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Assisted Surface-state Recombination of Orange-peel Carbon Nanodots in Various Matrices

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Abstract

The contentious origin of the luminescence of carbon nanodots (CDs) has attracted considerable attention. In this work, we synthesized CDs from orange peel by using a microwave-assisted technique. We investigated the optical properties of the synthesized CDs. Moreover, we studied the effect of matrix addition on the optical properties of CDs. We found that matrix addition significantly influences the absorbance and photoluminescence of CDs. Shifts in absorbance peak intensity and emission peak wavelength indicated that the bonding of matrix molecules on the surfaces of the CDs has changed the structures of CDs. This finding is supported by the extended half-life of CDs after matrix addition. Our results will expand research on the use of CDs as phosphorescent materials.

Abstrak

Rekombinasi Keadaan Permukaan Carbon Nanodots dari Kulit Jeruk pada Beberapa Matriks. Saintis tertarik mengamati asal usul pendaran carbon nanodots (CDs). Pada penelitian ini, kami mensintesis CDs dari kulit jeruk menggunakan teknik pemanasan gelombang mikro dan mengamati sifat optiknya. Selain itu, pengaruh penambahan matriks terhadap sifat optik dari CDs juga dijelaskan. Kami menemukan bahwa penambahan matriks mempengaruhi secara signifikan absorbansi dan fotoluminesens dari CDs. Pergeseran puncak absorbansi dan panjang gelombang emisi mengindikasikan perubahan struktur CDs yang diakibatkan oleh ikatan molekul matriks pada keadaan permukaannya. Temuan ini didukung oleh meningkatnya waktu peluruhan CDs setelah penambahan matriks. Hasil penelitian ini dapat menjadi acuan dalam memperluas penelitian tentang penggunaan CDs sebagai material yang dapat berpendar.

Keywords: carbon nanodots; matrix; surface state

Introduction

Carbon nanodots (CDs) are a type of carbon nanoparticles with diameters of less than 10 nm. CDs were first discovered through the purification of single-walled carbon nanotubes [1]. Carbon is a black material with poor water solubility and weak luminescence [2]. By contrast, CDs have strong luminescence that originates from their high fluorescence efficiency [3]. The fluorescence of CDs develops when electrons from the ground state are excited to the metastable state. Excited electrons in the metastable state can slowly return to the ground state by emitting photons in a process known as recombination. Recombination in CDs is predicted to follow a quantum confinement effect given the small volume of CDs. The ratio between the surface and volume of CDs affects energy trapping, which generates the strong luminescence of

CDs [4]. This phenomenon is similar to the production of emission by silicon nanocrystals. Emission originates from the surface of silicon nanocrystals as a result of the radiative recombination of electrons and holes [5].

Phosphorescence is another property of CDs. The process of phosphorescence emission begins with the excitation of electrons from the ground to excited state, which is the singlet state. However, because of the high probability of energy transition, electrons move from a singlet state to a surface state (triplet state) without emitting photons. Electrons are temporarily trapped on the surface of CDs, thus delaying recombination [6].

The unique properties of CDs have attracted attention from numerous researchers who aim to develop and investigate every aspect of CDs, including the synthesis of CDs. Several methods have been established to

synthesize CDs from various carbon sources. These methods include the microwave-assisted method using graphite oxide [7], hydrothermal method using soy milk [8], arc-discharge and electrochemical method using nitric acid [9], and ablation-laser method using coffee powder [10]. Various organic substances, such as flour [11] and eggshells [12], have been used to synthesize low-cost and eco-friendly CDs through the microwave-assisted method. Through this method, CDs with strong photoluminescence [13,14] can be synthesized from the original material without the use of chemical solvents.

The luminescence of CDs mainly originate from the core state and is less affected by the surface state of CDs [15,16]. Moreover, some material, such as polyvinyl alcohol (PVA) [22], and tetraethyl orthosilicate (TEOS) [17], can add to the energy of CDs. The additional energy is mainly derived from the surface state, which contributes to the luminescence of CDs.

