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COMMUNICATION

Photothermal synthesis of ultrafine Cu_xO nanoparticles on carbon nanotubes for photosensitized degradation

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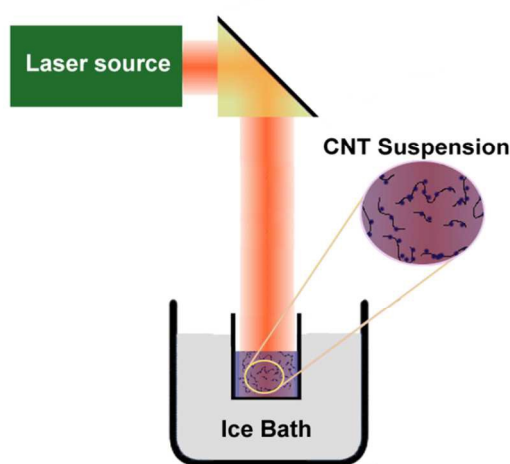
We exploit a facile strategy for photothermal synthesis (PTS) of Cu_xO nanoparticles (NPs) on carbon nanotubes (CNTs) suspended in solution, where the pulsed laser can penetrate through the liquid unimpeded and heat the CNTs selectively to a high temperature, thereafter, the hot CNTs trigger the chemical reactions to produce Cu_xO NPs directly on CNT surface. PTS yields ultrafine NPs with sizes of 3–5 nm, which distribute evenly and connect tightly with CNTs. The $\text{Cu}_x\text{O}/\text{CNTs}$ composite shows excellent photocatalytic property due to its cascade energy structure, smooth electron transfer between NPs and CNTs, and elimination of structural defects in CNTs by laser heating.

Copper oxides have been recognized as promising materials for photoelectrical applications.¹ Among various copper oxides, CuO and Cu_2O attract extensive attention due to their narrow band gaps (1.2 and 2.0 eV, respectively) for efficiently harvesting visible light.² Hitherto, Cu_xO ($x=1, 2$) materials have been applied in diverse fields such as lithium ion batteries, gas sensors, heterogeneous catalysts, and solar energy conversion.² Moreover, the combination of CuO and Cu_2O can promote the charge separation due to their type II band configuration,³ resultantly, $\text{CuO}/\text{Cu}_2\text{O}$ composite exhibits enhanced photoactivity superior to pure Cu_2O .⁴

Recently, several studies demonstrates that the combination of Cu_xO NPs with CNTs can improve the photocatalytic performance remarkably, because CNTs facilitate the dispersion of Cu_xO NPs as well as electron transport.⁵ $\text{Cu}_x\text{O}/\text{CNTs}$ composites have been prepared by several methods.⁶ For example, Yang et al obtained CuO/CNTs composite by two-step electrodeposition,^{6a} Luo et al synthesized CNTs beaded with Cu_2O nanospheres via a wet chemical route.^{6b} However, the reported methodologies usually involve complex precursors, and the Cu_xO NPs agglomerate seriously.⁶ Therefore, it is of practical importance to develop a facile strategy for the preparing high-quality $\text{Cu}_x\text{O}/\text{CNT}$ composite.

In previous works, we demonstrated that pulsed laser ablation in liquid is a simple and fast technique for the synthesis of nanostructures.⁷ More importantly, this technique shows unique advantage on achieving ultrafine and well-dispersed NPs because of the high heating and cooling rate created by the pulsed laser.^{7c} Accordingly, we propose to fabricate $\text{Cu}_x\text{O}/\text{CNT}$ composite by laser heating of CNTs suspended in the solution of Cu_xO precursors. As shown in Figure 1, the pulsed laser can penetrate through the solution unimpeded and heat the CNTs selectively to a high temperature, thus trigger the chemical reactions for the production of

Cu_xO NPs, which are more likely to grow in-situ on the hot CNTs, causing a tight connection. What's more, laser irradiation can remove the structural defects in CNTs,⁸ which benefits electron transfer and then final performance.⁹

Scheme 1. Experimental setup for PTS of $\text{Cu}_x\text{O}/\text{CNTs}$ composite.

