

Supporting Information:

Controlled Drug Release and Hydrolysis Mechanism of Polymer-Magnetic Nanoparticle Composite

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Table S1. SEM results on PLA and PLA-MNP composite film surfaces: mean pore density and size results of films after hydrolysis for 1, 39h and 60 h.

Samples	After hydrolysis for 1 h		After hydrolysis for 39 h		After hydrolysis for 60 h	
	pore's density (pores per μm^2)	pore's size (μm)	pore's density (pores per μm^2)	pore's size (μm)	pore's density (pores per μm^2)	pore's size (μm)
PLA	0.022±0.001	0.76±0.01	0.12±0.01	0.92±0.02	0.16±0.03	1.63±0.17
PLA-NPs1	0.062±0.002	1.54±0.01	0.19±0.01	1.65±0.02	0.21±0.02	1.91±0.42
PLA-NPs2	0.44±0.09	0.62±0.01	0.39±0.01	2.44±0.05	0.25±0.03	3.16±1.22
PLA-NPs3	0.036±0.001	0.73±0.01	0.08±0.01	2.03±0.06	0.10±0.07	1.86±0.13

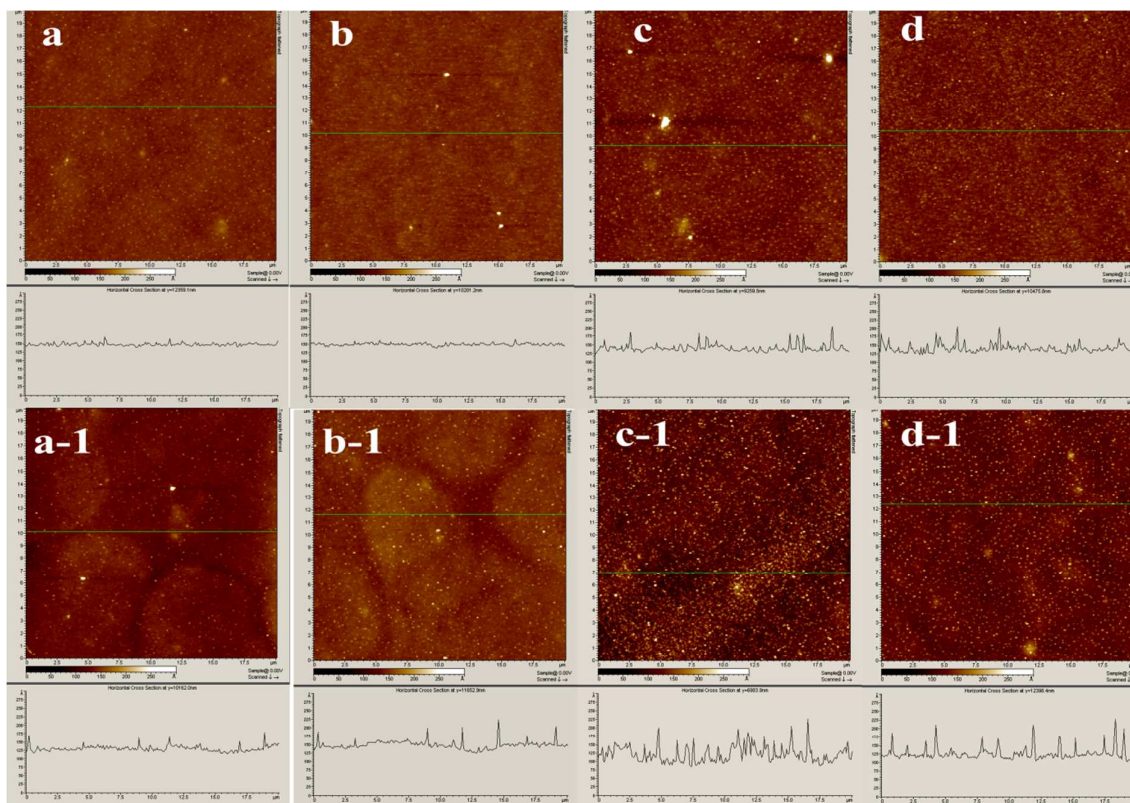


Figure S1. Surface topography of $20 \times 20 \mu\text{m}^2$ scanned area by the AFM and cross-section surface profile.

(a) pure PLA and PLA-MNP hybrid films with various MNP bulk concentrations ((b) ~2 %, (c) ~20 % and (d) ~50 %) before contact with water. Images labeled as a-1, b-1, c-1, d-1 are the corresponding results after immersion in water for 1 h, respectively, for hydrolysis.

