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TiO_2/carbon dot composites: Synthesis and photocatalytic phenol degradation performance

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Abstract

Carbonaceous nanomaterials can influence the photocatalytic activity of semiconductors and have consequently attracted much attention. Herein, TiO_2/carbon dot (CD) composites hydrothermally prepared from TiO_2 and electrolytically synthesized CDs were characterized in terms of structure, appearance, morphology, and light absorption properties. Moreover, we probed the performance of these composites for photocatalytic phenol degradation under UV-vis light and calculated the apparent activation energy of this process (63.71 kJ mol^{-1} for the composite containing 0.5 wt. % CDs) based on reaction kinetics.

Keywords: nanotechnology, photochemistry, Spectroscopic methods, Synthesis of materials

1. Introduction

Phenol, an important industrial chemical, is the main organic water pollutant [1]. Photocatalysis is viewed as an effective means of wastewater treatment, as it exhibits a high environmental restoration potential [2]. Among the multitude of photocatalysts, TiO_2 exhibits the benefits of high stability, low cost, and non-toxicity, promoting the room-temperature degradation of various organic pollutants to [CO_2 + H_2O] or small organic molecules [3–5]. However, the practical application of TiO_2 is hindered by its inherent disadvantages, e.g., wide band gap and fast electron-hole recombination [6], which decrease the efficiency of solar light utilization and hence, photo activity. Therefore, the enhancement of TiO_2 photocatalytic activity has become a hot research topic in the field of photocatalysis.

Carbon dots (CDs), spherical nanoparticles under 10 nm in diameter containing sp^2-hybridized carbon [7], are a new type of brightly photo luminescent nanomaterials with good optical absorption in UV and near-visible regions and are therefore promising photosensitizers for photocatalytic applications [8–10]. In particular, the combination of CDs with TiO_2 allows one to efficiently utilize the full solar spectrum, enhances the charge separation rate of TiO_2, and increases the efficiency of organic compound adsorption onto the TiO_2 surface, thus improving the catalytic activity of pure TiO_2. CDs can be prepared in a number of ways, most of which involve the carbonization of organic or other carbon-rich substances. Zhu et al. [11] prepared CDs by heating a solution of glucose and PEG in a microwave oven, while Dong et al. [12] synthesized CDs by one-step carbonization of citric acid and branched polyethylenimine and studied their chemical sensing performance. Shiral Fernando et al.[13] prepared CDs via surface functionalization of carbon nanoparticles with organic and polymeric molecules, demonstrating that these CDs showed high activity for photocatalytic water splitting. Li et al. [14] designed a carbon quantum dot (CQD)/semiconductor photocatalyst and applied it to the photo degradation of methylene blue, revealing that hybridization with CQDs can effectively improve the photocatalytic activity of semiconductors. Pan et al. [15] synthesized graphene quantum dots (GQDs) by a molecular fusion method and stably deposited them onto anatase TiO_2 nanoparticles under hydrothermal conditions, concluding that monodisperse QD–based heterojunctions can effectively inhibit the fast recombination of electron–hole pairs of GQDs with a large exciton binding energy. Although these methods are convenient, they exhibit the drawbacks of high energy consumption and low yields, which highlights the need for more environmentally friendly and effective syntheses.

Here, we electrolytically prepared CDs from a graphite rod and hydrothermally hybridized them with TiO_2 to afford TiO_2/CD composites, revealing that these composites showed a higher photocatalytic phenol degradation activity than pure TiO_2 and determining the optimal content of CDs. Degradation kinetics was fitted by a first-order model and used to calculate the

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apparent activation energy. Finally, the effect of irradiation time on the UV-vis absorption spectra of phenol solutions was analyzed to determine a plausible reaction mechanism.

1.1 materials and methods

CDs synthesis. CDs were electrolytically synthesized from a graphite rod using deionized water as the electrolyte. The applied current and voltage were maintained at 50 mA and 36 V for 24 h to obtain an aqueous solution of CDs that was subsequently concentrated at 100 °C for 12 h to afford CD powder.

