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A facile synthesis of waterborne polyurethane/silica/CdTe-QDs nanocomposites with excellent mechanical, thermal and optical properties

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Monodispersed waterborne polyurethane WPU/silica/CdTe-QDs nanocomposites were directly synthesized via the reaction between the groups of amine group (-NH_2) on the SiO_2-hybrided CdTe QDs surface and an isocyanate end group (-NCO) of polymer chains. The SiO_2-hybrided CdTe QDs were characterized by Dynamic Light Scattering, Transmission Electron Microscopy. The WPU/silica/CdTe-QDs nanocomposites were characterized by Fluorescence Spectroscopy, the results shows the nanocomposites could emit bright photoluminescence. These nanocomposites have notably up-conversion fluorescence properties. Dynamic mechanic alanalysis (DMA) reveals these nanocomposites also have excellent mechanical properties.

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Keywords: Nanocomposites, Polyurethane, Silica, CdTe, QD, TEM, Dynamic light scattering

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1. Introduction

It is well known that waterborne polyurethane (WPU), as an environmentally friendly material, has been widely used in many fields such as construction, biological and automobile. The introduction of inorganic nanoparticles into polyurethane (PU) matrices has been proved to be an effective approach to obtain PU nanocomposites with advantageous properties, since it can provide significant improvements in PU properties such as mechanical and thermal properties even at very low amount of inorganic nanoparticles [1]. Overviewing the previous literatures, the inorganic enhanced agents could be silicon dioxide (SiO_2), multi-walled carbon nanotubes [2], polyhedral oligomeric silsesquioxanes (POSS) [3] and graphene [4]. Among them, SiO_2 has always applied to prepare the PU/SiO_2 nanocomposites due to its low cost, high availability, large surface area and good mechanical response to stress.

Recently, fluorescent semiconductor nanocrystals known as quantum dots (QDs) also have attracted intensive attention because of their unique size-dependent optical properties and their potential application in solar cells [5], optoelectronic devices [6] and lasers [7]. However, in practical applications, QD-based materials must be nontoxic [8], and their metastable nanoparticles are required to be stabilized in an appropriate matrix with the retention of their initial photoluminescence (PL) efficiency, where the aggregation and agglomeration should be suppressed [9]. To satisfy these requirement, the QDs were often protected by inorganic materials or polymer. For example, zinc sulfide (ZnS) QDs with nontoxic protecting shell have been prepared [10]. Recently, the QDs with SiO_2 protecting shell have been developed [11], since SiO_2 with functional groups not only could protect QDs from outer environment but also could provide good solubility, biocompatibility and surface functionality. In addition, polymer was also used to pretect QDs, which can effectively stabilize the metastable QDs nanoparticles [12]. Xiaodong Cao and Su Chen reported the preparation of the QDs-containing PU composites with PU shell using the reaction between -NCO end group of polyurethane and the reactive group such as amine (-NH_2) [13] and hydroxyl (-OH) [14] on the surface of QDs, and they also found not only QDs can be proctected by polyurethane, but also QDs can endow PU with optical properties.

To obtain the PU/QDs with advantageous properties, we fabricate WPU/silica/CdTe-QDs nanocomposites. The synthesis of WPU/silica/CdTe-QDs nanocomposites has not reported yet. We used one-pot approach to prepare silica/CdTe-QDs first. Silica/CdTe-QDs was further functionalied to amine-modifying nanoparticles using 3-aminopropyltrimethoxysilane (APS). Finally, WPU/silica/CdTe-QDs nanocomposites were obtained via the reaction between amine group of silica/CdTe-QDs and -NCO end group of PU prepolymer in an aqueous solution. In our experiments, on the basis of the versatile properties of WPU and the PL originating from the QDs, it is envisioned that these materials could act as polymer coating, ink for the fabrication of ordered structures, envisaged optoelectronic devices, and so on.

