A Promising Clean Way to Textile Colouration: Cotton Fabric Covalently-bonded with Carbon Black, Cobalt Blue, Cobalt Green and Iron Oxide Red Nanoparticles

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Supplementary information

Irradiation facility

⁶⁰Co source, located in the campus of Shanghai Institute of Applied Physics, Chinese Academy of Sciences, with a radioactivity of 1 MCi was used as irradiation facility in this article. The dose rate in the irradiation process was 2.94 kGy/h.

The absorbed dose of the cotton fabrics in this article was 50 kGy, and the irradiation time need 17 hr by using ⁶⁰Co source as irradiation facility. However, the irradiation time can be reduced to several seconds for future scale-up industrial application by using electron beam accelerator which has much higher dose rate as the irradiation facility, because the radiation chemical effects of polymers which initiates graft polymerization using both ⁶⁰Co gamma-ray source and electron beam accelerator as irradiation facility are the same¹ and the RIGP method discussed in this article can be scaled up by using electron beam accelerator.

Instruments and characterization

Fourier transform infrared (FT-IR) spectra were conducted by attenuation total reflection (ATR) accessory of a Thermo Nicolet Avatar 370 FT-IR spectrometer. Scanning electron microscope (SEM) analysis was performed on a JEOL JSM-6700F SEM instrument. The samples with 5mm x 5mm were deposited of gold by sputtering under 10 kV for 150 seconds at room temperature. Thermogravimetry analysis (TGA) was performed from a Q500 Thermogravimetric Analyzer. Samples with 5 mg – 10 mg were held for 10 minutes at 100 °C and then heated to 600 °C with a rate of 10 °C min⁻¹ under nitrogen atmosphere. Transmission electron microscope (TEM) was used on a Tecnai G2 F20 S-TWIN field-emission instrument. The samples were dispersed in ethanol and then dropped on copper micro-grids followed by evaporation of the solvent. Chemical oxygen demand (COD) was calculated by a DR890 analyzer. Metal concentrations were measured by an inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, Nexion 300D). Wastewater color was measured by a U-3900 spectrophotometer. An HVF-350 padder was used to make colored cotton with the same weight of solutions. Centrifuge with HC-3513 was used, solutions was centrifuged for 15 min under 10000 RPM.

Modification of CB, CoB, CoG and FeR nanoparticles.

Pristine CB nanoparticles are easily agglomerate together (Fig. S1a and Fig. S1b). Modification of CB nanoparticles is necessary to retard aggregation and introduce other groups²⁻⁴. In this process, 10 g CB nanoparticle was weighed into a glass bottle followed by adding 100 mL acetone, the mixture was stirred for 10 minutes at room temperature. Then silane coupling agent KH570 (3-methacryloxypropyltrimethoxysilane) (5%, v/v) was added into the mixture. After stirring for 24 hours at room temperature, the modified CB nanoparticle (denoted as CB-C=C) was separated by centrifugation and washed by acetone for 3 times. Then modified CB nanoparticle was dried in a vacuum oven at 60 °C for 12 hours. The modified CB nanoparticle became a giant cross-linker with multiple C=C bonds, guaranteeing the CB nanoparticles to participate in the subsequent graft polymerization and being immobilized onto the cotton fabric by covalent bond networks. The agglomeration of the nanoparticles was retarded (Fig. S1c and Fig. S1d). The modification process of CoB, CoG and FeR nanoparticles were same as that of CB nanoparticles.

The existence of C=C double bonds was proved by the reaction between modified nanoparticles and Br_2 solution (Fig. S2). Br_2 solution was prepared by mixing 30 mL deionized water, 2 mL KBr-KBrO₃ (0.09mol/L) and 1m HCl (18%). The reaction between the modified nanoparticles and Br_2 was carried out by soaking 2.5 g modified nanoparticles into the Br_2 solution for 5 min at room temperature. The colour change and corresponding