In this communication, we verify the above hypothesis and succeed in preparing $\text{Cu}_x\text{O}/\text{CNTs}$ composite via PTS by utilizing a long-pulse-width laser (millisecond laser) to irradiate CNTs suspended in aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. Owing to the low power density of millisecond laser,^{7b} the CNTs are safe under laser irradiation, and PTS proceeds smoothly. We found that the product showed several merits over that by hydrothermal synthesis (HTS), such as ultrafine Cu_xO NPs, uniform distribution of Cu_xO NPs on CNTs, tight connection of Cu_xO NPs with CNTs, and reduced defect numbers in CNTs. Resultantly, the $\text{Cu}_x\text{O}/\text{CNTs}$ composite exhibits photocatalytic performance superior to that by HTS.

Three samples were prepared to investigate the PTS process. Sample A is the CNTs treated by mixed nitric acid and sulphuric acid, which were used as the starting materials for HTS and PTS. Samples B and C are $\text{Cu}_x\text{O}/\text{CNTs}$ composites by PTS and HTS, respectively. The morphologies of NPs synthesized by the two methods are quite different. As shown in Figure 1a,

ultrafine (3-5 nm) NPs by PTS distribute homogeneously on CNTs under 21.5 J/mm² laser irradiation. High resolution transmission electron microscope (HRTEM) image shows that NPs tend to grow at the wall steps on CNTs, forming a tight connection (Figure 1b). XRD pattern suggests that CuO and Cu₂O phases coexist in the product (Figure 1e). As the laser current increases to 45.4 and 65.2 J/mm², the Cu_xO NPs become larger and many of them aggregate together (Figure S2). However, the molar ratio of CNTs to Cu(Ac)₂ does not make an obvious impact on the size and distribution of Cu_xO NPs (Figure S3).

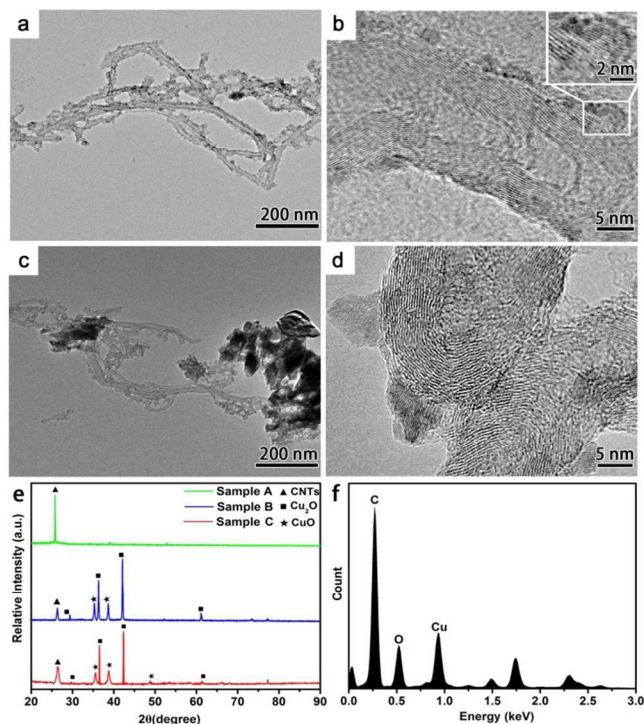


Figure 1. Characterizations on the products by PTS and HTS. (a) TEM image and (b) corresponding HRTEM image of sample B by PTS under 21.5 J/mm² laser irradiation for 2 min. (c) TEM image and (d) corresponding HRTEM image of sample C by HTS. (e) XRD patterns of samples A, B, and C, (f) EDS spectrum of sample B.

HTS produces CuO and Cu₂O NPs as well (Figure 1e), however, the NPs tended to agglomerate (Figure 2c), and tiny NPs were seldom found on CNTs. HRTEM image suggests a loose connection between NPs and CNTs (Figure 1d). Moreover, when the acid-treated CNTs were replaced as-received CNTs (see Figure S4a), Cu_xO NPs did not grow on the CNTs any more after HTS (Figure S4b)

FTIR spectra were measured to detect the change of functional groups (Figure 2a). The spectrum from sample A exhibits absorption bands at 1062, 1715, and 3436 cm⁻¹, which arise from the alkoxy C-O stretching,¹⁰ C=O stretching of carboxylic acid groups,¹¹ and O-H stretching of hydroxyl groups,¹² respectively, illustrating the presence of abundant carboxylic groups on the surface of CNTs. The composite by HTS displays a similar spectrum. On the contrary, the product fabricated by PTS shows much lower absorption intensity at 1062, 1715, and 3436 cm⁻¹, which suggests the removal of carboxylic acid groups after laser irradiation. Moreover, the weak band at 670 cm⁻¹ appeared in composite samples can be assigned to

Cu-O bonds of copper oxide structure,¹³ indicating the formation of Cu_xO NPs.