2. Experimental

2.1 Reagents

Ethylene glycol, polytetramethylene ether glycol (PTMEG, M_n = 2000, AR) which was dried for 5h at 105 ^oC in the vacuum oven before use, isophorone diisocyanate (IPDI, pure grade, 98%), dimethylol propionic acid (DMPA, pure grade, 99%), ethylenediamine (EDA, AR), triethylamine (AR) and rhodamine 6G (AR) were purchased from Aladdin-regant Co. Ltd, China. Tellurium powder (pure grade, 99%), sodium borohydride ($NaBH_4$), mercaptopionic acid (MPA, AR), tetraethlorthoslicate (TEOS, AR), 3-aminopropyltrimethoxysilane (APS, pure grade, 99%) were purchased from Sigma-Aldrich. Other regents and solvents in analytical grade were all obtained from Shanghai Chemical Reagents Company.

2.2 Synthesis of SiO_2/ CdTe-QDs nanohybrids

SiO_2/CdTe-QDs nanohybrids were synthesized using one-pot approach [15]. A typical procedure, 1.12 g of $NaBH_4$ and 105.0 mL of distilled water were charged into a flask with a magnetic stirring bar. After stirring for 30 min at 0 °C, 1.50 mg (11.8 mmol) of tellurium powder was added. During the reaction, a small outlet connected to the flask was kept open to discharge the pressure from the resulting hydrogen. After several hours at 0 °C, the black tellurium powder disappeared and white precipitate appeared on the bottom of the flask. The resulting fresh oxygen-free NaHTe aqueous solution was added to 4.0 L of N_2-saturated $CdCl_2$ solution (7.2 mmol) at pH 9.0 adjusted by NaOH (1.0 M) in the presence of MPA (49.6 mmol) at 100 °C. After 10 min, 65.2 mL of TEOS was injected into the mixture. After reflux for 10 h, the mixture was precipitated by ethanol. The supernatant was discarded, and the precipitates were centrifuged and washed with ethanol three times. The resulting orange solid was dried at 60 °C for 24 h under a vacuum.

2.3 Synthesis of amino-SiO_2/CdTe-QDs nanohybrids

100 mg SiO_2/CdTe-QDs nanohybrids, 0.5 mL of APS (2.86 mmol) and 50 mL of toluene was added into 100 mL of flask, and the mixture was stirred at 95 ^oC for 6h. The product was separated by centrifugation and washed with ethanol three times repeatedly. The resulting product was dried at 60 °C for 24 h under a vacuum.

2.4 Synthesis of WPU prepolymer

In a typical process, PTMEG and DMPA were introduced into a four-necked flask equipped with mechanical stirrer, condenser, and thermometer, the mixture was heated up to 85 ^oC until the PTMEG was melted completely, then IPDI was added dropwise. After the reaction was carried out for 3 h, ethylene glycol was added to this flask at 65 ^oC, and the reaction was carried out for 3 h until the -NCO content reached a desired value, which was determined by using a standard dibutylamine titration method. After neutralization of carboxylic groups with Triethylamine for 30 min, the product of -NCO terminated WPU prepolymer was obtained. This reaction was comfirmed by FT-IR measurements (Fig. 3).

2.5 Preparation of WPU/silica/CdTe-QDs nanocomposites

Amino-SiO_2/ CdTe-QDs nanohybrids and EDA were directly used to react with NCO-terminated WPU prepolymer in the aqueous solution. Fig. 1 shows the process for preparation of the WPU/silica/CdTe-QDs nanocomposites, starting from the aqueous SiO_2/ CdTe-QDs. The amino- SiO_2/ CdTe-QDs was got through silane-coupling reaction of SiO_2-h-CdTe QDS and APS. The -NCO terminated WPU can be attached on the surface of amino-SiO_2-h-CdTe QDS effectively via the reaction between the groups of -NH_2 and -NCO. This reaction was comfirmed by FT-IR measurements (Fig. 3). The formulations used to prepara the WPU/silica/CdTe-QDs nanocomposites was given in Table 1. It is noted that a fresh WPU prepolymer should be used here, otherwise, the -NCO groups are consumed by water slowly.

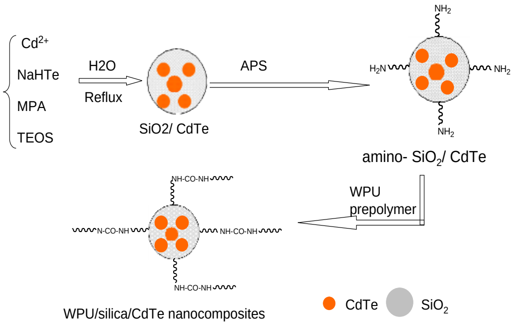


Fig. 1. Preparation of WPU/silica/CdTe nanocomposites.