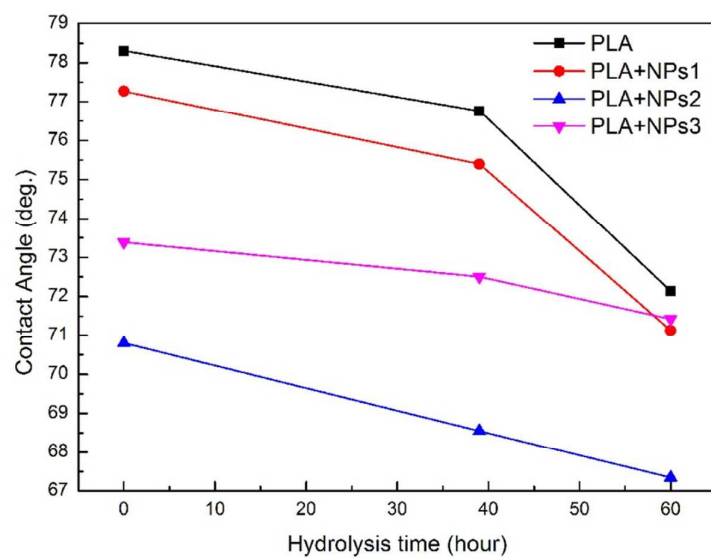


Figure S2. Static water contact angles on PLA and PLA-MNP hybrid films before (0 h) and after water hydrolysis for 39 h and 60 h.