In this work, we present a sustainable, inexpensive, and eco-friendly approach to the synthesis of fluorescent CDs from orange peel through the microwave-assisted method. We aim to increase emission from recombination on CD surfaces by adding various matrices, specifically PVA and TEOS. The addition of matrices is expected to affect the emission of surface-state CDs.

Experiment

Materials. Orange peels from Siam Orange, Pontianak, Indonesia. Distilled water. PVA powder. TEOS with 98% purity.

Preparation of CDs from Orange Peel. First, 15 g of orange peel was mixed and blended with 150 mL of DI water. The solution was filtered to remove orange-peel waste and to obtain 40 mL of orange-peel solution. The filtered solution was then heated in a microwave at 700 W for 50 min until the sample was dried. After the sample was cooled down, 40 mL of DI water was added to dissolve the dried sample. The surfactant and precipitate were separated through 30 min of centrifugation at 10,000 rpm. Finally, orange-peel CDs were ready for characterization.

Preparation of the CDs@powder PVA. To study the effect of the solid PVA matrix on the optical properties of CDs, 5 mL of CD solution was mixed with 2 g of PVA powder. The mixture was then ready for analysis.

Preparation of the CDs@liquid PV. To study the effect of the liquid PVA matrix on the optical properties of CDs, 0.2 mL of CD solution was mixed with 1.5 mL of PVA solution (10 g PVA + 15 mL aquades) and 0.3 mL DI.

Preparation of the CDs@TEOS. A magnetic stirrer was used to stir 1 ml of CD solution with 10 ml of

TEOS for 1 h. The mixture was then centrifuged for 30 min 10,000 rpm. After centrifugation, the clear top layer was separated from the bottom layer, which appeared as a brownish gel that contained some dregs. The brown gel solution was then ready for characterization.

Characterization. MAYA Ocean Optics Spectrophotometer was used to obtain absorbance, photoluminescence, and time-resolved photoluminescence measurements. Fourier transform infrared (FTIR) spectra were recorded by Thermo Scientific Seri Nicolet iS10 Smart iTR 500-4000. The morphological structure of CDs was visualized through transmission electron microscopy (TEM) using TECNAITM (G² Spirit FEI Company).

Results and Discussion

Orange-peel CDs. Figure 1a shows that the absorbance of CDs appear at 270 and 320 nm wavelength. Upon excitation by a 420 nm laser, the emission peak intensity of synthesized CDs from orange peel appears at 510 nm. FTIR spectroscopy was used to identify the functional groups present in the CD solution. As shown in figure 1b, the CDs exhibit the main characteristic absorption bands of O–H¹⁸ stretching vibration at 3448 cm⁻¹, that of C=C¹⁹ at 2364 cm⁻¹, that of C–N²⁰ at 2343 cm⁻¹, that of C=O²⁰ at 1637 cm⁻¹, and that of C–O²¹ at 1404 cm⁻¹. The absorbance peak at 270 nm is attributed to $\pi - \pi^*$, which corresponds to the C=C bond from the CD core. In addition, $n - \pi^*$, which is attributed to the C=O bond, exhibits an absorbance peak at 320 nm and represents the subshell with the strongest bond.

The C=O bond on the surfaces of CDs may generate photoluminescence [16]. TEM images reveal the dispersion of CDs in a specific location (figures 1c and 1d). The diameters of CD particles are predominantly distributed in the range of 2.50–8.75 nm, as shown in figure 1e. The average particle size, which was manually estimated from the TEM image, is presented in Figure 1. The particle sizes indicate that CD nanoparticles have been successfully prepared from orange peel through the microwave technique.

Effect of Matrix Addition on CDs. Photoluminescence occurs on the surfaces of CDs. Matrix addition affects the surface bonding and luminescence of CDs, as shown on Figure 2.