Synthesis of TiO_2/CD nanocomposites. The hydrothermally prepared TiO_2/CD composites had CD loadings of 0.1, 0.3, 0.5, and 1 wt%. Typically, a solution of tetrabutyl titanate (5.1 mL) in ethanol (27 mL) was dropwise added under continuous stirring to a homogeneous dispersion of CDs in 30 vol% aqueous ethanol prepared by 30-min sonication [16–18]. After 3-h stirring, the reaction mixture was transferred to a Teflon-lined autoclave (100 mL) and heated at 180 °C for 12 h. The obtained samples were centrifuged, and the solids were washed with water and then dried at 60 °C in a vacuum drying oven [19].In addition, individual anatase TiO_2 nanoparticles were prepared under identical conditions in the absence of CDs [20].

Characterization. X-ray diffraction (XRD) spectra were recorded on a Bruker AXS D2 PHASER diffractometer for $2\theta = 10–70°$ and a step size of $0.01° s^{-1}$ using Cu Kα radiation ($\lambda = 1.5406$ Å). UV-vis spectra (200–800 nm) were recorded on a THERMO EVOLUTION220 spectrophotometer, and optical absorption spectra were recorded on a Hitachi U-3310 UV-vis spectrophotometer.

Photocatalytic property evaluation. For photocatalytic property evaluation, TiO_2/CD composites were used to promote the photo degradation of phenol under irradiation with a 200-W Xe lamp at an intensity of 100 $mW{\cdot}cm^{-2}$. Typically, a 50-mg TiO_2/CD sample was added to a solution of phenol (0.25 mg) in water (50 mL), and the mixture was stirred for 30 min in dark to establish an adsorption-desorption equilibrium and then irradiated at temperatures of 303.13, 313.13, and 323.13 K. During the reaction, 5-mL aliquots were sampled at a given time interval, centrifuged for five times, and the absorption of phenol in the supernatant was recorded at 272 nm.

2. Results and Discussions

Structural characterization. Figure 1 displays the XRD patterns of pure TiO_2, pure CDs, and TiO_2/CD composites with different CD contents. Peaks at 2θ = 25.38, 37.80, 48.18, and 54.09° were ascribed to reflections from the (101), (004), (200), (105), and (211) planes of anatase TiO2, respectively (JCPDS No. 21-1272), and the small peak at 27.4° was ascribed to a negligibly small amount of rutile TiO_2. The positions of the above peaks did not change with CD content, i.e., hybridization with CDs did not affect the crystal structure of TiO_2; however, no peaks attributable to CDs were observed because of low CD content. These results agreed with those reported previously [21].

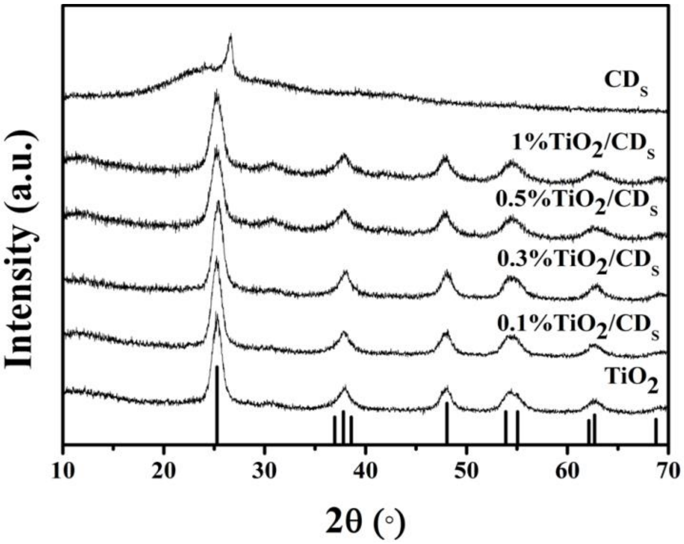

Figure 1: XRD patterns of TiO_2/CD nanocomposites.

