Laser-induced fabrication of highly branched CuS nanocrystals with excellent near-infrared absorption properties*

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We report on the successful fabrication of highly branched CuS nanocrystals by laser-induced photochemical reaction. Surprisingly, the single-crystalline nature with preferential alignment of the (107) orientation can be well improved during the moderate growth process. The branch length drastically increases from about 5 nm to 6 μm with an increase of photochemical reaction time (0–40 min). The absorption spectra of as-prepared CuS nanodendrites show that localized surface plasmon resonance (LSPR) peaks can be modulated from about 1037 nm to 1700 nm with an increase of branch length. Our results have a promising potential for photodynamic therapy and biological imaging application.

Keywords: laser-induced photochemical reaction, CuS nanodendrites, single-crystalline nature, near-infrared absorption

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1. Introduction

The possibility of using laser light as a convenient and versatile tool for sculpting micro- and nano-structures has prompted the recent renewed interest in the multi-functional material systems.[1–5] Many interesting works, such as micro-nano scale ripples,[3] nano-sponges,[6] and subwavelength ripples,[5] have been reported by laser direct writing technique. In 2016, Terakawa *et al.* demonstrated the construction of three-dimensional (3D) metal microstructures in biocompatible poly-based hydrogel by laser-induced photoreduction.[2] Moreover, the laser light is also an excellent source that can be adopted in photochemical reactions to convert soluble metal ions into their atomic state, which then facilitates the overgrowth of novel nano-materials.[1,2,4,7,8] Most recently, an outstanding work illustrated the anisotropic growth of Au nano-prisms via laser-induced photochemical reactions in methanol solution.[1] In addition, our groups have also confirmed that laser irradiation is an attractive green and versatile technique for the fabrication of Ag quantum dots,[9] Au/TiO_2 nanodendrites,[10] organic-metal Ag/P3HT,[11] Ag_2S/Ag nanoparticles,[12] porous ZnS/Zn,[13] tadpole-shaped Au nanoparticles,[14] and TiO_2 nanocages.[15] Compared with those standard chemical fabrications, the distinctive feature of the photochemical route is that the novel strategy is developed by laser irradiation without using any potential toxic issues and complicated stabilizers or soft directing agents.

Up to now, although a number of nanostructures have been synthesized by laser-induced fabrication, the shape-controlled synthesis of highly branched nanostructures has not been explored as extensively as for hybrid nanoparticles (core-shell shapes and porous-cages). Compared with other nanostructures, the anisotropic architectures, especially highly branched structures based on plasmonic metals (Ag, Au, and Cu), are anticipated to provide an ideal localized surface plasmon resonance (LSPR) in the near-infrared region (NIR) (> 1000 nm).[16–19] It has great potential as clinical cancer photothermal therapies. It should be noted that the Au/TiO_2 nanodendrites results[10] demonstrated that the laser irradiation only provided the generation of hydroxyl radical (OH) groups on TiO_2 surface. In fact, the branched Au@TiO_2 nanostructures have been generated by the reduction of $HAuCl_4$ and overgrowth of Au on the TiO_2 nanospheres with OH groups. To our knowledge, the direct fabrication of highly branched nanodendrites with controllable structures has not been reported through the laser-induced photochemical route.

Herein, for the first time, we expand the realm of anisotropic nanostructures accessible via laser-induced photochemical reaction with the demonstration of optical excitation-driven highly branched copper sulfide (CuS) nanocrystals synthesis. The hot electron–hole pairs produced via optical excitation play an important role in the subsequent anisotropic

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growth of CuS nanodendrites. After 40 min laser irradiation, the branch length increases from about 5 nm to 6 μm. Moreover, the CuS single-crystalline nature with preferential alignment of the (107) orientation can be well improved through the photochemical reaction. Meanwhile, the corresponding absorption spectrums reveal that the LSPR peaks can be effectively modulated from about 1037 nm to 1700 nm. The as-prepared CuS nanodendrites with excellent NIR absorption properties have promising potentials for developing important novel biomedical sensors. This is no doubt that the present results will be a breakthrough in the fabrication of anisotropic metal sulfide nanocrystals using laser light as an energy input.