Raman spectra were collected to clarify the influence of laser irradiation on the structure of CNTs (Figure 2b). The ratio of diamond-band intensity to graphite-band intensity (I_D/I_G) reflects the structural perfection of CNTs, the higher I_D/I_G value, the lower structural perfection. The CNTs after HTS give an I_D/I_G value of 1.49, while the I_D/I_G value of the samples by PTS first decreases and then increases with the laser intensity. At the laser current of 21.5 J/mm², the I_D/I_G value reaches the minimum, 1.32, which means the defect density was somewhat reduced.

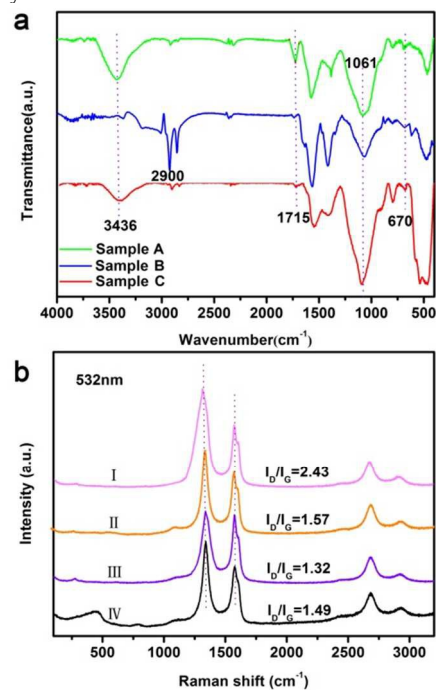
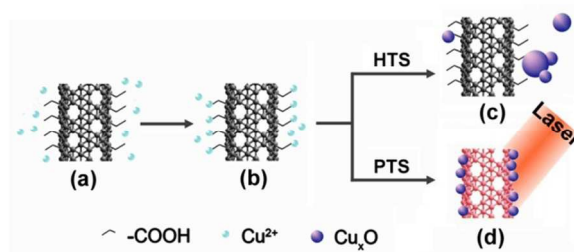
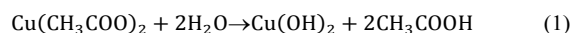


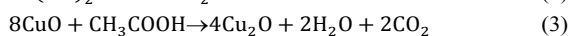
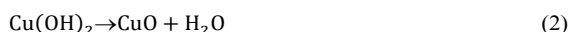
Figure 2. Surface and internal structure of CNTs. (a) FTIR spectrum, (b) Raman shift of CNTs treated by laser under current density of 65.2 J/mm², (II) 45.4 J/mm², (III) 21.5 J/mm², (IV) 0 J/mm².



Scheme 2. Proposed mechanism for HTS and PTS of Cu_xO NPs on CNTs.

On the basis of above, a possible mechanism can be rationalized for PTS of Cu_xO/CNTs composite. As shown in Scheme 2, CNTs with surficial carboxylic groups can capture Cu²⁺ ions by electrostatic force (Scheme 2b).¹⁴ In HTS, the Cu²⁺ ions were oxidized by acetic acid, and Cu_xO NPs were formed either on the surface of CNTs or in the solution according to the following equation¹⁵





The NPs collided and agglomerated into large particles, which linked with CNTs loosely through carboxylic groups (Scheme 2c). In PTS, CNTs were heated by the pulsed laser and induced the growth of Cu_xO NPs on their surface. Meanwhile, the pulsed laser can remove carboxylic groups and defects (see Figure 2), resulting in Cu_xO nanoparticles anchored directly on reprinted CNTs (Scheme 2d).^{8a} On the other hand, the pulsed laser heated the CNTs intermittently, and the final size of Cu_xO nanoparticles can be facilely controlled by adjusting pulse numbers, in favour of the preparation of tiny Cu_xO nanoparticles (see Figure 1a).

As an extension, we synthesized other two composites, $\text{Pb}_x\text{O}_y/\text{CNTs}$ and ZnO/CNTs , by PTS and using $\text{Pb}(\text{CH}_3\text{COO})_2$ and $\text{Zn}(\text{CH}_3\text{COO})_2$, respectively, as precursors. $\text{Pb}(\text{CH}_3\text{COO})_2$ could transform into Pb_xO_y NPs directly by the photothermal effect, while $\text{Zn}(\text{CH}_3\text{COO})_2$ first reacted with NaOH to give rise to an intermediate, $\text{Na}_2[\text{Zn}(\text{OH})_4]$, which then decomposed into ZnO NPs by the photothermal effect. TEM images and XRD patterns confirmed that ultrafine Pb_xO_y and ZnO NPs can be produced in-situ on the surface of CNTs (Figure S4). These results demonstrate that PTS can be generalized to synthesize different composites.