Figure 3 shows the absorbance spectra and PL of CDs after matrix addition. The absorbance spectra have significantly changed after matrix addition. The absorbance peaks of CDs in PVA powder are at 283 and 320 nm, whereas those of CDs in PVA solution are at 275 and 317 nm. The absorbance peaks of CDs in a TEOS matrix are observed at 283 and 316 nm. These findings indicate that the absorbance peak, which is attributed to $\pi - \pi^*$, shifts to long wavelengths and that luminescence

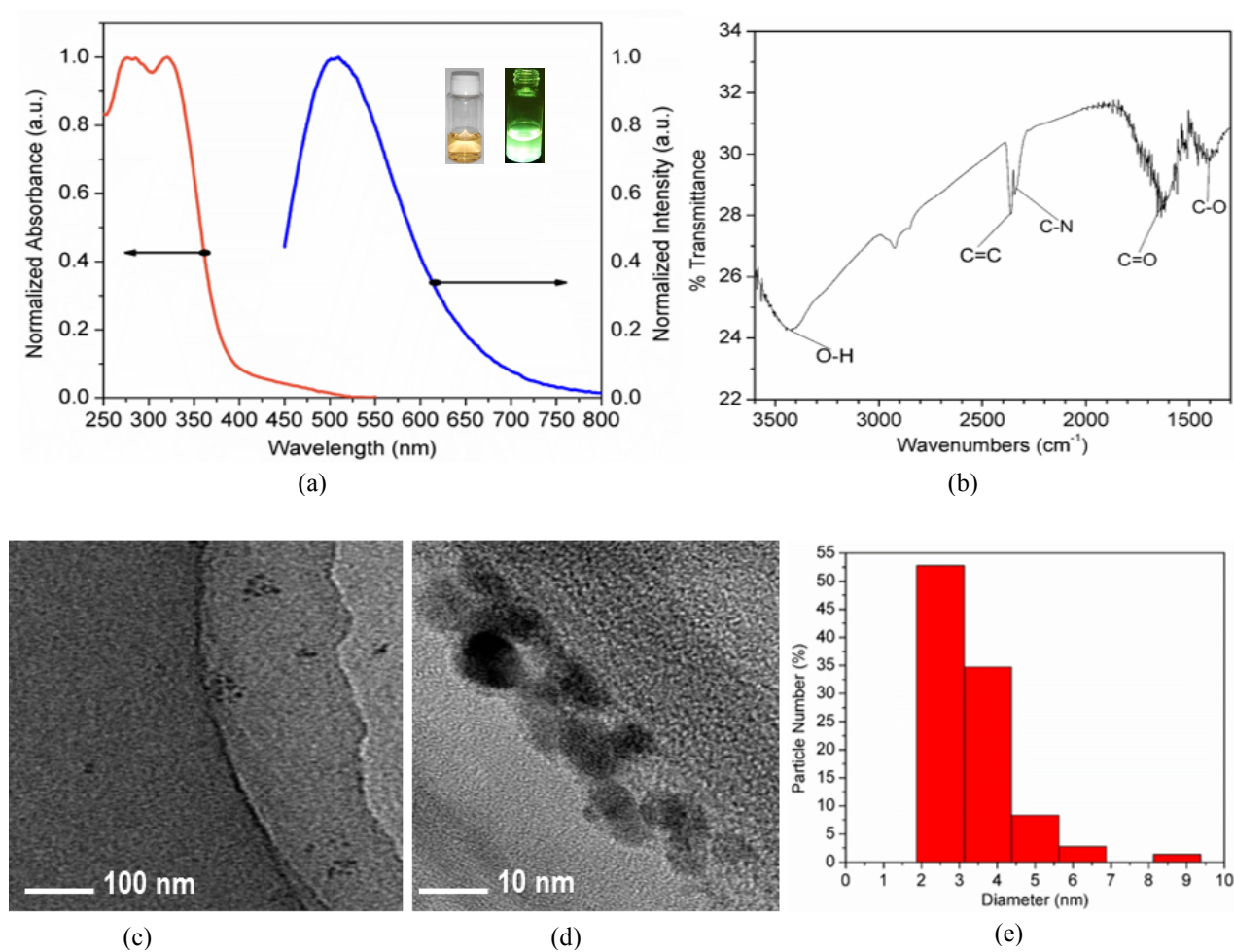


Figure 1. (a) Absorbance and Intensity. (b) Molecular Bonding of Orange-peel CDs and Morphology Characterization. Scale bar (c) 100 nm and (d) 10 nm. (e) Distribution of the Diameters of Orange-peel CDs