2. Methods

The experimental apparatus based on laser irradiation in liquid is similar to that described in our previous studies.[9–15] Briefly, a well-polished Cu metal as the target was placed on the bottom of a rotating glass dish with a speed of ∼ 200 rpm. It was filled with 4-mm depth of liquid solution containing 0.7 M thioacetamide (TAA) and 15 mL distilled water. The TAA will provide the sulfur sources for the construction of CuS nanodendrites. A Q-switch Nd-YAG (yttrium aluminum garnet) laser (Quanta Ray, Spectra Physcis) beam operating at wavelength of 1064 nm with a pulse duration of about 6 ns and 10 Hz repetition was focused onto the Cu target by a quartz lens with 60 mm focal length. The power density of the laser beam was about 1.6 GW/cm^2. The irregular CuS nanoparticles will be generated by laser ablation for 20 min. Then, the CuS colloidal suspensions were irradiated under different time region (0–40 min) by the non-focused laser beam with the same parameters in the laser ablation. The morphological investigations and chemical composition measurements of the products were performed by transmission electron microscope (TEM, JEOL-JEM-2100F), field emission scanning electron microscope (SEM, Hitachi S-4800), and energy-dispersive X-ray spectroscope (EDS). The detailed sample compositions were studied by X-ray photoelectron spectra (XPS) on a PHI Quantera SXM with an Al Kα = 280.00 eV excitation source. The crystallographic investigations of products were analyzed by x-ray diffraction (XRD) patterns (Rigaku RINT-2500VHF) using Cu Kα radiation. The absorption spectrums were recorded by a UV–IR spectrometer (Cary 50).

3. Results and discussion

After cumulative pulse laser ablation of Cu target in TAA solution, the obtained CuS nanomaterials were served as seeds for further fabrication of branched nanodendrites. The low- and high-resolution images of the as-prepared products are analyzed by TEM, shown in Figs. 1(a) and 1(b) respectively. The morphology in Fig. 1(a) clearly shows that numerous nanoparticles are irregular quasi-sphere and meatball-like structures. The meatball-like nano-structures with sizes varying from about 15 to 18 nm are likely to be fabricated one-by-one separately, and are almost not hinge joined. The average length of these protuberant parts in each meatball is about 5 nm by measuring the diameters of more than 300 nanoparticles in sight on the TEM images. The high-resolution TEM (HRTEM) image in Fig. 1(b) provides a typical structural detail of the nanoparticles. The regions marked by cyan lines in Fig. 1(b) with a d-spacing of 0.19 nm are indexed as the (107) plane in the CuS (covellite) structure. On the other hand, the areas marked by yellow lines with a periodicity corresponding to a d-spacing of 0.28 nm should be indexed with reference to the CuS (103) plane structure. Moreover, the XRD pattern of the CuS in Fig. 1(c) illustrates that a series of (102), (103), (105), (107), and (116) CuS (covellite, JCPDS, no.06-0464) diffraction peaks were indeed detected at 29.277°, 31.784°, 38.835°, 47.78°, and 59.345°, respectively. The inset in Fig. 1(c) shows the chemical compositions of the obtained nanoparticles. The result of EDS clearly demonstrates that the nanoparticles are composed of Cu and S elements. The ratio of Cu and S is calculated about 4.99:5.01, which is consistent with the CuS composition. Figure 1(d) depicts corresponding LSPR spectra of the obtained CuS colloidal solution. The LSPR peak can be detected at about 994 nm in NIR region, which is coincident with the previous reports.[14–16] The obtained CuS nanomaterials with meatball-like structures are beneficial to fabricate branched nanodendrites in the next process.