Morphological characterization. The morphologies of pure TiO_2 nanoparticles, CDs, and TiO_2/CD nanocomposites were characterized by TEM. As shown in Figure 2a, pure TiO_2 nanoparticles tended to aggregate and exhibited an average length and diameter of ~10 and ~20 nm, respectively. The lattice spacing of pure TiO_2 nanoparticles was determined as 0.35 nm (Figure 2b) and matched the interplanar spacing of the (101) anatase crystal plane. Well-dispersed spherical CDs had an average diameter of ~1.5 nm (Figure 2c) and featured an amorphous structure (Figure 2d). TEM imaging of TiO_2/CD nanocomposites (Figure 2e) revealed the presence of numerous dark CDs well dispersed on TiO_2 nanoparticles, and the related lattice spacing corresponded to that of the (101) anatase crystal plane (Figure 2f), which confirmed the hybridization of CDs with TiO_2.

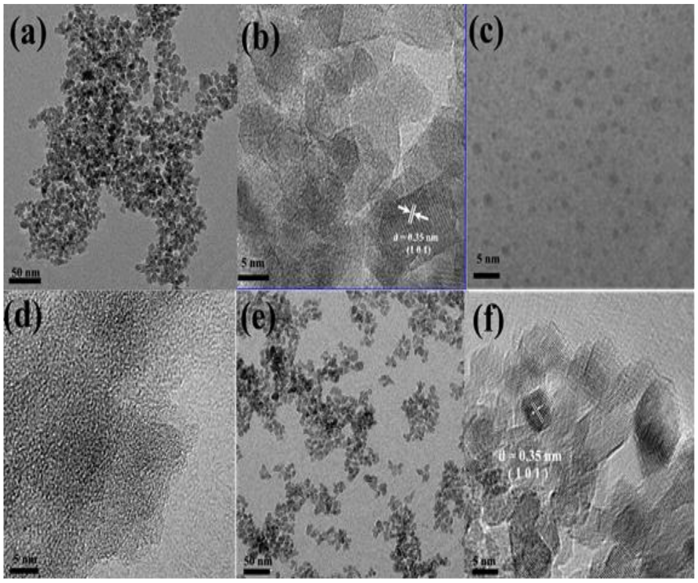

Figure 2. (a, c, e) low- and (b, d, f) high-magnification TEM images of (a, b) pure TiO_2 nanoparticles, (c, d) pure CDs, and (e, f) 0.5 wt% TiO_2/CDs.

UV-vis spectral analysis. The optical properties of TiO_2/CD nanocomposites were further probed by UV-vis diffuse reflectance spectroscopy (Figure 3). All samples presented good light absorption efficiency, which increased in the visible region upon CD introduction. Compared to that of bare TiO_2, the absorption edge of TiO_2/CD nanocomposites was significantly red-shifted. This shift was most obvious for 0.5 wt% TiO_2/CDs, in which case the absorption edge extended to 503 nm. Band gap energies (E_g, $E_g = 1240/\lambda_g$ (eV), where λ_g (unit) is the absorption wavelength threshold...) for CDs loadings of 0.1, 0.3, 0.5, and 1 wt% were determined as 3.08, 3.07, 3.06, 2.46, and 3.06 eV, respectively, and were lower than that of pure TiO_2 (3.10 eV). Therefore, the introduction of CDs increased the quantum yield and visible light utilization efficiency of TiO_2 and thus enhanced its photocatalytic activity, in agreement with previously reported results [22].

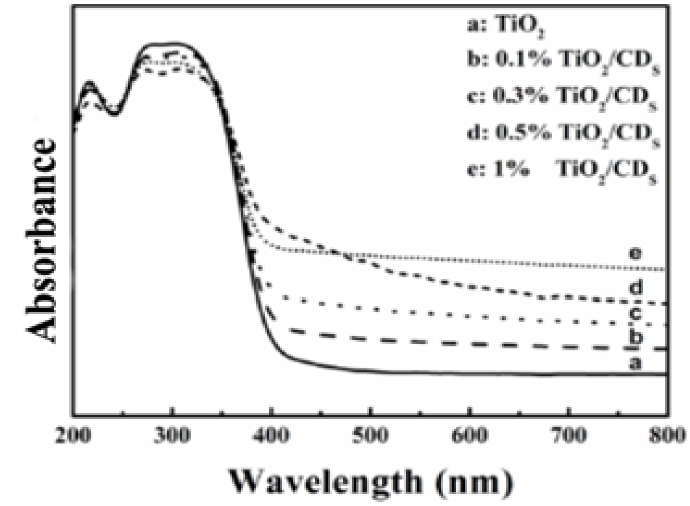

Figure 3. UV-vis diffuse reflectance spectra of TiO_2/CD nanocomposites.