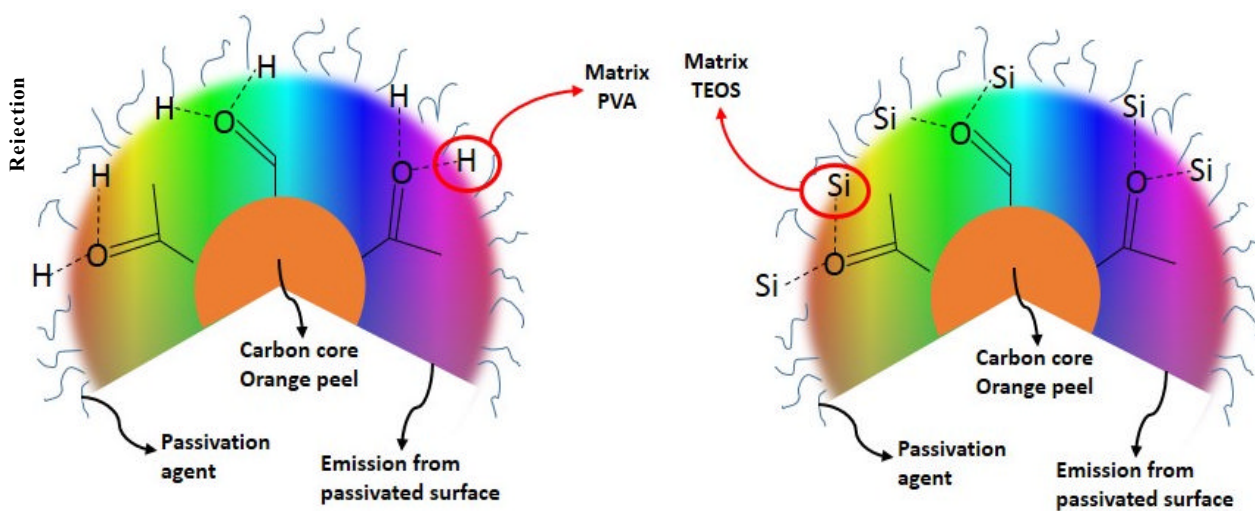


Figure 2. Effect of Matrix Type on the Surface State of CDs

is mainly generated from CD surfaces. The $n-\pi^*$ bond decreases because of the bonding between the H atoms of the PVA matrix and the Si atoms of the TEOS matrix with O atoms on CD surfaces. The results of characterization and analysis provide clear evidence that H and Si atoms are immobilized on CD surfaces through a covalent bond. These results demonstrate that covalent bond formation is a viable option for stabilizing triplet emissive species [22], as previously shown by experiments that used PVA [16] and Si [22] as CD matrices.

Matrix addition also changes the emission spectra of CDs. After matrix addition, the emission peak of CDs in PVA powder occurs at 516 nm, that of CDs in PVA solution matrix has shifted to 511 nm, and that of CDs in TEOS solution matrix has shifted to 510 nm. The wavelength of peak photoluminescence emission may have shifted because of the structural changes undergone by CDs in the presence of a matrix.

The effect of matrix addition on the absorbance of the CD surface is illustrated in Figure 4. Before matrix addition, the cores and surfaces of the synthesized orange-peel CDs exhibit the same absorbance peak intensity. After matrix addition, however, the absorbance peak intensity of the surface has increased. This result indicates that the luminescence of CDs is mainly contributed by the surfaces of CDs and originates from the $n-\pi^*$ bonds between CDs and the matrix.

The effect of matrix addition on the excitation lifetime of CDs is shown in Figure 5. Matrix addition extends the half-lives of CDs.