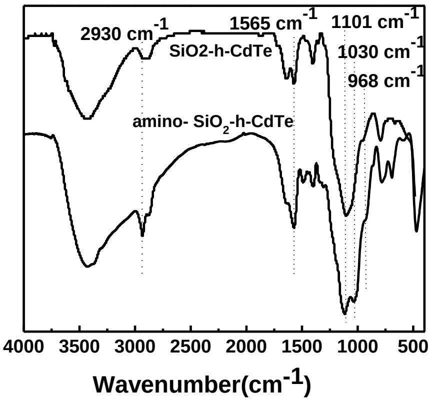


Fig. 2. FT-IR spectra of SiO_2-h-CdTe and amino- SiO_2-h-CdTe.

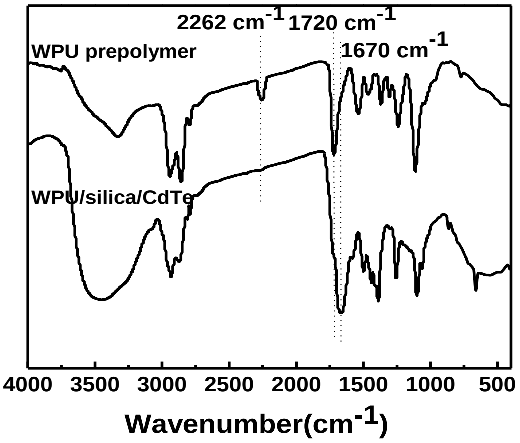


Fig. 3. FT-IR spectra of WPU prepolymer and WPU/silica/CdTe.

Table 1. The feeds of the preparation of WPU/silica/CdTe-QDs nanocomposites.

Sample	IPDI(g)	PTMEG(g)	DMPA(g)	EG(g)	amino-SiO2-h-CdTe	EDA(g)
Sample 0	37.33	90.42	7.37	2.25	0	1.88
Sample 1	37.33	90.42	7.37	2.25	1.42	1.81
Sample 2	37.33	90.42	7.37	2.25	2.85	1.74

2.6 Film samples preparation

Certain mass WPU/silica/CdTe-QDs nanocomposites emulsion was put into the glass model and allowed to dry at room temperature for 48 h. The WPU/silica/CdTe nanocomposites cast films were obtained after staying at oven about 3-4 h under 80 °C in normal oven, and then was further dried at vacuum oven for 24 h under 80 °C. The thickness of the cast films were about 0.3-0.4 mm.

2.7. Material tests and characterization

The test of Fourier Transform Infrared Spectroscopy (FT-IR) was recorded on a NICOLET-NEXUS 670 spectrometer. The samples were ground with KBr crystals, and the mixture was pressed into a flake for IR measurement. Transmission electron microscopic (TEM) observation was performed with a JEOL JEM-2100 transmission electron microscope. Photoluminescence (PL) spectra were measured on an Aminco Bowman Series 2 spectrofluorometer at room temperature. Ultraviolet-visible (UV-vis) absorption spectra were taken with a Perkin-Elmer Lambda 900 UV-vis spectrometer with the scan range 400-650 nm, and all the UV-vis samples were diluted 60 times with water for analysis. The thermo gravimetric analyses (TGA) were obtained with a NETZSCH STA 409 PC in N_2 flow in the temperature range 40-600 ℃, the heating rate being 10℃/min, and the TGA samples were prepared by drying under vacuum for solvent removal. Tensile test for the films wre carried out using Construction Materials Testing (CMT) methods at room temperature and the tensile speed was 200 mm/min. DMA measurements were carried out on a DMA 242 (Netzsch–Geratebau GmbH, Bavaria, Germany). The samples were quickly cooled to -100 °C and equilibrated at that temperature for 3 min, after they were heated to 150 °C at a frequency of 10 Hz with constant heating rate of 5 °C /min under nitrogen atmosphere. Shore *A* hardness was measured using an indentation hardness tester according to ASTM D2240-75.