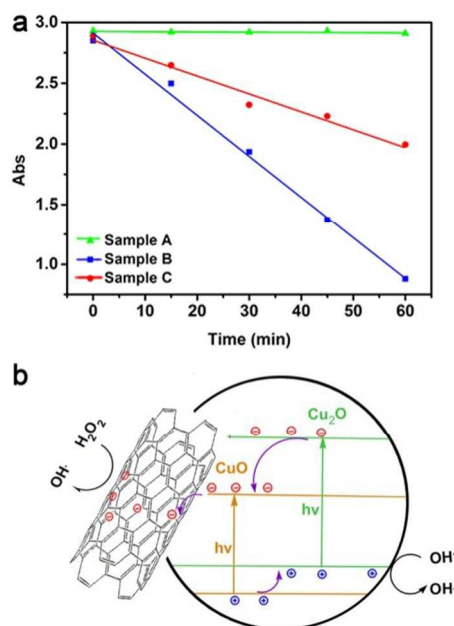


Figure 3. Photosensitized degradation of PNP by using $\text{Cu}_x\text{O}/\text{CNTs}$ composites. (a) The evolution of absorption intensity of PNP solution with respect to the light irradiation time. (b) Possible photodegradation mechanism.

We then detected the photodegradation performance of different products, the results were shown in Figure 3a and Figure S5. Merely with functionalized CNTs (sample A), p-nitrophenol (PNP) kept stable under visible light irradiation for 60 min. After adding $\text{Cu}_x\text{O}/\text{CNTs}$ composite by PTS (sample B), the absorption intensity of PNP solution decreased linearly with the irradiation time, and the decolorization ratio reached 70% after 60 min reaction. In comparison, sample C by HTS attained 31% decolorization after 60 min reaction. Similar results were found when the composite was used to degrade methylene orange (MO) molecules (Figure S6). The superior performance of the PTS composite can be understood from three aspects. First, the conductive band (CB) of Cu_2O is higher than that of CuO ,^{3,15} thus the photo-excited electrons in the CB of Cu_2O

can inject into CuO firstly, and then transfer into CNTs,¹⁶ which facilitates the electron-hole separation (Figure 3b). Second, Cu_xO NPs formed by PTS attach directly onto CNTs, which is conducive to electron transfer between the two components. Third, appropriate laser irradiation can eliminate the defects in CNTs, thus prolong the lifetime of free electrons.¹⁷ Accordingly, more electrons can reach the CNTs and reduce the H_2O_2 molecules, giving rise to $\text{OH}\cdot$ free radicals for PNP degradation.^{9,18} On the contrary, the Cu_xO NPs produced by HTS link with CNTs through carboxylic groups, which prevent the electron transfer, thus deteriorate the photocatalytic performance.

Conclusions

A PTS route was developed for the production of $\text{Cu}_x\text{O}/\text{CNTs}$ composite. Under moderate laser irradiation, the CNTs were heated to eliminate defects and functional groups, meanwhile, triggered the chemical reactions locally, resulting in fine Cu_xO NPs attached tightly to CNTs. The $\text{Cu}_x\text{O}/\text{CNTs}$ composite by photothermal synthesis exhibits high performance for decomposing organic dyes under visible light excitation due to its cascade energy structure, tight connection of Cu_xO NPs with CNTs, and laser elimination of structural defects in CNTs. Our study provides a simple route for achieving high quality composite.

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Notes and references

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Electronic Supplementary Information (ESI) available: [experimental details, TEM image of composites fabricated by PTS under different laser current densities, $\text{Cu}_x\text{O}/\text{CNTs}$ composite by PTS at different $\text{Cu}(\text{Ac})_2/\text{CNTs}$ molecule ratios, the as-received CNTs, and the product fabricated by HTS with as-received CNTs, characterizations of other oxide/CNTs composites by PTS, UV-vis absorption spectra of PNP solution with samples A, B, C at different time intervals, photosensitized degradation of MO by using $\text{Cu}_x\text{O}/\text{CNTs}$ composites]. See DOI: 10.1039/c000000x/

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