Based on the meatball-like CuS precursors, the anisotropic growth of branched CuS nanodendrites was carried out by laser-induced photochemical reaction. Figure 2 depicts a schematic growth diagram of CuS nanodendrites. At the moment of the pulse laser arriving at the Cu target, rapid boiling and vaporization of Cu element will result in the formation of explosive Cu plasma with ultra high temperature. The nucleation of Cu and S species (from TAA hydrolyzing reactions) can take place in the stage of rapid condensation of the plasma, and sharply terminate due to the expiration of the pulse laser. The CuS nanoparticles containing many twin planes and stacking faults are formed through the unique nucleation process.[9–13] In the next photochemical reaction, some larger CuS precursors are more stable against laser irradiation, and they grow at the expense of less stable nanoparticles with smaller sizes. The unstable CuS nanoparticles will be dissolved into Cu^{2+} and S^{2-} ions by laser fabrication, providing Cu^{2+} sources in solution for subsequent nanodendrites growth. It is well known that the optical excitation of surface plasmons in the photochemical synthesis can induce charge

separation (hot electron–hole pairs) on the nanoparticle surface. It can lead to face-selective reduced metal ions and anisotropic crystal growth, which is also coincident with our case.[14–17] The 1064 nm laser irradiation ensures that the incident excitation wavelength is commensurate with the LSPR (994 nm) of CuS precursors, which can efficiently separate photo-excited electron–hole pairs. The Cu^{2+} and S^{2-} ions in the colloidal solution will be separately reduced and oxidized by these hot electrons and holes, respectively. The laser irradiation can be used to convert soluble ions into their atomic states, resulting in the anisotropic growth of Cu and S species on the precursors. The photochemical reaction will propagate in the whole solution until all the CuS precursors are converted into much larger and more stable branched structures that can survive against the laser irradiation due to their higher redox potentials.

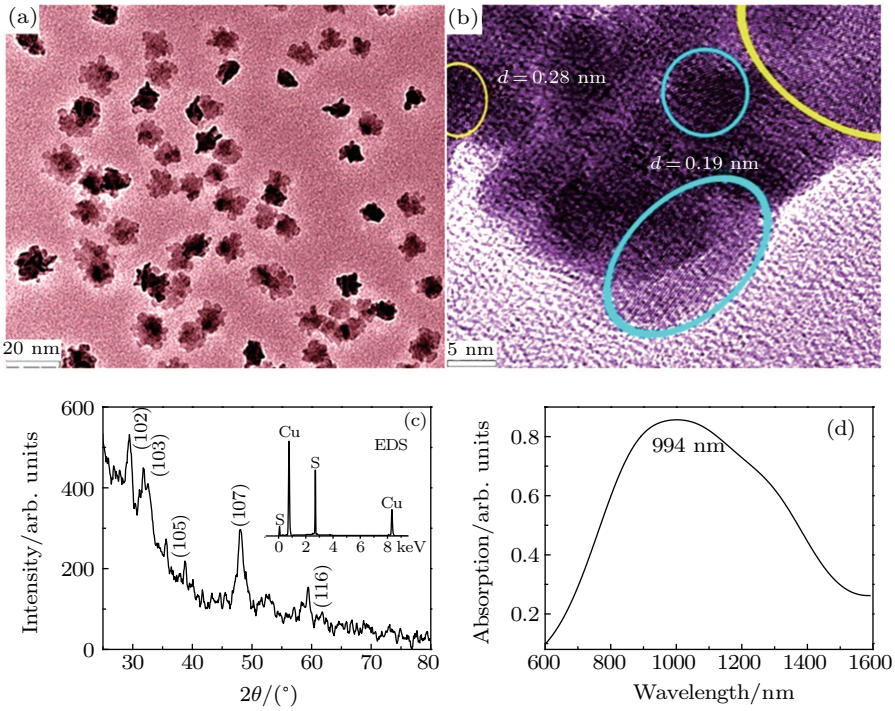


Fig. 1. (color online) The representative low-magnification (a) and enlarged (b) TEM images of the CuS nanoparticles by laser ablation of Cu in TAA solution. (c) XRD pattern of the products. The inset shows the EDS analysis. (d) The absorption spectra of the colloidal suspension.

