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One-step synthesis of solid state luminescent carbon-based silica nanohybrids for imaging of latent fingerprints

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ABSTRACT

Fluorescent carbon-based nanomaterials(CNs) with tunable visible emission are biocompatible, environment friendly and most suitable for various biomedical applications. Despite the successes in preparing strongly fluorescent CNs, preserving the luminescence in solid materials is still challenging because of the serious emission quenching of CNs in solid state materials. In this work, fluorescent carbon and silica nanohybrids (SiCNHs) were synthesized via a simple one-step hydrothermal approach by carbonizing sodium citrate and (3-aminopropyl)triethoxysilane(APTES), and hydrolysis of tetraethyl orthosilicate(TEOS). The resultant SiCNs were characterized through X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR, X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) spectroscopy. The SiCNs exhibited strong fluorescence in both aqueous and solid states. The luminescent solid state SiCNs power were successfully used as a fluorescent labeling material for enhanced imaging of latent fingerprints(LFPs) on single background colour and multi-coloured surfaces substrates in forensic science for individual identification.

1. Introduction

Fluorescent carbon-based nanomaterials(CNs), owing to their outstanding optical properties, less toxicity and biocompatibility, superior visible-light photocatalytic activity, and cost-effective preparation, have become popular materials in bioimaging [1,2], sensing [3], optoelectronics [4], and photocatalysis [5–7]. To date, many strategies like choosing different precursors and doping with other heteroatoms have been developed for improving the optical properties to expand their application of CNs [8]. Despite the successes in preparing strongly fluorescent CNs, preserving the luminescence in solid materials is still challenging. In past studies, the solid-state luminescent performance of CNs was not satisfactory because of the strong fluorescence quenching that occurs in the dry and aggregated states [9]. Therefore, the massive research efforts focusing on the applications of fluorescent CNs in aqueous environments, such as bioimaging and chemical sensing, and the development of their solid state properties and applications are in high demand.

Fingerprint detection in forensic sciences is an indispensable source of evidence for identification purposes. Fingerprints acts as the most powerful tool for identifying people because the ridge patterns of every print are unique and immutable. The most commonly found fingerprints at crime scenes are typically latent and can only be visualized and identified by certain techniques. Up to now, various methods, such as powder (metallic, magnetic, or fluorescent powder) dusting [10–12], iodine fuming [13] and mass spectrometry [14] techniques, have been studied and applied for detection of latent fingerprints(LFPs). For example, zinc oxide layer can be added around gold nanoparticles to get luminescent fingermarks [15]. Moret et al. reported application of the fluorescent dye incorporated silica nanoparticles to imaging of LFPs [16]. In particular, the use of quantum dots (QDs) as fluorescent labeling marks in LFPs detection has attracted significant research interest in forensic science; this is because of their unique physical and chemical properties such as small particle size, large surface area, good photochemical stability, and high fluorescent intensity. A series of QDs, including CdS, CdSe, and CdTe QDs, have been explored for LFPs development [17–19]. However, the toxicity of these QDs, especially with Cd^{2+} being classified as a carcinogen, is of increasing concerns. Moreover, these LFPs detection methods are also tedious. Therefore, a novel type of fluorescent nanoparticles with high efficiency and low toxicity is needed for the development

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of LFPs in the field of forensic chemistry.

Photoluminescent CNs have become popular imaging and sensing materials in the biomedical field, but their use in fluorescence imaging of LFPs has not been well-recognized. Up to now, several methods, including electrochemical [20], hydrothermal [21], and solid-phase synthesis methods [22], have been used for preparation of fluorescent CNs. Among these methods, the hydrothermal method has been widely applied to prepare various materials [23,24], because of the high reactivity of the reactants, easy control of the solution, little harm to the environment, and low energy consumption under hydrothermal conditions [25]. In this research, we used a typical hydrothermal method to chemically synthesize fluorescent carbon and silica nanohybrids (SiCNHs) powder with uniform size and strong fluorescent intensity that can be used to develop LFPs. Although carbon dots-based hybrid powders have been reported for LFPs detection, their fluorescence are too weak to be seen by naked eyes, and the developed fingerprints using the fluorescence microscopy images with point patterns were obtained [26]. For the first time we report the use of solid state SiCNHs as a novel fluorescent labeling agent for completely developing whole latent fingerprints. We successfully used SiCNHs to clearly image LFPs on various nonporous single background colour substrates, including marbles, transparent tape, white ceramic tiles, black plastic pages, stainless steel sheets, painted wood and multi-coloured surfaces materials (drink bottle foils and fresh fruits). LFPs detection using SiCNHs dry powder as fluorescent labeling markers can be well-defined in terms of finger ridge details, resulting in a good definition of enhanced detection.