absorption in UV-Vis before and after reaction (Fig. S3) proved C=C double bonds were successfully introduced onto pristine nanoparticles. Furthermore, pristine CB was also reacted with Br₂ solution to prove there were no C=C bonds on pristine CB. It can be seen that colour didn't change and absorption at 395 nm owing to Br₂ still existed (Fig. S2a and S3a). TGA curves of the nanoparticles before and after modification are given in Fig. S4. Pyrolysis temperature of 300 °C is attributed to the presence of KH570. The content of the KH570 attached on the surface of the CB, CoB, CoG, and FeR nanoparticles are 2.84 wt.%, 1.98 wt.%, 1.87 wt.% and 1.91 wt.%, respectively, which calculated according to the weight remain at 650°C on the TGA curves. FT-IR spectra of pristine nanoparticles and functional nanoparticles are given in Fig. S5. Compared to the spectrum of the pristine nanoparticles, a new band at 1730 cm⁻¹ appeared on the spectrum of functional nanoparticles. The remaining bands except for characteristic peaks of nanoparticles in Fig S5 were identified: 1730 cm⁻¹, stretching vibration of C=O; 1490 cm⁻¹ -1350 cm⁻¹, bending vibration of C-H; 1280 cm⁻¹ - 1100 cm⁻¹, stretching vibration of C-O and C-O-C; 1080 cm⁻¹, stretching vibration of Si-O.

References

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Figure S1: (a) and (b) TEM images of pristine CB with different magnification. (c) and (d) TEM images of CB-C=C with different magnification.



Figure S2. Image of Br_2 solvent reaction with pristine CB (a); CB-C=C (b); CoB-C=C (c); CoG-C=C (d) and FeR-C=C (e).



Figure S3. UV-Vis spectra of the Br₂ before and after reaction with pristine CB (a); CB-C=C (b); CoB-C=C (c); CoG-C=C (d) and FeR-C=C (e).







Figure S5: FT-IR of pristine Carbon black and CB-C=C (a); pristine Cobalt Blue and CoB-C=C (b); pristine CoG, CoG-C=C (c) and pristine FeR, FeR-C=C (d).



Figure S6. Set-up of the padder of HVF-350 (Samples were rolled between two rollers to squeeze out excess liquid and maintain same weigh of solution).



Figure S7. Relation between DG_{CB}, DG_{monomer}, Efficency_{CB}, Efficiency_{monomer} and concentration of CB (a); DG_{CoB}, DG_{monomer}, Efficency_{CoB}, Efficiency_{monomer} and concentration of CoB (b); Relation between DG_{CoG}, DG_{monomer}, Efficency_{CoG}, Efficiency_{monomer} and concentration of CoG (c); Relation between DG_{FeR}, DG_{monomer}, Efficency_{FeR}, Efficiency_{monomer} and concentration of FeR (d).



Figure S8. FT-IR spectra of pristine Cotton, CB5, CoB5, CoG5 and FeR5.







Figure S9. SEM images of sample pristine Cotton and Cotton-g-CB (CB1 to CB5) with magnification in 10000, 20000 and 50000.









н 2 μm

- 2 μm























Figure S10. SEM images of pristine Cotton, Cotton-g-CoB (CoB1 to CoB5), Cotton-g-CoG (CoG1 to CoG5) and Cotton-g-FeR (FeR1 to FeR5) with magnification in 10000, 20000 and 50000.



Figure S11. Chroma illustration of value *L*, *b* and *a*.



Figure S12. Image of scaled up sample CB6 (a) and after definite accelerated laundering cycles (b), Image of wastewater sample generated during the preparation of CB6 (c), laundering wastewater after 20 cycle accelerated laundering of sample CB6 (d).



Figure S13. Relationship of nanoparticles and fabric area ratio with nanoparticle concentration CoB (a), CoG (b) and FeR (c). Area ratios were estimated from SEM images by recognizing image elements of nanoparticles and whole fabric in Image recognition software, Area Ratio (%) = Area_{nanoparticle}/ Area_{fabric} × 100.



Figure S14. Ratio of the concentration of hazardous ions of wastewater samples from W_0-W_{CB5} (a) W_0-W_{COB5} (b), W_0-W_{COG5} (c) and W_0-W_{FeR5} (d) to the limits of ZDHC guideline (Cr:0.2 mg·L⁻¹; Cu:1 mg·L⁻¹; Zn:5 mg·L⁻¹; Ni:0.2 mg·L⁻¹).



Figure S15. Value pH of wastewater from W_0-W_{CB5} (a) W_0-W_{COB5} (b), W_0-W_{COG5} (c) and W_0-W_{FeR5} (d).



Figure S16. SEM images of CB5 (a); CoB5 (b); CoG5 (c) and FeR5 (d) after 20 cycles of accelerated laundering.