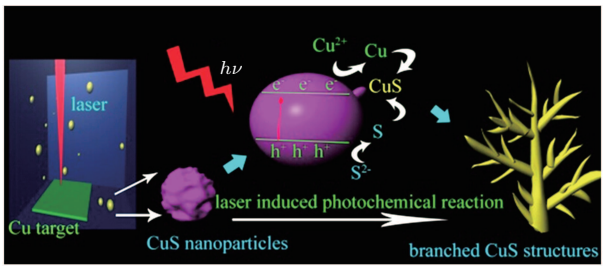


Fig. 2. (color online) Schematic growth of the branched CuS nanodendrites via laser-induced photochemical reaction.

To verify this laser-induced photochemical strategy, we increase the laser irradiation time to 10 and 40 min, respectively. The typical TEM images of the obtained products are illustrated in Figs. 3(a) and 3(b). The results show that the morphologies of meatball-like CuS nanoparticles have been significantly developed into branched nanostructures by laser-induced photochemical reaction. After 10 min reaction, the representative TEM image in Fig. 3(a) reveals that the individual CuS dendrite is composed of a solid body with multiple and elongated branches on its surface. Close view of these nanodendrites indicates that the branches are composed of numerous small nanoparticles, which are interconnected and accreted with each other. The average length of the branches (from the tops to the core surface) is about 200 nm by measuring the sizes of more than 300 nanodendrites in sight on the TEM images. It is clear that the photochemical reaction generated by laser irradiation of the CuS precursors will result in the anisotropic growth of Cu and S species on the surface of the stable nano-seeds. Increasing the reaction time should lead to highly branched nanodendrites. Figure 3(b) demonstrates the fascinating structures obtained by 40 min laser irradiation. The obvious branched CuS structures with large quantity (yield $> 99\%$) are uniformly well-defined multi-dendrites. Meanwhile, the morphology in the Fig. 3(b) also shows that the CuS dendrites are interconnected and accreted with each other, forming circular ring-like microstructures. The average length of the elongated branches is about 6 μm, which is about

1000 times longer than that of the protuberant parts in CuS precursors. Moreover, the less stable CuS nanoparticles with smaller sizes in original solution cannot be detected in the final products. It is reasonable to deduce that the stable meatball-like CuS precursors can be completely converted into highly branched structures via the laser-induced photochemical reaction.

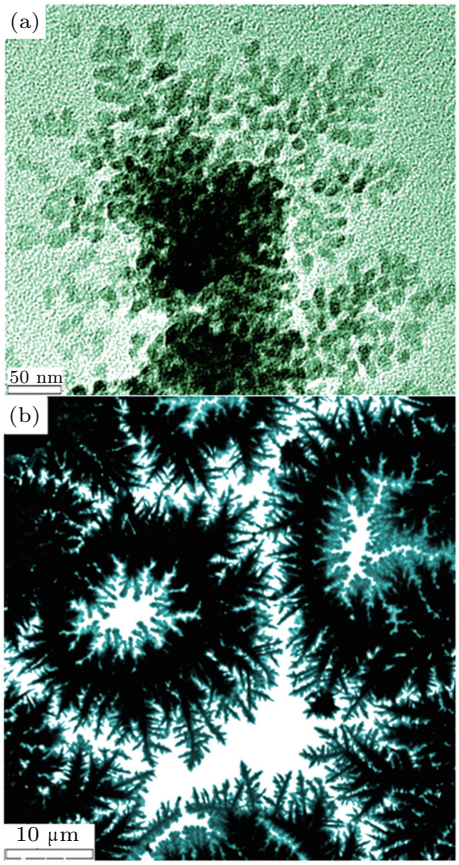


Fig. 3. (color online) The typical TEM images of the branched CuS nanodendrites obtained by laser irradiation for 10 min (a) and 40 min (b).