Photocatalytic properties. To examine the effect of CD loading on the photocatalytic activity of TiO_2/CD samples, these samples were used to promote the degradation of phenol under visible light irradiation (Figure 4). Notably, <5% degradation was achieved after 90-min irradiation of the blank sample, whereas significantly higher values were observed in the presence of the photocatalyst, with maximum degradation observed for a CD loading of 0.5 wt%. This behavior was ascribed to the fact that the introduction of CDs can extend the electronic path and enhance charge separation by promoting photoelectron trapping. The reduction of activity at an increased loading of 1 wt% implied that the adsorption of excess CDs on the surface of TiO_2 increases the adsorption performance of TiO_2/CD composites and hence, decreases their photocatalytic activity [23]. Analysis of UV-vis spectra. Figure 5 shows the absorption spectra of phenol solutions exposed to visible light for different times in the presence of 0.5 wt% TiO_2/CDs, revealing that degradation was almost complete in 90 min. With increasing time, the typical absorption peak at 272 nm lost intensity and disappeared, while the peak at 250 nm shifted to 240 nm, broadened, and ultimately disappeared.

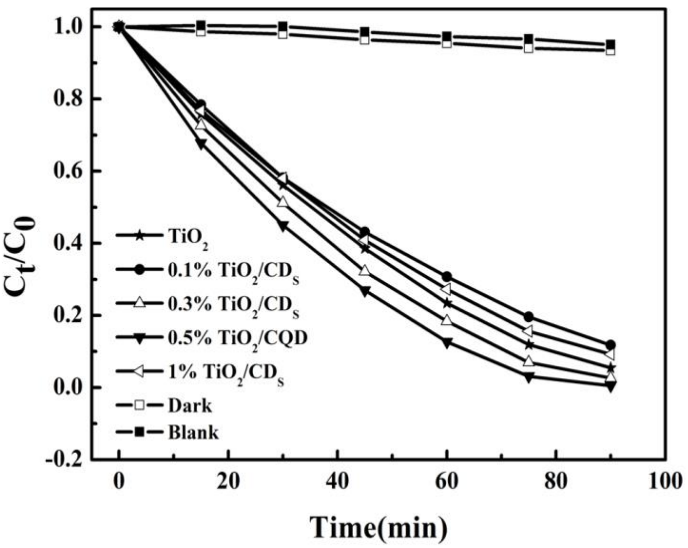

Figure 4. Photocatalytic degradation of phenol in the presence of TiO_2/CD composites (C_0 and C_t represent the initial concentration of phenol and that after time t, respectively).

These findings agreed with those of Peng et al [24]. This result caused by the hydroxyl groups out of from phenol and affect its conjugate structure, implying complete degradation of phenol by the photocatalysts.

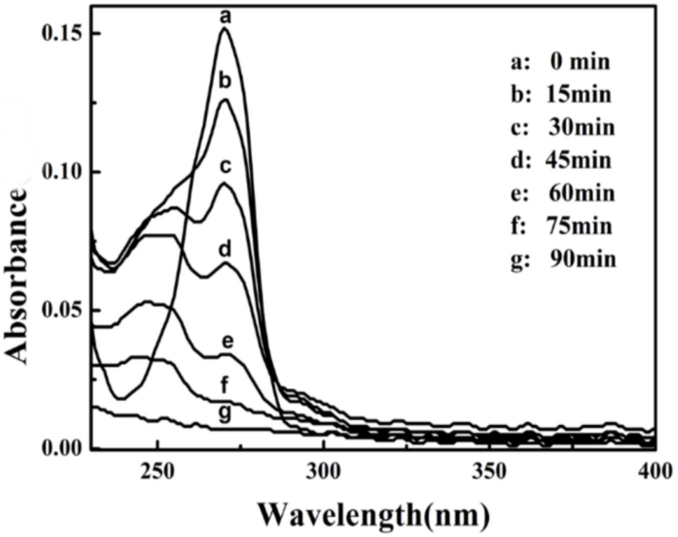

Figure 5. UV–vis absorption spectra of (phenol + 0.5 wt% TiO_2/CD) systems irradiated for different times.