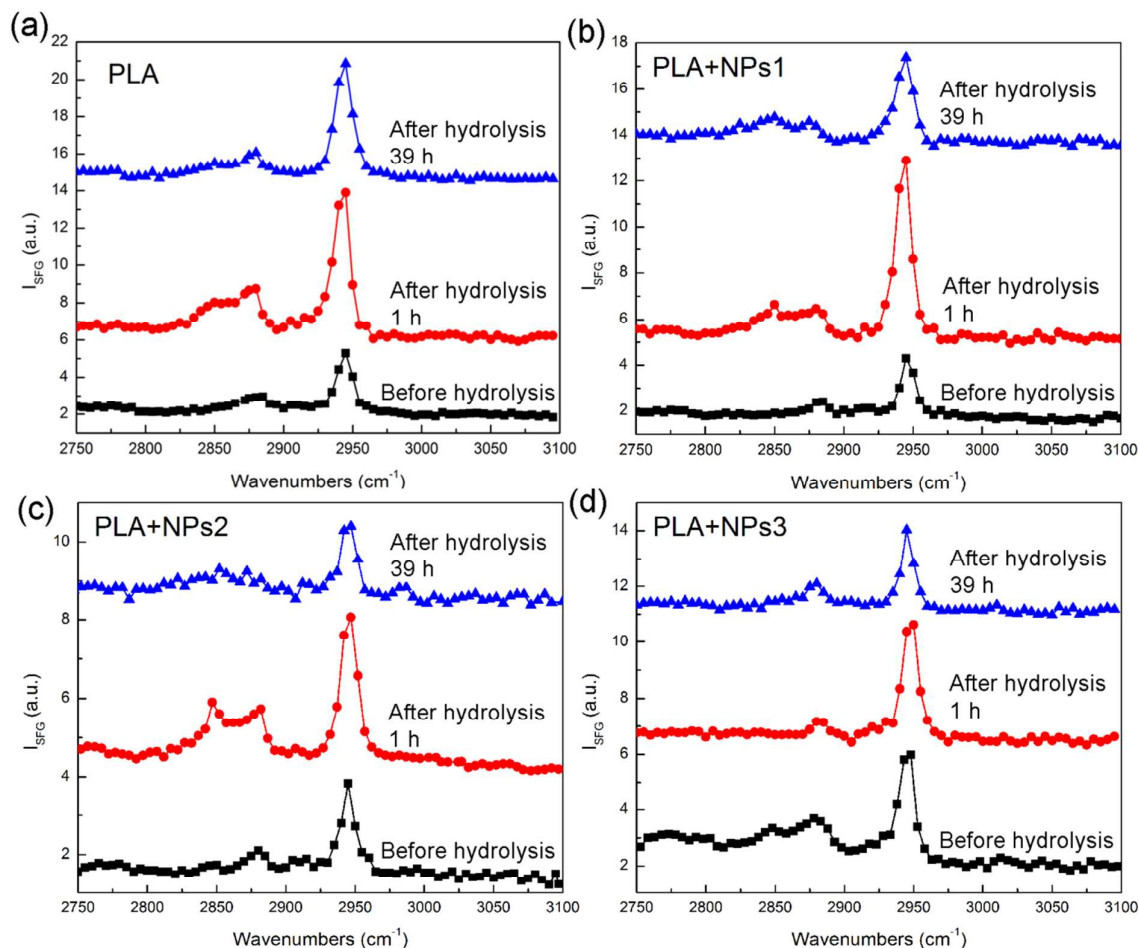


Figure S3. SFG ssp spectra collected from the surfaces of (a) pure PLA film, and PLA-MNP composites with different MNP bulk concentrations: PLA-NPs1 (b), PLA-NPs2 (c), and PLA-NPs3 (d) before and after water immersion for hydrolysis for 1 h and 39 h. Window geometry was utilized to collect SFG spectra for (a)-(d). Also, in (a)-(d), the spectra are offset for clarity.

For pure PLA (Figure S3a), after water immersion for 1 hour, the SFG spectral features are very similar to that of PLA-NPs3 before water immersion (Figure S3d). That is, a new peak was observed near 2850 cm^{-1} which may due to the symmetric CH_2 stretch.¹ Considering no CH_2 groups exist in PLA, this CH_2 peak may be contributed from PLA hydrolysis products remained at the film surface after water immersion. Besides, the SFG peak intensities increased after water immersion for 1 h hydrolysis (Figure S3a). The chain scission induced by hydrolysis may lead to more methyl groups on the surface which would result in higher peak intensities.² Moreover, after hydrolysis for 39 h, the spectrum features of pure PLA were still

very similar. However, the CH₂ peak became smaller and the intensities of other peaks reduced as well. As the hydrolysis time went up to 39 h, the amount of PLA molecules near the surface should be hydrolyzed, so the new surface might be similar as PLA before hydrolysis again. That is, the surface might be dominated by long-chain PLA molecules.

For PLA-MNP hybrid films, as the MNP concentration increased to ~2 % and ~20 %, a stronger CH₂ peak around 2850 cm⁻¹ was observed in SFG spectra after 1 h hydrolysis. Besides hydrolysis products, this CH₂ peak may also be assigned to the symmetric CH₂ stretch of oleic acids coated on the surfaces of MNPs. It is reasonable to observe this MNP peak enhanced after hydrolysis for PLA-MNP hybrid films because the chain scission of PLA might occur during hydrolysis of PLA in water, thus the MNPs buried in long chains of PLA might appear on the film surface again. Also, according to the SEM images shown in Figure 3, the hydrolysis processes were enhanced by MNPs, so it's reasonable to detect the strongest CH₂ peak on the surface of PLA-NPs2 film compared to other spectra after 1 h hydrolysis (Figure S3c) which had the quickest hydrolysis process from SEM results. Besides, in the case of PLA-NPs3, this CH₂ peak almost became undetectable after 1h hydrolysis. Meanwhile, the peak intensities were mostly unchanged rather than further increasing. If we assume the appearance of this CH₂ peak implies that the hydrolysis of PLA occurred on the film surface, then these results are consistent with the SEM and CA results.

One possible explanation for the case of the PLA-NPs3 film is that since the MNP concentration is as high as 50 %, there is a high chance that some of the MNPs would aggregate together in the PLA network. It's also possible that some MNPs aggregate at the PLA surface, so MNP signals can be detected by SFG as well. This can be supported by the rougher surface of PLA-NPs3 film observed by SEM (Figure 3d and Figure S1d). Also, after 1h hydrolysis, undetectable MNP signals in the SFG spectrum of PLA-NPs3 can be explained by loss of MNPs from film surface or total disordering of hydrophobic C-H long chains of oleic

acids on MNP surface. Whereas after hydrolysis for 39 h, the SFG spectra of three PLA-MNP hybrid films are very similar, except for various CH₂ peak intensities. Since the hydrolysis time was up to 39 h now and there were large pores on the film surfaces, the SFG signals must also be contributed from some of the inner surfaces of those pores. This may induce more complicated composition of SFG spectra, so it's hard to directly correlate these SFG data to hydrolysis behaviors here.

References:

- (1) Chen, C.; Wang, J.; Woodcock, S. E.; Chen, Z. Surface Morphology and Molecular Chemical Structure of Poly (n-butyl methacrylate)/Polystyrene Blend Studied by Atomic Force Microscopy (AFM) and Sum Frequency Generation (SFG) Vibrational Spectroscopy. *Langmuir* **2002**, *18*, 1302-1309.
- (2) Wiggins, J. S.; Hassan, M. K.; Mauritz, K. A.; Storey, R. F. Hydrolytic Degradation of Poly (d, l-lactide) as a Function of End Group: Carboxylic Acid vs. Hydroxyl. *Polymer* **2006**, *47*, 1960-1969.