Figure 4(a) shows the HRTEM image of the highly branched CuS structures generated by laser irradiation for 40 min. It provides a typical structural detail of the branches. Surprisingly, the insets in Fig. 4(a) illustrate that the obtained CuS nanodendrite is found to be highly crystalline according to the clear lattice fringes. The two different regions at top and stem both have a d-spacing of 0.19 nm, which should be indexed with reference to the CuS (107) plane. Moreover, the XRD pattern in Fig. 4(b) is also the best evidence for the fabrication of single-crystal CuS nanodendrites. Three distinct peaks are observed at 31.784°, 47.78°, and 59.345°, corresponding to (102), (107), and (116) lattice planes of CuS covellite structure. Because of the much higher peak at 47.78° in XRD pattern, the preferential alignment of the CuS (107) orientation should be formed in the final branched products. Compared with the crystallographic investigation in CuS precursors, after laser irradiation process, (103) and (105) plane-structures should be less stable structures, which cannot be detected in the final branched CuS nanodendrites. The single-crystalline nature with preferential alignment of the (107) orientation can be significantly improved during the overgrowth of branched CuS structures.

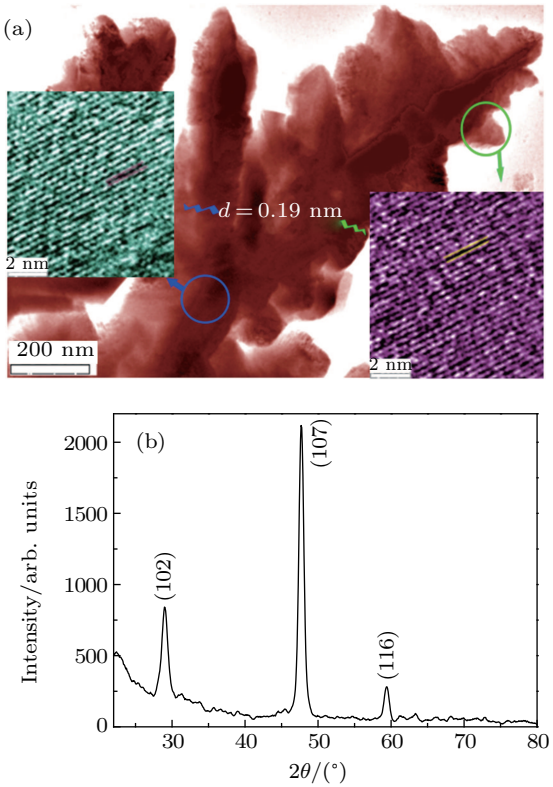


Fig. 4. (color online) (a) The enlarged TEM image of the highly branched CuS nanostructures. The insets show the HRTEM images of the top and stem region. (b) The XRD pattern of the obtained CuS nanodendrites.

In order to further verify the element valence state of CuS nanodendrites, the x-ray photoelectron spectroscopy (XPS) results are illustrated in Fig. 5. In the XPS spectra, the binding energies were calibrated by referencing the C1s peak (284.9 eV) to reduce the sample charge effect,[20–22] which is also coincident with our case. The oxygen impurity in the spectra (530.7 eV) is attributed to the surface oxide after keeping them in an oven. The peaks of Cu2p and S2p as well as Cu(A) (from Auger electrons) can be clearly detected in Fig. 5(a). In Fig. 5(b), the peaks at 932.6 eV ($Cu2p_{3/2}$) and 952.1 eV ($Cu2p_{1/2}$) reveal that the oxidation state of Cu^{2+} formed in the nanodendrites. Moreover, the $S2p_{3/2}$ peak at 161.9 eV and the $S2p_{1/2}$ peak at 163.1 eV prove the element valence state of S^{2-} in the final products. The above result is the best evidence for the formation of CuS structures by laser-induced photochemical reaction in this paper.