Figure S17. Wastewater of CB5 (a); CoB5 (b), CoG5 (c), and FeR5 (d) after definite accelerated laundering cycles.



Figure S18. Images of (a) 0 cycle accelerated laundering wastewater on filter membrane; (b) laundering wastewater after 20 cycles accelerated laundering of CB5 on filter membrane; (c) wastewater of CB5 after 20 cycles accelerated laundering and (d) centrifuged after filtration.



Figure S19 SEM image of the filter residue of the laundering wastewater of CB5 after 20 cycles of accelerated laundering (in Fig S18b).

Sample/site	L/AL	a/∆a	b/∆b	ΔΕ
CB5/1	38.6	0.19	0.41	
2	-0.15	-0.03	-0.02	0.16
3	-0.28	-0.05	-0.09	0.29
4	0.16	-0.05	-0.03	0.17
CoB5/1	57.51	-3.93	-43.12	
2	0.12	-0.12	0.24	0.29
3	-0.11	-0.19	-0.28	0.35
4	0.21	0.15	-0.25	0.36
CoG5/1	59.44	-30.27	17.66	
2	-0.11	-0.22	0.12	0.27
3	0.12	-0.24	-0.12	0.29
4	-0.14	0.21	-0.26	0.36
FeR5/1	43.57	30.97	24.15	
2	0.05	0.13	-0.13	0.19
3	-0.11	-0.08	0.06	0.14
4	0.08	-0.02	-0.11	0.13

Table S1. Chromaticity distortion of the CB5, CoB5, CoG5 and FeR5 by measuring 4 sites on each fabric.

Table S2. Value *Lab* and ΔL of sample CB5, CB6 and laundered CB6; ΔE between CB6 and laundered CB6.

 $(\Delta L/\% = (L_{CB5} - L')/L_{CB5} \times 100, L' \text{ is } L_{CB6} \text{ or } L_{\text{laundering CB6}})$

Sample	L	а	b	ΔL/%	ΔΕ
CB5	38.6	0.19	0.41	0	-
CB6	36.8	0.17	0.35	4.67	0
laundering CB6	37.5	0.18	0.38	2.85	0.70

		Limits			Data of wastewater			
Sum	ZDHC	GB8978-	Sample	Sample	Sample	Sample	Sample	Sample
parameters		2002	W ₀	W _{CB5}	W _{CB6}	W _{Cob5}	W_{CoG5}	W_{FeR5}
(mg·L ⁻¹ ,ppm)								
рН	6-9	6-9	9.82	6.54	6.67	6.34	6.51	6.45
COD	150	200	1650	110	125	132	125	118
Color [m ⁻¹]	7;	-	1897;	0.18;	0.21;	0.42;	0.41;	0.38;
(436nm; 525 nm;	5;		1400;	0.17;	0.18;	0.43;	0.45;	0.59;
620nm)	3		1101	0.25	0.22	0.53	0.51	0.22
TSS/ total suspended solids	50	150	1410	38	32	42	35	40
Chromium/Cr	0.2	0.5	1.47	0.0018	0.0008	0.0019	0.0018	0.0023
Copper/Cu	1.0	1.0	0.041	0.0011	0.0018	0.0008	0.0005	0.0006
Zinc/Zn	5.0	5.0	1.04	0.063	0.037	0.0805	0.1255	0.015
Nickel/Ni	0.2	1.0	0.81	0.0081	0.0067	0.0013	0.0023	0.0021
Cobalt/Co	0.2	-	-	-	-	0.0076	0.0084	-
Titanium/Ti	0.2	-	-	-	-	0.0176	0.0126	-
Iron/Fe	0.2	-	-	-	-	-	-	0.0215

Table S3. Limits of wastewater according to Wastewater Guideline of ZDHC, GB8978-2002 and the parameters of sample W₀, W_{CB5}, W_{CB6}, W_{CoB5}, W_{CoG5} and W_{FeR5}.

Table S4. Parameters of laundering wastewater of CB5, CoB5, CoG5 and FeR5 after 20 cycles acceleratedlaundering.

Sample/mg·L ⁻¹	CB5	CoB5	CoG5	FeR5
COD	46	52	55	58
Cobalt/Co	-	0.0023	0.0015	-
Titanium/Ti	-	0.0012	0.0014	-
Iron/Fe	-	-	-	0.001