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Full Length Article

α-Fe_2O_3@dopamine core-shell nanocomposites and their highly enhanced photoacoustic performance

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ABSTRACT

In this work, multifunctional α-Fe_2O_3@dopamine core-shell nanocomposites consisting of α-Fe_2O_3 core surrounded by a thin dopamine (DA) shell have been successfully fabricated. The crystal structure, surface morphology and optical properties of the samples were determined by XRD, SEM, TEM and UV–vis, respectively, indicating that the presence of thin DA shell could affect the optical properties of Fe_2O_3 nanostructures. When it was incubated with NIH3T3 cells and injected in living body, the concave shape Fe_2O_3@dopamine nanocomposites exhibited the highest cell viability (94.6% within 16 h), and harmless to the living body. Moreover, the concave shape Fe_2O_3@dopamine nanocomposites also displayed the highest image contrast and distinguishability (3.74 times of control group, and 1.5 times of purchased Au nanoparticles). Thus, α-Fe_2O_3@dopamine core-shell structures are promising candidates for precise photoacoustic imaging and therapeutic process.

1. Introduction

Photoacoustic imaging (PAI), as a promising technique, combines the spectroscopic capability of light with the penetrability of ultrasound can provide high resolution functional information such as hemoglobin and blood oxygenation relevant to physiology and pathology [1–5]. This method, however, may have a limited detection depth and lack of effective endogenous contrast. The exogenous contrast agents are often needed to effectively enhance the imaging contrast and potentially break through the imaging depth limit [6–9].

Nanomaterials, especially that with broad absorption band in near infrared region (NIR) window, like Au nanoparticles [10,11], sulfide or selenide nanostructures [12,13], polymer nanoparticles [7,10,14], hybrid nanosystems [15–17], etc., have attracted great interest in biomedical sciences for applications such as (CT), PAI, fluorescence imaging (FI) and photothermal therapies (PTT). However, fancy cost, complicated chemistries coating, biodegradable and potential long-term toxicity restrain their wide application in clinical [12,18,19]. Super-paramagnetic iron oxide nanoparticles, combine low cost, hypotoxicity, good stability, superior magnetic and optical properties within a single nanostructure, offer an opportunity for multimodal bioimaging and theranostic applications [20–23]. For instance, nanoclusters of superparamagnetic iron oxide nanoparticles coated with poly (dopamine) have been prepared and successfully used for ultrasensitive magnetic resonance imaging (MRI) guided PTT [20]. Likewise, magneto-optical nanoparticles have been designed for cyclic magnetomotive PAI, which can dramatically reduce the influence of the background signals and produce high-contrast molecular images [22]. However, there are more efforts to improve the biocompatibility performance of the relative iron oxide nanoparticles.

Dopamine (DA), a typical organic chemical from the phenethylamine families, plays several important roles in the brain (neurotransmitter) and body (a small-molecule mimic of the adhesive proteins of mussels) [24,25]. Under alkaline pH and oxidative conditions, DA can be self-polymerized to form polydopamine (pDA), which is chemically stable, biocompatible and can be deposited onto different surfaces [20,24–29], allowing for its use in various biomedical applications. Recently, pDA has been used as a photothermal therapeutic agent for in vivo cancer therapy because of its strong NIR absorption and high photothermal conversion efficiency (40%) [26]. Considering these features, it is hypothesized that DA could be a useful material in the preparation of multi-functional nanocomposites for theranostic applications.

In this work, various shapes of multifunctional α-Fe_2O_3@DA core-

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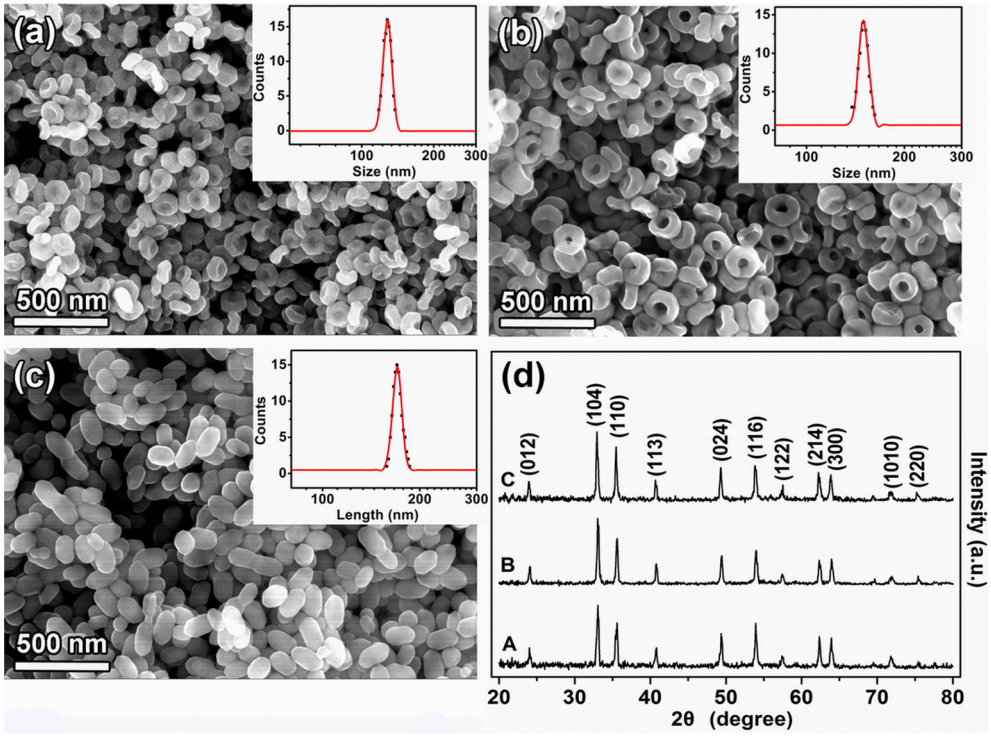