3. Results and discussion

As shown in Fig. 2, the observed features at about 1101 cm^{-1} and 968 cm^{-1} are respectively ascribed to Si-O-Si and Si-O-H stretching vibrations. The peak at 1030 cm^{-1} is associated with the stretching of Si-O-C bond. The presence of adsorption water was reflected by -OH vibration at 3438 cm^{-1} and 1632 cm^{-1}. The characteristic peaks of the amino-SiO_2/CdTe-QDs when compared with SiO_2/CdTe-QDs are -NH_2 band around 1565 cm^{-1}, -CH_2 band around 2930 cm^{-1} and Si-O-C bond around 1030 cm^{-1} [16]. These results suggested APS has been grafted onto the surface of silica/CdTe after modification.

Fig. 3 shows FT-IR spectra of WPU prepolymer and WPU/silica/CdTe-QDs nanocomposites. The peak at 2262

cm^{-1} is ascribed to -NCO groups of WPU prepolymer, but it completely disappeared in the spectrum of WPU/silica/CdTe-QDs nanocomposites, which indicates that the -NCO groups was reacted completely. The peak at 1720 cm^{-1} is corresponding to C=O groups of WPU, which resulted from the free C=O and hydrogen bonded C=O groups in the urethane bonds. However, in the spectrum of WPU/silica/CdTe-QDs nanocomposites, the peak shift to 1670 cm^{-1}. This confirms the formation of urea carbonyl via the reaction between the amino groups of silica/CdTe-QDs and NCO end group of WPU chains in an aqueous solution. This result is agreeable to the previous literature [17-18].

TEM image of SiO_2/CdTe-QDs nanohybrids was shown in Fig. 4a. The nanohybrids with spherical shape are well dispersed and their diameters are in the range of 4~20 nm, which would be beneficial to SiO_2/CdTe-QDs solubility. As shown in Fig. 4b, CdTe quantum dots were well coated by the SiO_2. Similar to the TEM results, the size histogram (Fig. 4c) of the SiO_2-h-CdTe particles prove that the diameters of the particles are less than 20 nm.

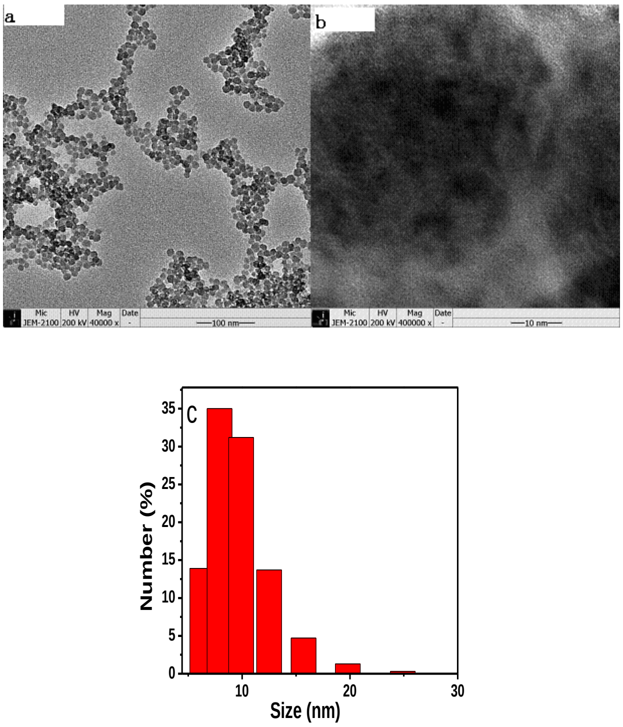


Fig. 4. Images of SiO_2-h-CdTe: (a) and (b) TEM image; (c) size distribution.