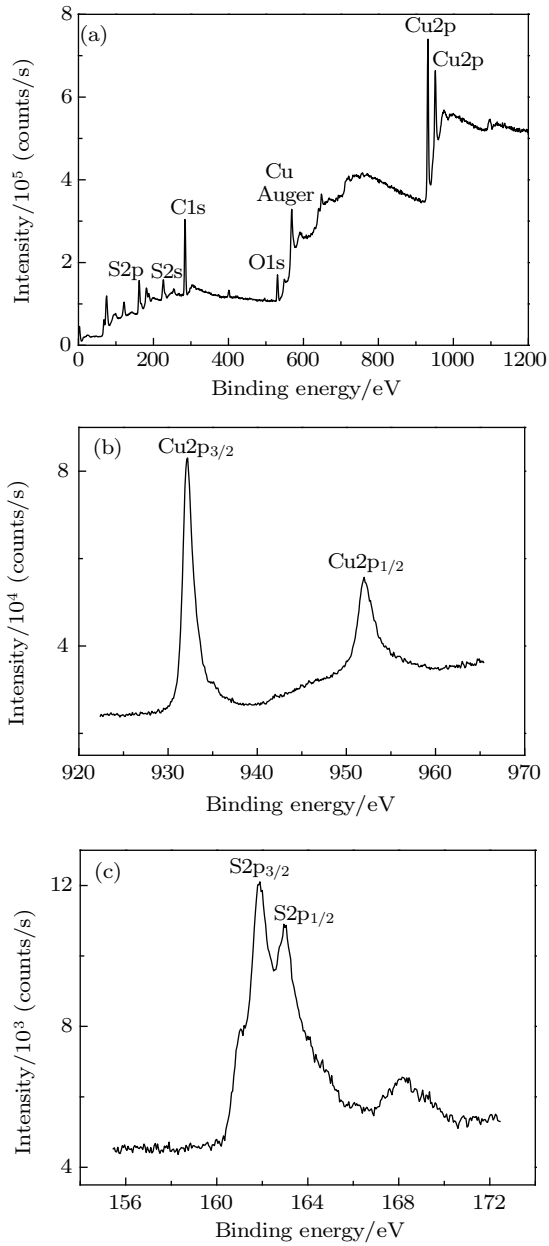


Fig. 5. XPS spectra of the CuS nanodendrites. (a) Survey structure, (b) $Cu2p_{3/2}$ and $Cu2p_{1/2}$ of the nanodendrites, and (c) $S2p_{3/2}$ and $S2p_{1/2}$ of the products.

The formation of highly branched CuS nanodendrites is also highly related to the laser parameters (laser power density and wavelength). If a higher-power ($\sim$ 3 GW/cm^2) 1064 nm laser beam was adopted in our experiments, the aggregated/agglomerated CuS nanomaterials with less obvious branched structures will be formed, as shown in Fig. 6(a). The most likely reason is that the higher laser energy significantly increases the temperature around the nano-seeds and gives rise to uncontrollable overgrowth of Cu and S species. On the other hand, the laser beam with wavelength in the visible region (532 nm) is also not suitable for the accurate growth of highly branched CuS nanodendrites. As shown in Fig. 6(b), 532 nm laser beam will lead to the formation of unpredictable poly-dispersed nanomaterials with irregular rugged structures. Compared with 1064 nm laser beam, the higher photon energy of 532 nm laser beam will result in the drastic overgrowth process, which will destroy and damage the highly branched structures. Therefore, the relatively low-power 1064 nm laser beam would be applicable to the controllable accurate growth of highly branched CuS nanodendrites.