Fig. 1. Typical morphology and structure of α-Fe_2O_3 nanoparticles. (a) concave; (b) ring; (c) short rod; (d) XRD patterns of the prepared α-Fe_2O_3 nanoparticles, 'A', 'B', and 'C' represent concave, ring and rod shape α-Fe_2O_3, respectively.

shell nanocomposites (consisting of α-Fe_2O_3 core surrounded by a thin DA shell) have been successfully fabricated. The α-Fe_2O_3 core enhances the capacity of the nanocomposites as contrast agents for PAI, and the DA shell can also be employed for PAI and PTT, due to its NIR absorption. Although the synthesis of iron oxide coated with poly (dopamine) have been reported [20,30,31], to the best of our knowledge, the PAI applications of α-Fe_2O_3@DA have not been systemically explored. Our results suggest a high potential use of DA in the construction of multifunctional nanocomposites for PAI and PTT.

2. Experimental section

2.1. Preparation of Fe_2O_3 nanocrystals

All chemicals (unless specified) were all purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. Fe_2O_3 nanocrystals were synthesized by a modified hydrothermal method [32,33]. In a typical procedure (Sample A, Fe_2O_3 nanoconcaves), 0.324 g ferric chloride hexahydrate (0.02 M), 0.0047 g sodium sulfate (0.55 mM) and 0.00048 g sodium dihydrogen phosphate (0.05 mM) in a 100 mL flat-bottomed flask. The mixture was stirred with a magnetic blender for about 10 min and then transferred into a stainless-steel autoclave with a capacity of 100 mL, sealed and heated at 220 °C for 5 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The brick red precipitate was centrifuged, washed several times with distilled water and absolute alcohol, and finally dried in a dry oven at 60 °C for 5 h for further characterizations. Likewise, the Fe_2O_3 nanorings (Sample B) and short rods (Sample C) could also be obtained by changing the dosage of sodium dihydrogen phosphate as 0.075 mM and 0.2 mM, respectively.

2.2. DA modification of Fe_2O_3

First, iron oxide nanoparticles were soaked by ammonium hydroxide for 24 h. The production was centrifuged, washed several times with distilled water and finally dried in a drying oven for further application. Then, 3.793 g of dopamine hydrochloride (0.02 M) was dissolved in 2 mL of acetonitrile solution, followed by the addition of 2 mL suspension of hydroxylated Fe_2O_3 nanoparticles (30 mg mL^{-1}) in acetonitrile, and finally adjusted the pH value to about 8.5. After sonicating for 30 min, the DA decorated iron oxide nanoparticles were centrifuged and washed several times with acetonitrile and absolute alcohol.

2.3. Characterization

The morphology and structure of the prepared Fe_2O_3 nanoparticles were identified by scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, JEOL 2100F, 200 kV). UV–Vis absorbance of various Fe_2O_3 nanoparticles, were identified by spectrophotometer (Shimadzu, 3100 UV–Vis-NIR). The photoacoustic signals were recorded and normalized by the unit rotation scanning photoacoustic detection system (Fig. S1), which contains laser device (Surelite I-20, Continuum), optical parametric oscillator (OPO) (Surelite OPO Plus), non-focused ultrasonic transducer (PMUT) (V310-SU, Olympus, 5 Hz), motor step rotating table and its motor control box (MC) (M600, Beijing Zhuo Li Han Guang Instrument Co., Ltd.), preamplifier (5077PR, Olympus), PCI4732 data acquisition (DAQ) card, etc. 532 nm laser was directly launched from the laser device, and further multi-wavelength lasers were oscillated by the OPO.