In order to examine the effect of silica on the thermal stability of WPU/silica/CdTe-QDs nanocomposites, thermogravimetric analysis (TGA) was carried out. Fig. 5 shows the thermogravimetric curves of Sample 0 (silica/CdTe-QDs 0%) and Sample 1 (silica/CdTe-QDs 1%) and Sample 2 (silica/CdTe-QDs 2%) with different nanohybrids contents. For pure PU, the first decomposition stage occurs at the temperature range of 200-270 ^{o}C, which results from the vaporization of residual water, and the loss of oligomer and by-products in the WPU and hybrid materials. The second decomposition stage at the temperature range of 270-345 ^{o}C is corresponding to the decomposition of the hard segment of polyurethane. The third decomposition stage at the range of 345-600 ^{o}C is attributed to the decomposition of the soft segment of polyurethane [19]. Fig. 5 shows the incorporation of the surface treated silica/CdTe-QDs into PU doesn't improve the first decomposition temperature, but improve the second decomposition temperature. The Sample 2's second decomposition temperature at around 370 ^{o}C, delayed by 25 ^{o}C compared with the pristine PU. This is presumably due to an increase in particle-matrix interaction, better dispersion and less tendency toward aggregation, more interaction between silica/CdTe-QDs particales and macromolecular chains [20]. On the other hand, the chemical crosslink points of silica/CdTe-QDs, which limit the movement of the molecular chain of PU. After adding silica/CdTe-QDs with a high melting point to the polymer matrix, the silica/CdTe-QDs can work as a good thermal cover layer, avoiding the direct thermal decomposition of PU matrix. In addition, the silica/CdTe-QDs is a nanoscale particle, which offers a larger surface area and improves the effect of thermal cover. The higher residue content of all the WPU/silica/CdTe-QDs nanocomposites at high temperature (600 °C) is attributed to the excellent thermal stability of inorganic silica (Si–O–Si) part, which would be accumulated on the surface of the polymer and thus prevent from further thermal decomposition of the inner organic network.

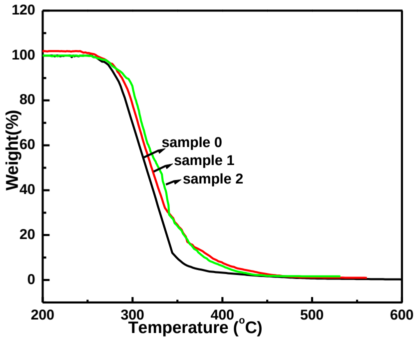
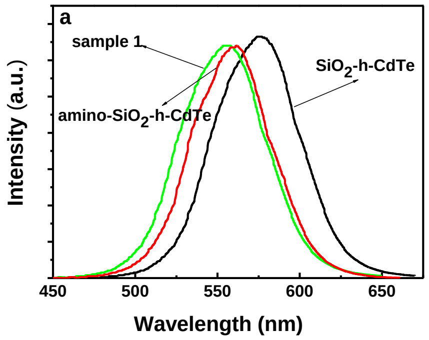


Fig. 5. TGA analysis of WPU/silica/CdTe.

The UV-Vis and PL emission spectra of amino-SiO_2/CdTe-QDs nanohybrids and WPU/silica/CdTe-QDs nanocomposites (Sample 1) are respectively shown in Fig. 6a and Fig. 6b. Compared with the free QDs in aqueous solution, we can see that amino-SiO_2/ CdTe-QDs nanohybrids and WPU/silica/CdTe-QDs nanocomposites the maximum emission peak became blue shift and broader obviously, it had been demonstrated that the blue shift was due to the corrosion of QDs during reaction. Since thiol ligands may be removed partly from their surfaces, thus resulting in this blue-shift in the maximum of emission spectra [21].



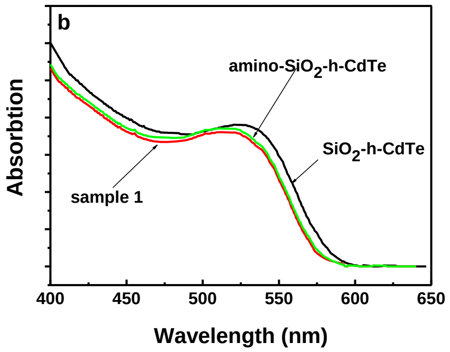


Fig. 6. PL and UV-vis absorption spectra of SiO_2/ CdTe, amino- SiO_2/ CdTe, Sample 1.

Remarkably, besides the strong PL in visible range, the WPU/silica/CdTe-QDs nanocomposites also exhibit excellent upconversion fluorescence (UPL) property. Fig. 7 shows the PL spectra of nanocomposites excited by long wavelength light (from 650 to 1000 nm) with the up-conversion emissions located in the range from 500 to 650 nm. This UPL property of nanocomposites may be attributed to the multiphoton active process similar to previous reported [22]. Compared with the nanocomposites prepared in other methods [23], The WPU/silica/CdTe-QDs nanocomposites prepared in this paper with a simple method are relatively inexpensive and have excellent PL properties, such as the strong PL in visable range and excellent UPL property which are reported firstly. These results suggest that the nanocomposites may be used as a powerful energy-transfer component in photocatalyst design for applications in environmental and energy issues.