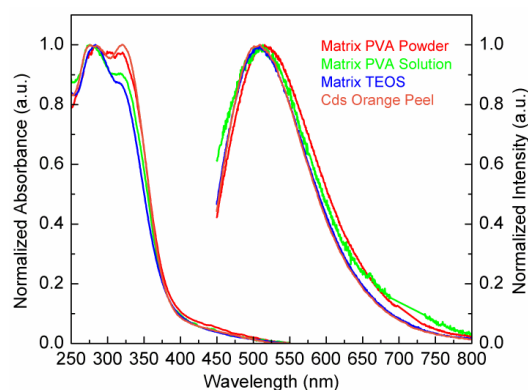


Figure 3. UV-Vis Spectrum of the Absorbance and Photoluminescence of CDs before and After Matrix Addition

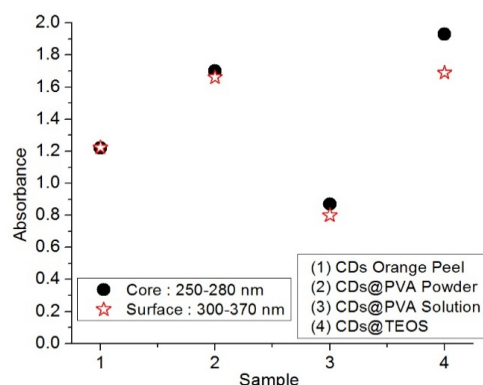


Figure 4. Distribution of Absorbance and Wavelength of CDs Before and After Matrix Addition

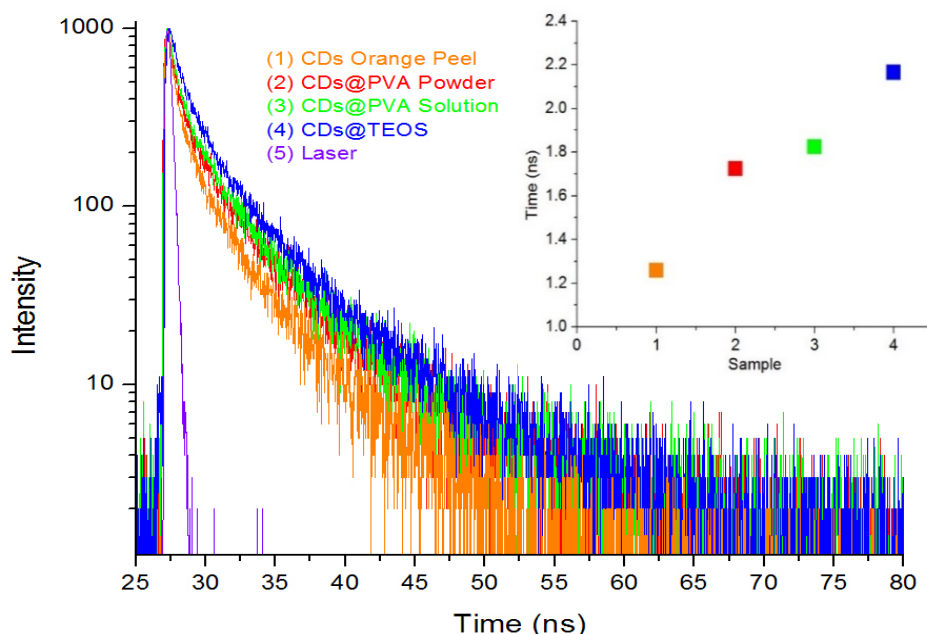


Figure 5. Half-lives of CDs Before and After Matrix Addition. Inset: Half-life of Each Sample

Orange-peel CDs have a half-life of 55 ns. However, the addition of PVA powder, PVA solution, or TEOS has extended the half-lives of CDs to 89, 80, and 83 ns, respectively. The extension of half-lives can be attributed to bonding of the H/Si atoms on the matrix molecule to the surfaces of CDs. Electrons in the singlet state transition to a triplet state. This transition extends the half-life of the CDs@matrix.

Conclusions

We have successfully fabricated CDs from orange peel by using a simple microwave technique and have shown the effect of matrix addition on the optical properties of CDs. The changes exhibited by CDs after matrix addition provide evidence that the luminescence of CDs mainly originates from CD surfaces. Matrix addition affects the surface bonding and luminescence of CDs. The addition of PVA powder or solution and of TEOS shifts the wavelength of absorbance peak intensity and photoluminescence. These behaviors indicate changes in CD structure. In addition, matrix addition extends the half-life of CDs. This result indicates that an energy trap is present in the CD surface. Our results will expand research on the use of CDs as phosphorescent materials.

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