

THE NEAR-IR LIGHT INITIATED FREE RADICAL PHOTOPOLYMERIZATIONS USING 2D BLACK PHOSPHORUS

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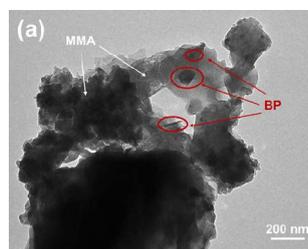
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The search for semiconductor photo-catalysts in a wide variety of uses has attracted great attention since the first discovery of the use of TiO₂ under ultraviolet (UV) light irradiation. As heterogeneous photo-catalysts, significant efforts have been made in the development of semiconductor materials and in increasing their usage areas. However, most of the traditional semiconductors have a wide bandgap, which means UV light irradiation is needed to activate their photocatalytic activities. Therefore, more than 90% of incident rays are not able to activate the traditional semiconductor photocatalysts since only a small range of the incoming solar spectrum covers UV irradiation. The development of a new photocatalyst systems absorbing solar light at much longer wavelength, especially in the visible and NIR has aroused widespread interest. The use of solar energy as a power source and semiconductor materials for polymerization has afforded improvements to minimize the fabrication processes and promise a way to produce a hybrid material by *in-situ* polymerization [1]. In this study, we report for the first time the utilization of exfoliated BP as photocatalysts for the polymerization of (meth)acrylate monomers under white LED and NIR light irradiation using onium salts as co-initiators (Table 1). Moreover, the yielded polymers contain few-layered 2D BP nanosheets (BPNs) as reflected by various analyses. (Figure 1). We suggest that a novel methodology to identify promising concept to the other polymerization modes and click chemistry where PET reactions play a crucial role.

Table 1. White LED/ NIR Light Induced Free Radical Polymerization of MMA in the presence of onium salts.

Oxidant (E _{red}) ^b	White Led		NIR Light	
	Conv. (%) ^c	M _n x 10 ⁻³ (g.mol ⁻¹) ^d	Conv. (%) ^c	M _n x 10 ⁻³ (g.mol ⁻¹) ^d
NO ₂ PhN ₂ ⁺ B F ₄ ⁻ (-0.1)	23	10.5	52	83.9
Ph ₃ S ⁺ PF ₆ ⁻ (-1.2)	np ^e	-	np ^e	-
Ph ₂ I ⁺ PF ₆ ⁻ (-0.2)	-1	173.3	18	372.6

Figure 1. TEM image of BP/MMA nanocomposite.



[1] Kiskan, B.; Zhang, J.; Wang, X.; Antonietti, M.; Yagci, Y., *ACS Macro Letters* **2012**, 1 (5), 546-549.