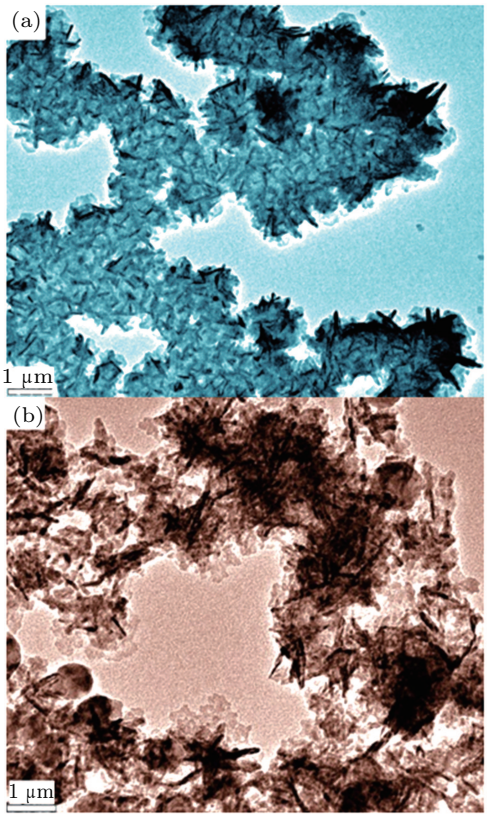


Fig. 6. (color online) The typical TEM images of CuS nanomaterials generated by (a) 1064 nm laser beam with a higher power density of 3 GW/cm^2 and (b) 532 nm laser beam.

Finally, the unique optical properties of the as-prepared CuS nanodendrites are illustrated by the absorption spectra in Fig. 7. It is interesting to note that the LSPR peaks can be modulated from about 1037 nm to 1700 nm with an increase of the photochemical reaction time. The increasing reaction time (0–40 min) results in the formation of higher branches in CuS nanodendrites, which leads to a significant change in the solution color from yellow to brown (inset in Fig. 7). Compared with the LSPR (994 nm) of CuS precursors, the highly branched CuS nanodendrites show excellent red-shifted absorption in NIR region. The enhanced NIR absorption property should be attributed to longitudinal plasmon wavelength of the highly branched CuS nanostructures with elongated branches. It is reasonable to deduce that the obtained CuS nanodendrites with excellent NIR absorption properties will be very suitable for developing a biomedical sensor in photodynamic therapy and biological imaging application.

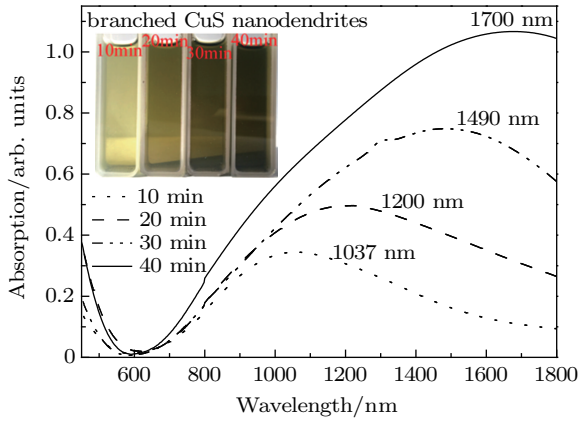


Fig. 7. (color online) The absorption spectra of the branched CuS nanodendrites fabricated by laser irradiation for 10, 20, 30, and 40 min, respectively. The insets show the corresponding photographs of CuS colloidal suspensions.

4. Conclusion

In this work, highly branched CuS nanocrystals have been successfully fabricated by laser-induced photochemical reaction. The moderate and anisotropic overgrowth process is based on the hot electron–hole pairs generated during optical excitation of surface plasmons on the CuS nano-precursors. Thanks to the highly branched CuS nanodendrites, the LSPR peak significantly red-shifts from about 1037 nm to 1700 nm. It is essential for the photodynamic therapy applications in the future. In the absence of any complicated stabilizers or soft directing agents, the report presents a green and effective route of wielding laser light as a versatile tool for sculpting highly branched nanostructures.

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