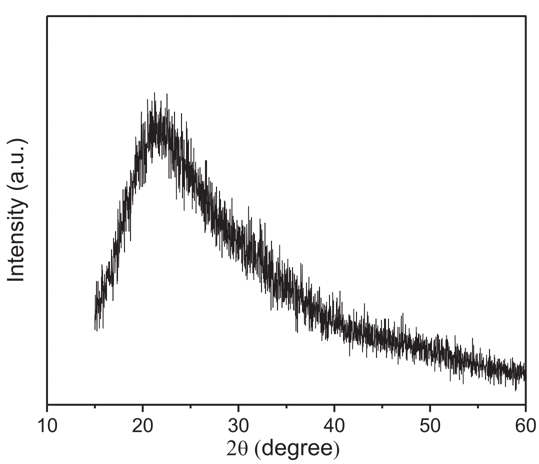

Fig. 1. XRD pattern of the SiCNHs.

2. Materials and methods

2.1. Materials and reagents

Sodium citrate, 3-Aminopropyltriethoxysilane (APTES), tetraethyl orthosilicate (TEOS), ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). All the reagents were of analytical grade and were used as received without further purification.

2.2. Preparation of luminescent SiCNs powder

1.0 g sodium citrate was dissolved in 50 mL deionized water in a 100 mL glass beaker, and then 1.0 mL APTES was added into the solution to form a homogeneous solution under magnetic stirring. Then, 1.0 mL TEOS was added dropwise into the solution followed by further stirring for 30 min. After that the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 4 h in a constant temperature drying oven. After the above reaction, the reactor was cooled down to room temperature naturally. Subsequently, the prepared SiCNs were collected by centrifugation at 8000 rpm for 5 min and washed with deionized water twice and with ethanol once, and then dried at 50 °C for 12 h. The solid luminescent SiCNs dry powder was thus obtained.

2.3. Imaging of latent fingerprints with SiCNs

To collect fingerprints from volunteers, fingers from clean hands were gently wiped across the forehead. Then latent fingerprints were pressed on several different surfaces of objects. For the supreme step, single appositions were collected from one donor on selected substrates. For studying aged fingerprints, the fresh fingerprints were left open to air in Petri dishes at room temperature. To detect the latent fingerprints, SiCNHs in the form of dry powder were carefully deposited onto the surfaces of the substrates, followed by a light brushing action to remove the excess powder. Then the prepared samples were illuminated with UV lamp (6W, 365 nm) and the images of the fingerprints were photographed using a Canon EOS 500D digital camera with a Canon 10–55 zoom lens.

2.4. Characterization

The SiCNHs were characterized by XRD on an X'Pert Pro diffractometer (PANalytical Co., Holland) with graphite monochromatized Cu K_{α} radiation ($\lambda = 0.15406$ nm). They were imaged under a JEM-2100 transmission electron microscopy (JEOL Ltd.,

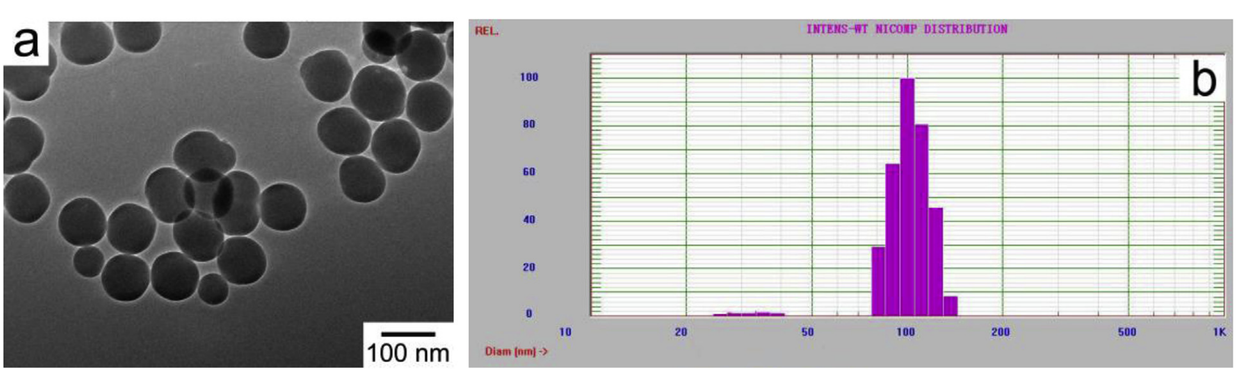

Fig. 2. (a) TEM image and (b) DLS particle size distribution of SiCNHs.