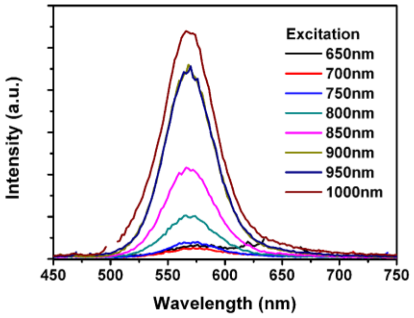
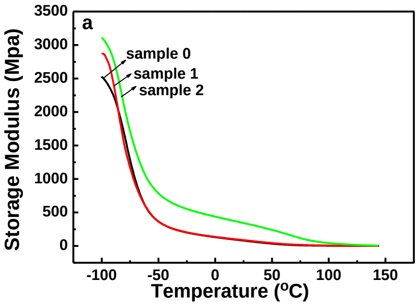


Fig. 7. Upconversion fluorescence spectra of WPU/silica/CdTe nanocoposites.

In Fig. 8a, we can see the presence of silica/CdTe-QDs evidently enhances the values to develop rubbery plateau. The interaction between pure WPU and silica/CdTe-QDs seems to prohibit the flow of pure WPU and sustain the rubbery state even at the temperature range. This confirms that the -NH_2 of silica surface provide reaction sites with WPU prepolymer to form network structure with silica being the cross-linking center. When subjected to a sinusoidal dynamic stress, a polymeric beam in clamps will exhibit a sinusoidal tension that lags behind the applied stress with a phase angle δ_0. From the relation between stress and strain, the storage modulus *E'* and the loss modulus *E"* can be calculated. The ratio of *E"/E'* is the loss tangent tanδ, which reflects the viscous-elastic characteristic of a polymeric material. Dynamic mechanical properties of WPU/silica/CdTe-QDs nanocomposites are also shown in Fig. 8. In Fig. 8b, the peak temperature at tanδ (around -67℃) which can be used as an indication of the glass transition temperature (Tg). The peak temperature positions do not vary much in WPU/silica/CdTe-QDs nanocomposites compared with pure WPU. This suggests that the degree of phase mixing between soft and hard segment does not vary much in the presence of nanosilica compared with pure WPU.



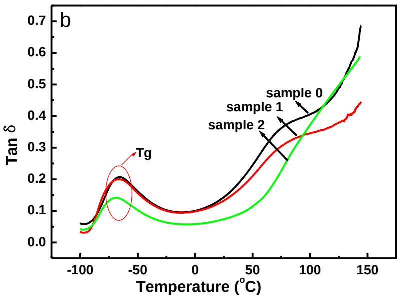


Fig. 8. Storage modulus (a) and Tanδ (b) of WPU/silica/CdTe nanocomposites versus temperature.

From Table 2, the 100 % secant modulus and tensile strength increase generally as the content of silica/CdTe-QDs nanoparticles is increased, and the elongation at break is reduced in the presence of silica/CdTe-QDs nanoparticles compared with pure WPU. These results of tensile properties measured at room temperature (20.0) show that the reinforcing effect of silica/CdTe-QDs nanoparticles is more evidently observed in tensile test with large deformation compared *E'* with measured with small deformation by DMA. This seems to be due to the fact that alignment and extension of PU polymer in rubbery state under large strain may cause the improved performance of silica/CdTe-QDs nanoparticles. The enhancement in the elongation may be due to the effect of the dispersed silica/CdTe-QDs nanoparticles particles which can act as cross-linking center and chain extenders. This result is similar to previous study on PU/silica nanocomposites [18]. In addition, we can see that the Shore *A* hardness is increased as the content of nanosilica is increased by the reinforcing effect of dispersed nanosilica.

Table 2. Physical properties of WPU/silica/CdTe.