Photo degradation kinetics. Figure 6 illustrates the effect of temperature on phenol degradation in the presence of 0.5 wt% TiO_2/CDs, revealing that degradation rate, and hence, photocatalytic activity, increased with increasing temperature and further showing that reaction kinetics could be well modeled by mono exponential decay (Eq. 1).

$$\ln(C_0/C_t) = kappt \quad (1)$$

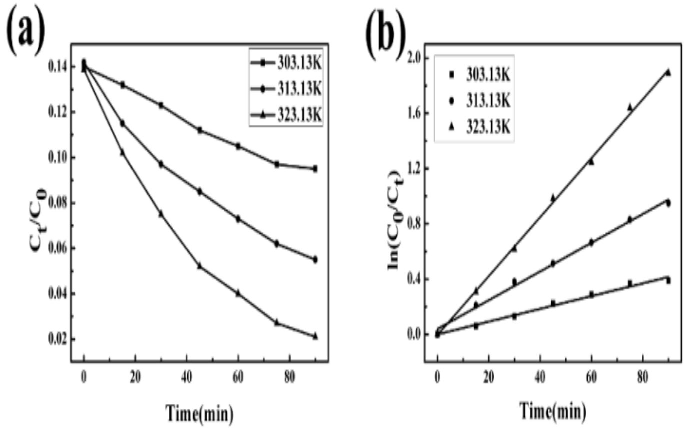

Figure 6. Effect of temperature on the kinetics of phenol degradation in the presence of 0.5 wt% TiO_2/CDs.

Where kapp (min^{-1}) is the apparent rate constant of phenol degradation. The obtained data and the Arrhenius equation (Eq. 2) were used to determine the activation energy (Ea) based on Eq. 3:

$$k = A\exp(-Ea/RT) \quad (2)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

Where R is the universal gas constant, T_1 and T_2 are two arbitrarily chosen reaction temperatures, and k_1 and k_2 are the corresponding rate constants. Additionally, the half-life of phenol ($\tau_{1/2}$) was determined as

$$\tau_{1/2} = \ln 2/k \quad (4)$$

Table 1 lists the kinetic data of photocatalytic phenol degradation, showing that the half-life of phenol decreased from 150.68 to 32.54 min as the temperature increased from 303 to 323 K. The average apparent activation energy ($\bar{E}a$) was calculated as 63.71 $kJ\cdot mol^{-1}$.

Table 1. Phenol photo degradation data obtained at different reaction temperatures

Temperature (K)	Kinetic equation	R^2	k_{app} (min^{-1})	$\tau_{1/2}$ (min)	$\bar{E}_a$ ($kJ\cdot mol^{-1}$)
303.13	KE1	0.984	0.0046	150.68	
313.13	KE2	0.994	0.0104	66.65	63.71
323.13	KE3	0.998	0.0213	32.54	

Note: KE1: $\ln C_t = \ln C_0 - 0.0046t - 0.0077$
KE2: $\ln C_t = \ln C_0 - 0.0104t - 0.0391$
KE3: $\ln C_t = \ln C_0 - 0.0213t + 0.0048$

3. Conclusions

CDs and TiO_2/CD nanocomposites were successfully synthesized by electrolytic graphite rod and hydrothermal methods, respectively. Compared to pure TiO_2, TiO_2/CD nanocomposites (CD loading = 0.1–0.5 wt%) exhibited an increased activity for photocatalytic phenol degradation, with maximal activity observed at a CD content of 0.5 wt%. Kinetic studies revealed that the degradation rate constant increased with increasing temperature, and the average apparent activation energy was determined as 63.71 $kJ\cdot mol^{-1}$. The obtained results provide a firm basis for further studies on the photocatalytic degradation of organic pollutants by TiO_2-based carbonaceous nanomaterials.

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