remove free dye molecules,

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