Sample	100% Secant Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Shore A Hardness
Sample 0	1.63	20.69	805	72
Sample 1	1.87	27.1	955	80
Sample 2	2.04	29.9	985	85

4. Conclusion

The first facile synthesis of WPU/silica/CdTe-QDs nanocomposites has been achieved by using the -NCO terminated WPU prepolymer as a matrix. The reaction between -NH_2 on the QDs surface and the -NCO terminated WPU creates the silica/CdTe-QDs as cross-linking centers, which could disperse uniformly in PU matrix and significantly improve the mechanical and thermal properties. We have found that WPU/silica/CdTe-QDs nanocomposites have the strong PL and excellent UPL property. This work could offer a novel approach to fabricate highly fluorescent QD-polymer composites from aqueous QDs without any post-preparative treatment. On the basis of the versatile properties of WPU/silica/CdTe-QDs nanocomposites, it is envisioned that these materials could be used as functional coating resins and optoelectronic devices.

Reference

[1] S. H. Hsu, H. J. Tseng, Y. C. Lin, Biomaterials **31,** 6796 (2010).
[2] H. Koerner, W. D. Liu, M. Alexander, P. Mirau, H. Dowty, R. A. Vaia. Polymer **46**, 4405 (2005).
[3] Q. Guo, T. P. Knight, J. Wu, T. P. Mather, Macromolecules **43**, 4991 (2010).
[4] Y. R. Lee, V. A. Raghu, H. M. Jeong, B. K. Kim, Macromol. Chem. Phys **210**, 1247 (2009).
[5] W. C. W. Chan, S. Nie. Science **281**, 2016 (1998).
[6] K. Boeneman, J. B. Delehanty, J. Am. Chem. Soc. **132**, 5975 (2010).
[7] R. E. Beckham, M. A. Bevan, Langmuir **26**, 3779 (2010).
[8] M. Wang, M. Zhang, J. Jieshu Qian, F. Zhao, L. Shen, G. D. Scholes, M. A. Winnik, Langmuir **25**, 11732 (2009).
[9] X-S. Wang, T. E. Dykstra, M. R. Salvador, I. Manners, G. D. Scholes, M. A. Winnik, J. Am. Chem. Soc. **126**, 7784 (2004).
[10] B. Dubertret, P. Skourides, D. J. Norris, V. Noireaux, A. H. Brivanlou, A. Libchaber, Science **298**, 1759 (2002).
[11] S. J. Tan, N. R. Jana, S. Gao, P. K. Patra, J. Y. Ying, Chem. Mater. **22**, 2239 (2010).
[12] T. Hirai, T. Saito, I. Komasawa, J. Phys. Chem. B. **105**, 9711 (2001).
[13] X. Cao, C. M. Li, H. Bao, Q. Bao, H. Dong, Chem. Mater. **19**, 3773 (2007).
[14] S. Chen, J. Zhu, Y. Shen, C. Hu, L. Chen, Langmuir **23**, 850 (2007).
[15] L. Zhou, C. Gao, X. Hu, W. Xu, Appl. Mater. Interfaces **2**, 1211 (2010).
[16] H. H. Yang, S. Q. Zhang, F. Tan, Z. X. Zhuang, J. Am. Chem. Soc. **127**, 1378 (2005).
[17] J. A. Miller, S. B. Lin, K. S. Hwang, K. S. Wu, P. E. Gibson, S. L. Cooper, Macromolecules **18**, 32 (1985).
[18] S-I. Lee, Y. B. Hahn, K. S. Nahm, Y-S. Lee, Polym. Adv. Technol. **16**, 3281 (2005).
[19] N. Gaponik, D. V. Taplapin, A. L. Rogach, A. Eychmuller, H. Weller, Nano. Lett. **2**, 803 (2002).
[20] X. Cao, C.M. Li, H. Bao, Q. Bao, H. Dong, Chem. Mater **19**, 3773 (2007).
[21] G. Wang, C. Wang, W. Dou, Q. Ma, P. Yuan, X. Su, J. Fluoresc **19**, 939 (2009).
[22] H. T. Li, X. D. He, Z. H. Kang, H. Huang, Y. Liu, J. L. Liu, S. Y. Lian, A. Chi Him, C. H. A. Tsang, X. B. Yang, S-T. Lee, Angew, Chem. Int. Ed. **49**, 4430 (2010).
[23] Y. F. Liao, W. J. Li, S. L. He, Nanotechnology **18**, 375701 (2007).

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